NBS MONOGRAPH 105

Acid-Base Behavior in Aprotic Organic Solvents

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

UNITED STATES DEPARTMENT OF COMMERCE • C. R. Smith, *Secretary*

NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

Acid-Base Behavior in Aprotic Organic Solvents

Marion Maclean Davis

Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

t.
U.S. National Bureau of Standards Monograph 105.

Issued August 1968

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price $2.25

Library of Congress Catalog Card No. 67–62078

Foreword

During the past 50 years the American chemical industry has made available for common uses a great variety of organic solvents, in some of which acids and bases behave very differently than in water. For example, the order of relative strengths of a series of acids or bases may be altered by a change of solvent. This is especially evident when acid-base behavior in water is compared with that in hydrocarbons and halogenated hydrocarbons. To the latter two groups, which are often called "inert" or "aprotic" solvents, belong important liquids like benzene, toluene, cyclohexane, and carbon tetrachloride. Industrially important materials such as drycleaning solvents, lubricants, motor fuels, refrigerants, and transformer oils are additional examples.

From 1941 to the end of 1965 the National Bureau of Standards maintained, in response to requests from industry and other Government agencies, a research program designed to ascertain and explain acid-base behavior in aprotic organic solvents, as well as to develop methods and reference materials for determining total acid and base content and relative strengths of acids and bases in such media. Supplementing the experimental program, a record was maintained of relevant work being performed in other laboratories. The Office of Naval Research and the Air Force Office of Scientific Research contributed financial support.

This Monograph consists of a comprehensive, critical survey of present knowledge in this area, based on numerous kinds of chemical and physical measurements. More than 90 tabulations of data are included. The conclusions reached have broad scientific applicability, and the Monograph will be a useful guide both for those concerned with practical chemical programs and those engaged in fundamental researches. Its detailed discussion of the varied types of hydrogen bonds which form in aprotic media will be valuable to scientists attempting to develop an improved theory of hydrogen bonding.

A. V. Astin, *Director.*

Contents

Contents—Continued

Acid-Base Behavior in Aprotic Organic Solvents

Marion Maclean Davis

A unified picture of acid-base behavior in aprotic organic solvents is presented, based on an extensive survey of the literature and experimental results of the author and associates. Evidence given to support this picture includes data pertaining to colligative properties of acids, bases, and salts and also conductance, dielectric constants, distribution between immiscible solvents, and spectral absorption in the infrared, visible, and ultraviolet. The acids upon which attention is centered are proton-donor compounds that are measurably ionized in water, such as aliphatic and aromatic carboxylic acids, substituted phenols, and mineral acids. The bases of principal interest are likewise compounds capable of forming ions in water, for example, aliphatic and aromatic amines and derivatives of guanidine or pyridine. The solvents emphasized are hydrocarbons and halohydrocarbons, but data for dipolar aprotic solvents (for example, acetone, acetonitrile, and nitrobenzene) are included. Contrasts in acid-base behavior and in acidity and basicity scales in aprotic and water-like solvents are discussed.

The role of hydrogen bonding in aprotic solvents is discussed at length. Important types of hydrogen-bonded structures include chelate rings; self-associated acids, bases, and salts; hydrogen-bonded ion pairs; and homo- and heteroconjugate cations and anions. Examples are given in which hydrogen bonding of these types affects such properties as the absorption spectrum of a salt, the catalytic effect of an acid, and the accurate location of a titration endpoint.

Key Words: Acid-base behavior, acidity and basicity scales, aprotic organic solvents, hydrogen bonding, titrations

1. Introduction

At the present time increasing attention is being given to physicochemical investigations of acid-base behavior in organic solvents of comparatively inert character. Such solvents include aliphatic and aromatic hydrocarbons and halogenated hydrocarbons, which commonly have dielectric constants (ϵ) in the range 2 to 10 and are almost devoid of acidic or basic properties. A second group of solvents of somewhat higher dielectric constant (21 to 36) is also comparatively inert in character. Examples of the latter group are acetone, acetonitrile, and nitrobenzene. (Di)methyl-sulfoxide ($\epsilon = 46$) is sometimes included in the second group.

Having only feeble acid-base properties, these two groups of solvents do not interact strongly with acidic solutes such as carboxylic acids, phenols, and mineral acids, or with basic solutes like amines and derivatives of guanidine or pyridine. Consequently, they are not "masking" or "leveling" solvents like water and low molecular weight alcohols, but instead are "differentiating" solvents. (Solvents of the first group have also been referred to as "inert" or "indifferent.") The differentiating behavior of the two groups of solvents has proved to be very valuable in chemical analyses and separations, as well as in fundamental investigations of chemical equilibria and kinetics.

The current activity in studying acid-base systems in these solvents follows a long period of neglect, which was partly caused by overemphasis on the role of ionization in chemical reactions. One consequence of this overemphasis on ionization has been a widespread belief, slow to expire, that acid-base activity is practically nonexistent in nonionizing solvents like benzene. Later, after this belief was recognized as being incorrect, attempts were made to apply the quantitative acid-base formulations found to be highly satisfactory for aqueous solutions to solutions in benzene, chloroform, etc. The failure of such attempts discouraged further investigations in this area.

An example of beliefs which are now recognized as erroneous can be found in a noted textbook on qualitative analysis which was widely used into the 1920's [1] [1]:

"A solution of hydrogen chloride in a poorly ionizing medium, like benzene or toluene, is an extremely poor conductor . . . indicating only a trace of ionization. Such a solution behaves chemically, also, quite differently from the aqueous solutions of hydrogen chloride with which we are familiar: dry steel nails, dropped into it, remain almost unchanged—there is no marked evolution of hydrogen . . . We find thus . . . in the anhydrous benzene solution an absence of ionization, as indicated by lack of conductivity, and along with this, a lack of the familiar action of hydrogen chloride as an acid . . . ."

---

[1] All references are listed at the end of the review.

Later it was recognized that such tests, using heterogeneous systems, were not valid criteria of chemical reactivity, and it was readily demonstrated—for example, by tests using indicator dyes—that hydrogen chloride and other acids function as acids in benzene and similar solvents.

In justice to the noted author of the above citation, it should be pointed out that this textbook predated the chemical revolution initiated by the newer acid-base concepts of Brønsted, Lowry, and Lewis and also predated awareness of the important role of hydrogen bonding in acid-base behavior. Moreover, in later pages of the same book the author acknowledged that certain experiments by others suggested that hydrogen chloride in benzene *can* react as nonionized molecules, and he advocated reserving decision as to whether the observed reactions were caused by nonionized molecules or by traces of hydrogen ion until after more extensive investigations.

As is well known, the Brønsted-Lowry concept of acid-base relationships paved the way for systematic investigations of chemical behavior in all types of nonaqueous solvents. However, Brønsted's equation representing an acid-base reaction,

$$A_1 + B_2 \rightleftharpoons A_2 + B_1, \qquad (1)$$

cannot be applied without modification to benzene and similar media. This topic will be discussed further in section 2. The role of hydrogen bonding will be reviewed in section 4.

Through the combined efforts of many investigators, applying modern concepts and varied techniques, a great deal has been learned in recent decades about the interactions of hydrogen ("Brønsted") acids with bases in inert organic solvents. The principal objective of this review is to present a unified picture of our current knowledge in this area, with examples of the kinds of evidence obtained by different types of physicochemical investigations. Particular emphasis will be placed on acid-base behavior in hydrocarbons and halogenated hydrocarbons. Attention will be centered on systems consisting of strong or moderately strong protogenic and protophilic compounds—that is, acids and bases for which pK_a and pK_b values in water are obtainable.

2. Acid-Base Concepts

2.1. Present-Day Concepts

Irrespective of the particular acid-base definitions adopted, there is general agreement at the present time that *basic properties* in compounds are associated with (a) the presence of lone pair ("*n*-") electron donor atoms, such as nitrogen or oxygen, and also with (b) the presence of delocalized ("π-") electron systems, as in aromatic and unsaturated aliphatic hydrocarbons. Classes (a) and (b) differ very greatly in basic strength, however, so that the basic properties of *n*-electron donors can be studied very satisfactorily in benzene and other aromatic solvents.

There is also general recognition that the behavior of *hydrogen acids* with bases often parallels closely that of *nonprotogenic "acids"* like boron trichloride or sulfur trioxide [2]. This parallelism can be illustrated by the reaction of tri-*n*-butylamine with hydrogen chloride and with sulfur trioxide in benzene:

$$Bu_3N + SO_3 \rightleftharpoons Bu_3\overset{+}{N}{\cdot}\overset{-}{S}O_3, \qquad (2)$$

$$Bu_3N + HCl \rightleftharpoons Bu_3\overset{+}{N}H\overset{-}{Cl}. \qquad (3)$$

The products of reactions 2 and 3 have almost identical dipole moments in benzene—7.2 and 7.17, respectively [3, 4, 5]. However, tributylammonium chloride differs from tributylamine-sulfur trioxide in having the capacity to undergo ionic dissociation in suitable solvents:

$$Bu_3\overset{+}{N}H\overset{-}{Cl} \rightleftharpoons Bu_3NH^+ + Cl^- \qquad (4)$$

(ignoring solvation of ions).

Equation 4 indicates a major reason for treating protogenic and nonprotogenic acids separately. Additional reasons have been pointed out by various authors [6, 7, 8, 9, 25, 26].

Appropriately, nonprotogenic acidlike compounds have come to be known as "Lewis acids," while the term "Brønsted acids" has become a synonym for "hydrogen" or "protogenic" acids. There is no dualism in the case of bases—Lewis emphasized [2] his agreement with Brønsted's views [10] in regarding organic bases, as well as such ions as halide and acetate, as being true bases.

2.2. Formulation of Acid-Base Reactions in Ionizing Solvents

In applying the Brønsted-Lowry acid-base concept, Brønsted [10, 11, 12, 13] formulated acid-base reactions in ionic terms. Doing so has proved to be satisfactory for reactions in *ionizing* media, but a different formulation is needed for acid-base reactions in *inert* solvents. To bring out the contrast, let us first recall the essence of how Brønsted stated and applied his acid-base concept:

1. The definition of acids and bases is given by the scheme

$$A\ (\text{acid}) \rightleftharpoons B\ (\text{base}) + H^+. \qquad (5)$$

A and B are called a "conjugate pair."

2. Acids and bases can be neutral or ionic, as illustrated below.

Type of acid or base	Examples of acids	Examples of bases
Cationic	NH_4^+	$H_2NC_6H_4 \cdot C_6H_4NH_3^+$
Neutral	CH_3COOH	NH_3
Anionic	$HOOC.COO^-$	CH_3COO^-

3. Acids and their conjugate (corresponding) bases (see eq 5) cannot have the same electrical charge.

4. Equation 5 illustrates a "simple" acid-base equilibrium. A mixture of two simple systems gives a "double" acid-base system and acid-base equilibrium. Thus,

$$A_1 \rightleftharpoons B_1 + H^+, \qquad (6)$$

$$B_2 + H^+ \rightleftharpoons A_2, \text{ and} \qquad (7)$$

adding eqs 6 and 7,

$$B_2 + A_1 \rightleftharpoons B_1 + A_2. \qquad (8)$$

The reaction between triethylamine and hydrogen chloride may serve as a practical illustration of the general eqs 6–8:

$$HCl \rightleftharpoons Cl^- + H^+, \qquad (9)$$

$$Et_3N + H^+ \rightleftharpoons Et_3NH^+, \qquad (10)$$

and

$$\underset{(\text{base}_2)}{Et_3N} + \underset{(\text{acid}_1)}{HCl} \rightleftharpoons \underset{(\text{acid}_2)}{Et_3NH^+} + \underset{(\text{base}_1)}{Cl^-}. \qquad (11)$$

The equilibrium constant corresponding to eq 11 is

$$K = (Et_3NH^+)(Cl^-)/(Et_3N)(HCl), \qquad (12)$$

where the symbols enclosed in *parentheses* signify the stoichiometric concentration of the species concerned multiplied by the activity coefficient. (*Brackets* will be used in place of parentheses whenever activity coefficients are assumed to be approximately 1, or to be cancelled.)

We should bear in mind that all such formulations ignore any acidic or basic role played by the solvent.

2.3. Formulation of Acid-Base Reactions in Nonionizing Solvents

When acid-base reactions occur in relatively inert solvents like benzene, the data are found *not* to fit an equation patterned after eq 12. To illustrate, the association of triethylamine with the phenolic indicator bromophthalein magenta E (3′,5′,3″,5″-tetrabromophenolphthalein ethyl ester) in benzene, studied by spectrophotometry in the visible region, was found to conform instead to eqs 13–14:

$$Et_3N + HIn\ (\text{the indicator}) \rightleftharpoons Et_3NHIn, \qquad (13)$$

$$K_{\text{assocn.}} = [Et_3NHIn]/[HIn][Et_3N]. \qquad (14)$$

The equilibrium constant, $K_{\text{assocn.}}$, for this reaction has the value 2.74×10^4 (25°, molar units) [14, 15].

In general terms, eqs 13–14 can be formulated, respectively, as

$$B\ (\text{base}) + HA \text{ or } A\ (\text{the acid}) \rightleftharpoons S\ (\text{salt}), \qquad (15)$$

$$K_{\text{assocn.}} = [S]/[A][B]. \qquad (16)$$

The reaction between triethylamine and bromophthalein magenta E in benzene is but one of many that have been studied in hydrocarbon and halogenated hydrocarbon solvents and found to conform to eqs 15–16. In such solvents any tendency to react in the sense of eq 11 is usually of negligible importance.

A simple way of demonstrating that acid-base reactions conform to the general pattern of eqs 15–16 is to plot log [S]/[A] against −log [B], as in figure 1. The six sets of points were obtained for acid-base equilibria in benzene in which *triethylamine* was the base and the acid was one of the six *isomeric dinitrophenols* [16]. It is easily seen that if the six reactions conform to eqs 15–16 the experimentally obtained points should fall—as they do—on or near straight lines with the slope −1. Then, where log [S]/[A] = 0, −log [B] = log $K_{\text{assocn.}}$.

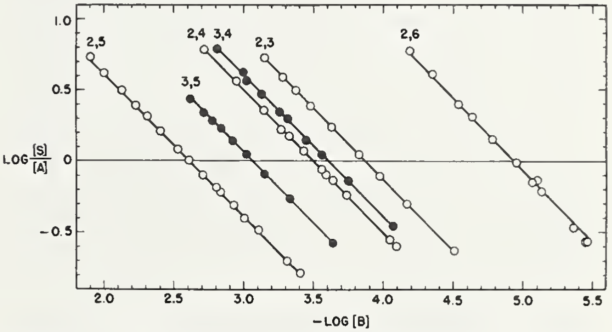


FIGURE 1. *Conformance of acid-base equilibria in mixtures of triethylamine with the isomeric dinitrophenols in benzene, to the assumed pattern of reaction: B (base) + A (acid) ⇌ S (salt).*

See M. M. Davis, J. Am. Chem. Soc. **84**, 3623 (1962). (Ref. No. 16.)

To measure the relative strengths of acids (bases) in a comparatively inert solvent like benzene, a suitable reference base (acid) must be added. From figure 1 it is apparent that, with triethylamine as the reference base, 2,6-dinitrophenol is the most acidic, and 2,5-dinitrophenol the least acidic, of the isomers. The same relative order of strengths in benzene has been obtained with diphenylguanidine as the reference base [17].

2.4. Hantzsch's Views [18–21]

Hantzsch maintained that a *chemical* method, such as the tendency toward salt formation with indicator bases in an inert solvent, gives the most logical measure of the relative strengths of acids, and he estimated the relative strengths of several acids by semiquantitative measurements of the extent of formation of colored salts with basic indicator dyes in solvents like benzene and chloroform [18, 19]. Two of his associates, Weissberger and Fasold [22], hoped to demonstrate the correctness of Hantzsch's views as applied to salt formation between trichloroacetic acid and methyl yellow (*p*-dimethylaminoazobenzene, *N,N*-dimethyl-*p*-phenylazoaniline) in benzene and chloroform. However, the values obtained for $K_{\text{assocn.}}$ (eq 16) were not constant and showed a trend. With the benefit of our much more complete knowledge about such systems, several possible explanations can now be seen for the failure of the particular system studied to conform to eq 16. These include the monomer-dimer equilibrium of trichloroacetic acid, complex anion formation, and the *cis-trans* isomerism of methyl yellow. A much more favorable system is the equilibrium mixture of tribenzylamine, picric acid, and tribenzylammonium picrate, for which $K_{\text{assocn.}}$ values were obtained by dielectric polarization measurements [23] and by spectrophotometry in the visible region [20]. The results by the two methods were in excellent agreement. Slightly less accurate association constants had been obtained earlier for mixtures of amines with bromophthalein magenta E [14].

In nitrobenzene, ionic dissociation is *not* negligible. Witschonke and Kraus [24] studied the equilibria involving anilinium, dimethylanilinium, and pyridinium picrates by the conductance method, and deduced that two equilibria coexist for these salts in nitrobenzene:

$$BHA \rightleftharpoons BH^+ + A^-, \qquad (17)$$

$$\text{and } BHA \rightleftharpoons B + HA. \qquad (18)$$

The equilibrium constant corresponding to eq 18 is, of course, the reciprocal of $K_{\text{assocn.}}$ (eq 16). The ionic dissociation constant and the equilibrium constant for dissociation of the salt into the component base and acid were *both* evaluated from the conductance data. To illustrate, for dimethylanilinium picrate the following values were obtained (molar units, 25°[2]): $K_{\text{ion.}}$ (eq 17) $= 4.1 \times 10^{-5}$. $K_{\text{dissocn.}}$ (eq 18) $= 2.5 \times 10^{-4}$.

There is now an abundance of evidence that *strong* acids (for example, picric acid) and bases (for example, triethylamine or diphenylguanidine)—and not merely the weak acids and bases previously known to associate through hydrogen bonding—interact according to the pattern of eqs 15–16 when dissolved in inert solvents, and the stoichiometry indicated is widely accepted as being correct. However, sometimes the schematic formula of the salt formed by association of a base B with an acid HA is written as BH^+A^-, the process of association is referred to as "ionization," and the salt is said to consist of "ion pairs." Other investigators (including the writer) believe this practice oversimplifies the situation, considering the evidence (see sec. 4.3) that many, at least, of such salts consist of *hydrogen-bonded* ion pairs. To indicate the role of hydrogen bonding, the structure of the salt may be written as $BH^+ \ldots A^-$, the process may be referred to as "partial ionization" or "partial proton transfer," and the salt may be said to consist of "hydrogen-bonded ion pairs." Shatenshtein [25], the late N. A. Izmailov [26], and N. D. Sokolov [27] are among proponents of such views.

2.5. The Role of the Solvent in Ionization

Brønsted wanted to formulate acid-base reactions independently of any specific solvent, as in eq 11, and in doing so he deliberately ignored the role of the solvent in promoting ionization. He was well aware, of course, that ionization of solutes depends on the dielectric constant of the solvent and on its acidic and/or basic character, also. The oversimplification was sometimes criticized, notably by Izmailov, who wrote [26]: "Our investigations have shown that Brønsted's theory is too schematic and provides for only one type of chemical interaction between dissolved acids and the solvent (only the exchange of protons), with the result that this theory does not allow the explanation of all the peculiarities in the effect of solvents, and in particular, does not explain the differentiating action on the strengths of acids, which is the result of more complex individual interactions in solvents of different types." Izmailov developed a "theory of the dissociation of acids and bases" [26], which he formulated in considerable detail. The theory was based on exhaustive studies by Izmailov and co-workers of the relative strengths of acids in different types of solvents, using such varied physical methods as cryoscopy, Raman spectroscopy, and emf measurements. The essence of the theory is that acids themselves are not ionized, but instead, the ionizing species consist of molecular compounds of the acids with the solvent. The structures of these molecular compounds may vary according to the chemical structures of the solute and solvent, thus accounting for differences in the acid strength of a given solute in different solvents. A number of investigators, notably Kendall (see ref. [28] and later papers), have also argued that the ionization process involves association of solutes with the solvent.

Shatenshtein has presented a complete, concise discussion of Brønsted's formulation of acid-base processes, together with his own comments and criticisms [25].

Davis has pointed out [5, 14–17, 20–21, 29–33] that results obtained in studying the behavior of hydrogen acids with bases in organic solvents

---

[2] Throughout this review temperatures are in °C.

(mainly benzene) by means of spectrophotometry in the visible region are in harmony with the evidence from other kinds of physicochemical investigations reported in the literature. The accumulated evidence points very convincingly to an important and varied role of hydrogen bonding in acid-base interactions involving hydrogen acids. When the role of the solvent in acid-base interactions was ignored, it was difficult to reconcile the Brønsted concept with the Lewis concept of acid-base reactions. This can be illustrated by comparing the reaction of triethylamine with hydrogen chloride as formulated by the Brønsted scheme with the formulation of the reaction of triethylamine with a typical Lewis acid, boron trichloride (eqs 11, 19).

$$Et_3N + HCl \rightleftharpoons Et_3NH^+ + Cl^-, \qquad (11)$$

$$Et_3N + BCl_3 \rightleftharpoons Et_3N \cdot BCl_3 \qquad (19)$$

However, applying what has been learned about the stoichiometry of acid-base reactions in nonionizing solvents (eqs 15–16) and taking into account the part played by an ionizing solvent such as water led Davis to formulate a scheme [5, 21] by which the two concepts may be harmonized, as illustrated by eqs 20–25.

1. *The Ionization of an Acid*, HA, *in Water.*

$$\underset{\text{(base)}}{H_2O} + \underset{\text{(acid)}}{HA} \rightleftharpoons H_2OH^+ \ldots A^-, \qquad (20)$$

$$H_2OH^+ \ldots A^- + \underset{\text{(base)}}{H_2O} \rightleftharpoons H_2OH^+ \ldots OH_2 + A^-, \qquad (21)$$

Combining eqs 20 and 21 gives:

$$2H_2O + HA \rightleftharpoons H_2OH^+ \ldots OH_2 + A^- \qquad (22)$$

2. *The Ionization of a Base*, R_3N, *in Water.*

$$\underset{\text{(base)}}{R_3N} + \underset{\text{(acid)}}{HOH} \rightleftharpoons R_3NH^+ \ldots OH^-, \qquad (23)$$

$$R_3NH^+ \ldots OH^- + \underset{\text{(base)}}{H_2O} \rightleftharpoons R_3NH^+ \ldots OH_2 + OH^-, \qquad (24)$$

Combining eqs 23 and 24 gives:

$$R_3N + 2H_2O \rightleftharpoons R_3NH^+ \ldots OH_2 + OH^-. \qquad (25)$$

In these two sets of equations water represents the solvents which are capable of functioning both as a base and as an acid. The first equations (eqs 20 and 23) represent associations which are analogous to Lewis acid-base reactions, while the second equations (eqs 21 and 24) show separation into solvated ions. The third equation in each set is the sum of the first two. Those who accept these formulations as valid look upon the *primary* acid-base reaction as being an *association*, and formation of separate, solvated ions as constituting a secondary reaction.

Equation 21 is based on the assumption [5] that in water solutions protons are likely to be associated with *at least two* water molecules, rather than just the one molecule implied by the formula H_3O^+. This assumption has found added support in work of the past decade which has led to the conclusion that H_3O^+, the hydronium ion, associates with further water molecules, forming the fairly stable species $H_3O^+ \cdot 3H_2O$ when sufficient water is present [34]. Likewise, there is strong experimental evidence in support of eq 24 [5].

In proposing concrete pictures of how water can bring about ionization of acids and bases through specific hydrogen bonding reactions it is not essential that solvation of anions be considered. It is obvious, however, that the two sets of equations would have been still more complete if attention had also been paid to solvation of A^- and OH^-. Structures such as $HOH \ldots A^-$ are highly probable.

Important effects of hydrogen bonding on acid-base behavior will be discussed in greater detail in section 4.

3. Classification of Organic Solvents

In the preceding discussion water and chemically related solvents like the alcohols have been referred to as *masking*, *leveling*, or *ionizing* solvents. In comparison, benzene and chemically related solvents have been referred to as *indifferent*, *inert*, *differentiating*, or *nonionizing*. In an earlier day benzene was also characterized as an "associating" solvent.

3.1. Dielectric Constants of Pure Solvents

A more definite basis for classifying solvents is according to the magnitude of the dielectric constant. Table 1 contains available values of the dielectric constant, ϵ, of eight homologous series of organic solvents, and table 2 contains the dielectric constants of additional currently important organic solvents. Water, formerly considered to have an extremely high dielectric constant, has been overshadowed in this respect by some of the newer solvents, for example, *N*-methylpropionamide ($\epsilon = 176$) [39a]. As would be expected, aliphatic hydrocarbons have the lowest dielectric constants ($\epsilon \leq 2$).

The most familiar organic solvents—usually compounds of low molecular weight—may differ

TABLE 1. *Values of dielectric constant (°C) for homologous solvents having the general formula* normal-$C_nH_{2n+1}X$ [a]

n=	X=							
	H	Br	CN	$COCH_3$	COOH	$COOC_2H_5$	NH_2	OH
0	....	3.8 (25)	115 (20)	21.1 (21)	58 (16)	7.2 (25)	16.9 (25)	78.54 (25)
1	1.7 (−173)	9.82 (0)	37.5 (20)	20.7 (25)	6.15 (20)	6.02 (25)	9.5 (25)	32.63 (25)
2	....	9.39 (20)	27 (20)	18.5 (20)	3.30 (10)	5.65 (19)	6.94 (10)	24.30 (25)
3	1.61 (0)	8.09 (25)	20 (21)	15.4 (20)	2.97 (20)	5.10 (18)	....	20.1 (25)
4	....	7.07 (20)	17 (21)	[b] 13.1 (20)	2.7 (20)	4.71 (18)	5.3 (21)	[c] 17.5 (25)
5	1.84 (20)	6.32 (25)		12.0 (20)	2.63 (71)	....	4.5 (22)	[c] 14.8 (25)
6	1.89 (20)	5.82 (25)		10.4 (20)	2.59 (71)	....		[c] 13.0 (25)
7	1.92 (20)	5.33 (25)			2.4 (20)	....		12.1 (22)
8	1.95 (20)	5.00 (25)				....		[c] 9.96 (25)
9	1.97 (20)	4.74 (25)				....		....
10	1.99 (20)	4.44 (25)				3.55 (20)		8.1 (20)
11	2.00 (20)	4.73 (−9)				3.44 (20)		....
12	2.01 (20)	4.07 (25)						6.5 (25)
14		3.84 (25)						4.72 (38)
15		3.89 (20)						....
16		3.71 (25)						3.82 (50)
18		3.53 (30)						3.42 (58)

[a] Unless indicated otherwise the data were taken from reference [35].

[b] 4-Methyl-2-pentanone (methyl isobutyl ketone).

[c] From reference [36].

REFERENCES:

[35] A. A. Maryott and E. R. Smith, Table of Dielectric Constants of Pure Liquids, *NBS Circ.* 514, Aug. 10, 1951.
[36] C. G. Malmberg, NBS, unpublished data.

appreciably in the value of the dielectric constant depending on the polar groups present (for example, compare the values of ϵ for CH_3COOH, CH_3NH_2, CH_3OH, CH_3CN, and CH_3NO_2). However, in aliphatic homologous series there is generally a trend toward very low values with increasing carbon content (see tables 1 and 2). The hydrocarbons show a slight trend in the opposite direction (table 1, second column). From consideration of the examples given in these tables it is apparent that if solvents with $\epsilon \geqslant 20$ were arbitrarily regarded as having high constants, and those with $\epsilon < 20$ as having low constants, most of the common organic solvents would belong to the second class. That is, besides the hydrocarbons and brominated hydrocarbons, the second class would include valeronitrile and higher nitriles, all of the ketones except acetone and methyl ethyl ketone, all of the aliphatic carboxylic acids except formic acid, all of the ethyl esters, and all of the primary aliphatic amines, as well as *n*-butanol and higher alcohols. The dielectric constants of secondary and tertiary aliphatic amines are still lower than those of primary aliphatic amines.

Schlundt [42] seems to have been the first person to report that a decrease in the value of the dielectric constant with increasing molecular weight is the general rule for homologous series, though similar observations had been made still earlier for a few series. It is not surprising, of course, that the value of ϵ drops off as polar groups become increasingly screened by aliphatic groups.

The value of ϵ also depends on the *location* of polar groups in the molecule. To illustrate, the following values of ϵ (22°) were obtained for 1-, 2-, 3-, and 4-heptanol, respectively: 12.1, 9.21, 6.86, and 6.17 [35]. Analogously, values of ϵ (20°) found for twenty of the isomeric octanols [35] range from 10.3 for 1-octanol or isooctanol to 2.87 for 4-methyl-4-heptanol.

The relation between dielectric constant and structure has been treated exhaustively by Smyth [43].

Enough has been said to indicate that, by itself, the magnitude of the dielectric constant does not provide a very helpful basis for classifying solvents.

3.2. Dielectric Constants of Mixed Solvents

Mixed solvents are used frequently in acid-base titrations and in studying solute-solvent interactions. For instance, "ASTM Medium," which is

TABLE 2. *Values of dielectric constants (t °C) of selected organic solvents*[a]

Alcohols		Halogenated Hydrocarbons		Nitro Compounds	
Benzyl alcohol	13.1 (20)	Benzotrifluoride	9.18 (30)	Nitrobenzene	34.82 (25)
iso-Butyl alcohol	17.7 (25)	Carbon tetrachloride	2.23 (25)	Nitroethane	28.1 (30)
tert.-Butyl alcohol [36a]	12.5 (25)	Chlorobenzene	5.62 (25)	Nitromethane	35.9 (30)
Cyclohexanol	15.0 (25)	Chloroform	4.81 (20)	1-Nitropropane	23.2 (30)
Ethylene glycol	38 (25)	*o*-Dichlorobenzene	9.93 (25)	2-Nitropropane	25.5 (30)
iso-Propyl alcohol [36]	19.2 (25)	1,1-Dichloroethane [38]	9.90 (25)		
		1,2-Dichloroethane [38]	10.23 (25)	Phenols	
Amines		Dichloromethane	9.08 (20)		
		Hexachloro-1,3-butadiene	2.55 (25)	Phenol	9.78 (60)
Aniline	6.89 (20)	Tetrachloroethylene	2.30 (25)	*o*-Cresol	11.5 (25)
Benzylamine	4.6 (21)			*m*-Cresol	11.8 (25)
Dibenzylamine	3.6 (20)	Hydrocarbons		*p*-Cresol	9.9 (58)
Ethylenediamine	14.2 (22)				
2-Methylpryidine	9.8 (20)	Benzene	2.27 (25)	Miscellaneous	
Morpholine	7.33 (25)	Cyclohexane	2.02 (25)		
Piperidine	5.8 (22)	Decahydronaphthalene	2.2 (20)	Benzonitrile	25.20 (25)
Pyridine	12.3 (25)	Mesitylene	2.28 (20)	Carbon disulfide	2.64 (20)
Pyrrole	7.48 (18)	Phenylacetylene	2.98 (25)	Cyclohexanone	18.3 (20)
Triethylamine	2.42 (25)	Tetrahydronaphthalene	2.76 (20)	Dimethylformamide [39]	36.7 (25)
		Toluene	2.38 (25)	Formamide	109 (20)
Ethers		2,2,4-Trimethylpentane	1.94 (20)	*N*-Methylformamide [39]	182.4 (25)
		o-Xylene	2.57 (20)	*N*-Methylpropionamide [39a]	176 (25)
Anisole	4.33 (25)	*m*-Xylene	2.37 (20)	Methyl sulfoxide [40]	46.4 (25)
1,4-Dioxane	2.21 (25)	*p*-Xylene	2.27 (20)	Tetramethylguanidine [39b]	11.5
Ethyl ether	4.34 (20)			Tetramethylurea [41]	23.1
Tetrahydrofuran [37]	7.39 (25)			Tributyl phosphate	7.96 (30)

[a] Unless otherwise indicated data were taken from reference [35].

REFERENCES:

[35] A. A. Maryott and E. R. Smith, Table of dielectric constants of pure liquids, NBS Circ. 514, Aug. 10, 1951. Supt. of Documents, U.S. Govt. Printing Office, Washington, D.C.
[36] C. G. Malmberg, Natl. Bur. Std., unpublished data.
[36a] W. Dannhauser and L. W. Bahe, J. Chem. Phys. **40**, 3058 (1964).
[37] F. E. Critchfield, J. A. Gibson, Jr., and J. L. Hall, J. Am. Chem. Soc. **75**, 6044 (1953).
[38] J. T. Denison and J. Ramsey, J. Am. Chem. Soc. **77**, 2615 (1955).
[39] G. R. Leader and J. F. Gormley, J. Am. Chem. Soc. **73**, 5731 (1951).
[39a] T. B. Hoover, J. Phys. Chem. **68**, 876 (1964).
[39b] A. Popov, M. L. Anderson, and R. N. Hammer, Abstrs. Papers 145th Meeting Am. Chem. Soc., New York, N.Y., Sept. 1963, p. 21N.
[40] J. J. Lindberg and J. Kenttämaa, Suomen Kemistilehti **B33**, 104 (1960).
[41] A. Lüttringhaus and H. W. Dirksen, Angew. Chem. Intern. Ed. Engl. **3**, 260 (1964).

used in standard methods for determining the acid and base numbers of petroleum products [44], as well as in determining the acid numbers of marine and vegetable oils [45], consists of 50.0 percent of toluene, 49.5 percent of isopropanol, and 0.5 percent of water, by volume. The dielectric constant is about 8 [46]. In the area of fundamental investigations, Fuoss and co-workers have been investigating electrolyte-solvent interactions systematically since about 1950, using various mixed solvents so as to gain insight into interactions between solvents as well as between solvent and solute [47–49].

Figures 2 to 5 contain curves showing the dielectric constants of some important binary solvent mixtures as functions of the composition. It is clear that the magnitude of ϵ does not vary with changing composition in a quantitatively predictable way. This is not surprising, considering that the structure of a mixture at any given temperature will depend on the size, the shape, and the relative orientations of component molecules, as well as the strengths of intermolecular forces of attraction. Additional structural changes will occur, of course, when solutes are added.

By interpolation in the curves, a rough idea of the dielectric constants of some of the solvent mixtures currently popular can be obtained. For example, the value so obtained for 4:1 benzene-methanol by volume, a solvent mixture which has been recommended for titrating carboxylic acids [50], is about 6.7, assuming the absence of impurities and negligible volume change on mixing.

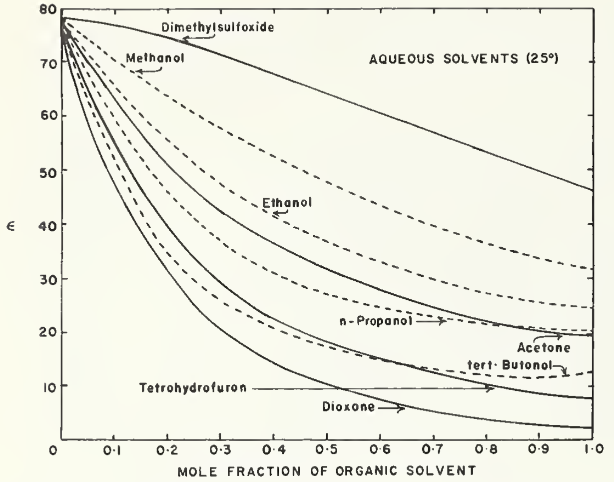


FIGURE 2. *Dielectric constants of aqueous organic solvents as a function of composition* (25°).

Sources of data: Water-methyl sulfoxide, ref. 40; water mixed with methanol, ethanol, *n*-propyl alcohol, or acetone, ref. 51; water-*tert*.butyl alcohol, ref. 52; water-dioxane, ref. 53; water-tetrahydrofuran, ref. 37.

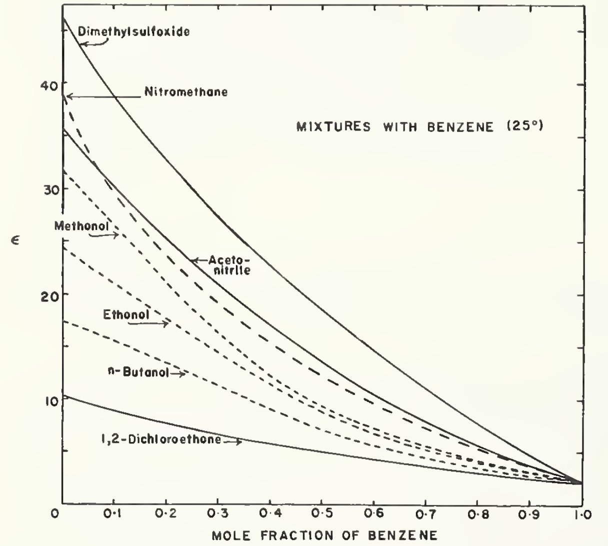


FIGURE 3. *Dielectric constants of binary solvent mixtures as a function of composition* (25°).

Sources of data: Benzene-methyl sulfoxide, ref. 54; benzene-nitromethane, ref. 55; benzene-acetonitrile, ref. 56; benzene-methanol, ref. 57; benzene-ethanol, ref. 58; benzene-*n*-butyl alcohol, ref. 59; benzene-1,2-dichloroethane, ref. 60.

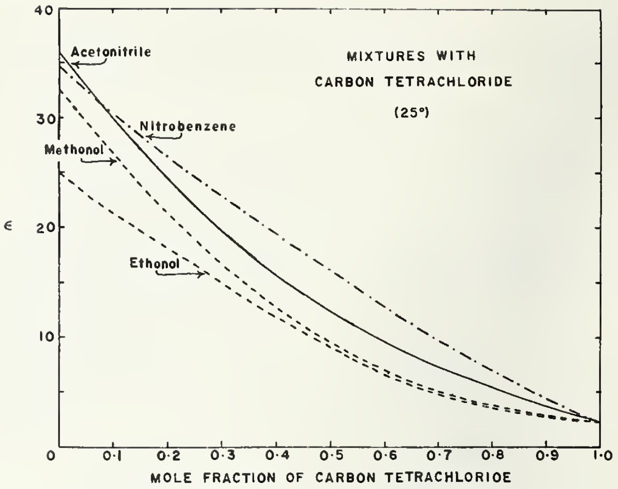


FIGURE 4. *Dielectric constants of binary solvent mixtures as a function of composition* (25°).

Sources of data: Carbon tetrachloride-acetonitrile, ref. 61; carhon tetrachloride-nitrobenzene, refs. 62–63; carbon tetrachloride-methanol, ref. 64; carbon tetrachloride-ethanol, ref. 65.

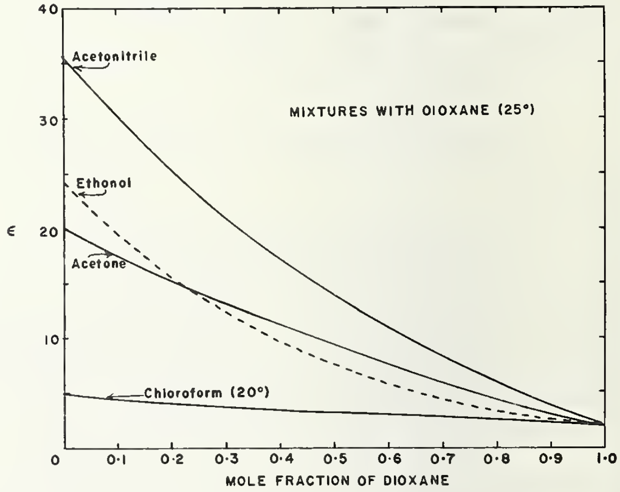


FIGURE 5. *Dielectric constants of binary solvent mixtures as a function of composition* (25°).

Sources of data: Dioxane-acetonitrile, ref. 66; dioxane-ethanol, ref. 67; dioxane-acetone, ref. 68; dioxane-chloroform (20°), ref. 69.

3.3. Brønsted's Eight Classes

Brønsted proposed [12] subdividing solvents into eight types, taking into consideration the acidic and/or basic properties and the values of the dielectric constant. This scheme is shown in table 3. *Plus* and *minus* signs indicate a "higher or lower value" of the property referred to. Suggested examples of the eight types have been added.

For solvents of type 1 Brønsted [13] coined the designation "amphiprotic," to signify that they are both protogenic and protophilic and are therefore "completely active protolytically." Solvents of type 8 represent the opposite extreme in properties. To these solvents Brønsted applied the adjective "aprotic," to signify that they are "completely indifferent protolytically."

Benzene, cited as an example of type 8, is now well known to be a π-electron donor, and thus a base according to the most modern concept. However, its basicity is very low relative to that of n-electron donors [5].

Brønsted recognized, of course, that all sorts of transitions between the eight main classes of sol-

TABLE 3. *Brønsted's Scheme for Classifying Solvents* [12][a]

Type No.	Dielectric Contant, ϵ	Relative Acidity	Relative Basicity	Examples (ϵ, approx.)
1	+	+	+	Water (78), methanol (33).
2	+	+	−	Hydrogen cyanide (115), hydrogen fluoride (84, 0°).
3	+	−	+	*N*-Methylpropionamide (176), tetramethylurea (23).
4	+	−	−	Acetone (21), acetonitrile (36), dimethylformamide (37), methyl sulfoxide (46), nitrobenzene (35).
5	−	+	+	*tert.*-Butyl alcohol (11), cyclohexanol (15), *tert.*-pentyl alcohol (6).
6	−	+	−	Acetic acid (6), propionic acid (3).
7	−	−	+	*n*-Butylamine (5), pyridine (12), tetramethylguanidine (11), dioxane (2), ethyl ether (4), tetrahydrofuran (7).
8	−	−	−	Benzene (2.3), cyclohexane (2.0), 2,2,4-trimethylpentane (1.9), carbon tetrachloride (2.2), 1,2-dichloroethane (10).

[a] *Plus* and *minus* signs indicate a comparatively high or low value of the property referred to. In the selection of examples, solvents of $\epsilon \geqslant 20$ were arbitrarily regarded as having a comparatively high dielectric constant, that is, to have a "plus" value for this property. Correspondingly, solvents of $\epsilon < 20$ were regarded as having a low ("minus") value. Compounds commonly considered to be good proton donors (acceptors) are assigned plus values for relative acidity (basicity).

REFERENCE:

[12] J. N. Brønsted, *Chem. Ber.* **61**, 2049 (1928).

vent are conceivable. For the study of acid and base properties, he said [12], a medium of type 4 would be of special interest, and he emphasized the importance of solvents of type 8 in these words [13]: "The properties of acids and bases may then by no means, as is generally believed, be investigated in aqueous solutions, but must on the contrary be investigated in solutions of benzene-like, aprotic character if we would gain the most comprehensive and deepest insight into the nature of these substances." Moreover, he said [12]: "A thorough study of the molecular state [in benzene and similar solvents] must precede an exact quantitative investigation of acid and base strength [in such solvents]."

This rough classification is useful, even though few would be in complete agreement about the most suitable categories for particular solvents. It will be noted that in the selection of examples for table 3, the value $\epsilon = 20$ was arbitrarily taken as separating solvents of relatively high and relatively low dielectric constants. The dielectric constant of a solvent bears a relationship, of course, to its acid-base character.

As previously indicated, this review is mainly concerned with acid-base behavior in solvents of type 8. Solvents of type 4, on account of their comparatively slight acidic and basic character, are the most nearly similar in their influence on solute behavior, and useful parallels can be drawn between the two types.

3.4. Comparisons of Aprotic Solvents

The behavior of solutes dissolved in acyclic saturated hydrocarbons is generally found to resemble closely that of the gaseous solutes, but in other hydrocarbons there is evidence of more or less solvent-solute interaction. For this reason, the qualifying adverb "comparatively" or "relatively" should always be understood when cycloparaffins and aromatic or other unsaturated hydrocarbons are referred to as "inert" solvents. At the same time, any acid-base properties of these solvents should not be overstressed, for all have far less acid-base character than such familiar acids and bases as carboxylic acids, phenols, amines, ethers, and the like.

Halogenated hydrocarbons, likewise, are inert only in a comparative sense. Proton donor capacity in halogenated compounds containing C–H, such as chloroform, has been amply demonstrated, and more recently, evidence of hydrogen bonding to halogen has been presented. Furthermore, in the last several years there has been increased realization of the tendency of halogenated hydrocarbons to react with nitrogen bases and with oxygen. Such reactions are accelerated by irradiation.

3.4.1. Aromatic Solvents as Bases

While benzene is the most commonly used hydrocarbon solvent, occasionally it is replaced by a related aromatic solvent like toluene or chlorobenzene, for such reasons as a more desirable boiling point or dielectric constant. Recognition that these solvents differ slightly in basic character is helpful in accounting for solvent effects sometimes observed. The comparative basicities of aromatic solvents will be discussed only briefly here. This topic has been reviewed recently by Shatenshtein [25], Briegleb [70], Arnett [71], and many others.

Basic tendencies in benzene have been recognized for at least 25 years (see Davis's summary of the evidence [5]). Considerable knowledge of the basic character of aromatic hydrocarbons has resulted from many investigations of the past 15 years, stimulated by Benesi and Hildebrand's experimental studies of the association of aromatic hydrocarbons with the Lewis acid iodine [72] and the theoretical studies of "charge-transfer complexes" by Mulliken and co-workers [73–76]. In these investigations two of the most widely used criteria are (a) the stability constants of complexes with Lewis or Brønsted acids, determined by measuring spectral changes in the ultraviolet or visible regions, and (b) the comparative magnitudes of shifts in infrared stretching frequencies. (The interacting materials are generally diluted with solvents like heptane, cyclohexane, or carbon tetrachloride.)

The examples of comparative stability constants given in table 4[3] are representative of many data which show that the basic character of the benzene ring increases with increasing number of methyl substituents. For example, analogous results were obtained by selective extraction from heptane with the reagent $HF{-}BF_3$ [79], and by determining the capacities of methylbenzenes to dissolve hydrogen chloride at −78.5° [80]. Such results would be expected because of the well-known electron-releasing capability of the methyl group [81]. Halogen atoms, on the contrary, tend to attract electrons from the benzene ring, and it is not surprising to find (table 4, last column) that bromobenzene and *m*- and *p*-chlorotoluenes are poorer π-electron donors toward iodine monochloride than benzene and methylbenzenes.

TABLE 4. K_c *(liter/moles) values for associations in* CCl_4 (25°)[a]

π-Electron Donor	Electron Acceptor	
	I_2	ICl
Benzene	0.15	0.54
Toluene	0.16	0.87
o-Xylene	0.27	1.24
m-Xylene	0.31	1.39
p-Xylene	0.31	1.51
Mesitylene	0.82	[b]3.70
Pentamethylbenzene	0.88	6.43
Hexamethylbenzene	1.35	[b]13.2
Bromobenzene	0.13	0.32
m-Chlorotoluene	....	[b]0.32
p-Chlorotoluene	....	[b]0.24

[a]Data are from Andrews and Keefer [77] except as noted otherwise.

[b]From Ogimachi, Andrews, and Keefer [78].

REFERENCES:

[77] L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc. **74**, 4500 (1952).

[78] N. Ogimachi, L. J. Andrews, and R. M. Keefer, J. Am. Chem. Soc. **77**, 4202 (1955).

Olah and co-workers [82], from their own and published data on shifts of infrared fundamental H-X stretching frequencies, concluded that the relative order of decreasing basicity of halobenzenes is as follows:

$$C_6H_6 > C_6H_5I > C_6H_5Br > C_6H_5Cl > C_6H_5F.$$

Table 5 indicates there to be a consistency of infrared results with various proton donors. Olah has pointed out [82] that occasional inconsistencies—as, for example, the relatively high stability of the iodobenzene-Ag^+ complex—probably can occur because of the capacity of halobenzenes to act both as π-electron and *n*-electron donors. Part of the results cited in table 5 are from investigations by Josien and co-workers. Additional results of interest may be found in the original papers [83–84].

Differences in the π-electron donor (hydrogen bond acceptor) capacities of benzene, toluene, and chlorobenzene provide a highly reasonable explanation for Popovych's results [85] in determining the extent of association of several pyridine-type bases with the reference acid tetrabromophenolsulfone-

TABLE 5. *Shift* (cm^{-1}) *of infrared fundamental* H–X *stretching frequencies of proton donors in halobenzenes*[a]

Electron Donor	Proton Donor								
	HCl	HBr	HI	PhOH	MeOH	MeOD	*n*-BuOH	Pyrrole	PhC≡CH
CCl_4	−55	−40	−26	−44	−42	−31	−40	−35	−25
C_6H_5F	−76	−40	−40	−48	−44	−33	−50	−42	−33
C_6H_5Cl	−107	−77	−48	−76	−63	−43	−64	−55	−36
C_6H_5Br	−117	−82	−54	−86	−69	−51	−70	−60	−38
C_6H_5I	−125	−90	−63	−95	−77	−53	−71	−63	−40
C_6H_6	−130	−106	−66	−97	−80	−60	−74	−70	−41

[a] Adapted from the compilation by Olah and co-workers [82]. Values given are for the shift in stretching frequency upon transfer from the gaseous state to solution.

REFERENCE:

[82] G. A. Olah, S. J. Kuhn, and S. H. Flood, J. Am. Chem. Soc. **83**, 4581 (1961).

---

[3] Unless stated otherwise, constants cited in the tables and text are either values calculated by the original authors or logarithmic equivalents of these values.

phthalein (bromophenol blue). The association constants (see eq 16) are given in table 6. Values for log K_B (log $K_{\text{assocn.}}$) in the three solvents are linearly related, but the $K_{\text{assocn.}}$ values are greatest in chlorobenzene and least in toluene. Thus, in this particular reaction chlorobenzene is the most nearly inert of the three solvents, as it competes the least with the pyridine-type bases.

TABLE 6. *Effect of solvent on some acid-base association constants* (25°) [a]

$K_{\text{assocn.}} \times 10^{-3}$ (liter/mole)

Base	Chlorobenzene (5.62)	Benzene (2.27)	Toluene (2.37)
Pyridine	2.50	1.88	1.40
Isoquinoline	....	4.75	3.64
2-Picoline	....	19.8	12.9
3-Picoline	14.6	9.51	6.67
4-Picoline	28.6	18.0	11.8
2,4-Lutidine	438	179	113

[a] From O. Popovych, J. Phys. Chem. **66**, 915 (1962). Dielectric constants are given in parentheses. The *reference acid* was bromophenol blue (tetrabromophenolsulfonephthalein), first color change (colorless to yellow).

REFERENCE:

[85] O. Popovych, J. Phys. Chem. **66**, 915 (1962).

There has been considerable interest in geometrical aspects of the interaction of benzene and other aromatic hydrocarbons with electron acceptor molecules. Proton magnetic resonance techniques have been found to be particularly suitable for such studies [86–87]. The π-electron system in aromatic molecules is commonly regarded as being a relatively exposed region of negative charge, effective in a direction perpendicular to the aromatic ring. In the interaction of benzene with chloroform, acetonitrile, and acrylonitrile, Schneider [86] has interpreted the observed proton shifts as being indicative of the structures shown in figure 6. Hatton and Richards [87] have proposed structures representing the directed interactions between benzene and three amides (*N,N*-dimethyl- and diethylformamide, *N,N*-dimethylacetamide).

Recently, Creswell and Allred [88] studied the association of benzene with chloroform in cyclohexane solution by means of nuclear magnetic resonance spectroscopy. The equilibrium constant (25°) is about 1.1 (m.f.)$^{-1}$ or about 0.11 liter/moles.

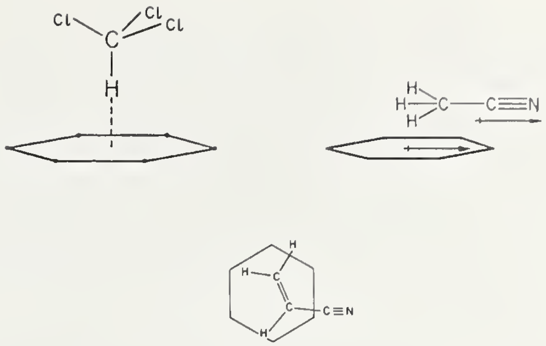


FIGURE 6. *Examples of directed solvent-solute interactions involving benzene. Top, left and right: Interaction with chloroform and acetonitrile, respectively. Bottom: Interaction with acrylonitrile.*

Reproduced from W. G. Schneider, J. Phys. Chem. 66, 2653 (1962), with the permission of the author and the publisher. (Ref. No. 86.)

3.4.2. Unsaturated Aliphatic Hydrocarbons as Bases

Using phenol and *p*-fluorophenol as reference proton donors, West [89] obtained infrared spectroscopic evidence that weak hydrogen bonding to unsaturated aliphatic hydrocarbons occurs in carbon tetrachloride solution. Part of West's results is given in table 7. From the relative shifts of the O–H band the following conclusions seem justified: (a) *p*-fluorophenol is a slightly better proton donor than phenol; (b) olefins are better proton acceptors than aromatic hydrocarbons; (c) basicity increases with increasing alkyl substitutions at the double bond; (d) conjugation (as in isoprene) would appear to reduce basicity; (e) the triple bond in 1-hexyne confers greater basic character than the double bond in 1-hexene. Conclusions (a)–(d) fulfill expectations. Conclusion (c) is the same as the earlier conclusion of Brown and Brady [80], based on the comparative solubilities of hydrogen chloride in various hydrocarbons at −78.5°.

TABLE 7. *Shifts* (*cm*$^{-1}$) *of* O–H *band for associations in* CCl_4 [a]

Hydrocarbon	Proton Donor	
	C_6H_5OH	*p*-F-C_6H_4OH
1-Me-cyclohexene	113	....
2-Me-2-butene	108	116
2-Me-1-butene	104	106
Cyclohexene	95	99
2-Hexene	85	....
1-Hexene	69	74
1-Octene	62	69
Isoprene	52	59
1-Hexyne	92	96
Mesitylene	73	78
p-Xylene	66	69
Toluene	58	61
Benzene	47	49

[a] Data of West [89], abridged and rearranged.

REFERENCE:

[89] R. West, J. Am. Chem. Soc. **81**, 1614 (1959).

Basic properties of acetylene groups will be referred to again in section 3.4.5.

3.4.3. Halogen Compounds as Bases

Haloaromatic compounds as *π-electron donors* were discussed briefly in section 3.4.1.

a. Alkyl halides. Recently several investigators have determined values of $\Delta\nu$ (shifts in infrared O–H stretching frequencies) and ΔH for hydrogen bonding to halogen which is covalently bonded to carbon—that is, for hydrogen bonding to halogen in alkyl halides, RX. A full discussion of such comparatively weak interactions is outside the intended scope of this review, but examples of results obtained are given in tables 8 to 10.

Table 8 gives values of $\Delta\nu$ and thermodynamic constants, obtained by West and co-workers for hydrogen bonding of phenol to four cycloalkyl halides, and also to *n*-butyl ether, in carbon tetrachloride solution [90]. As the authors pointed out, the spectral shifts indicate that the relative basicities of the monohalocyclohexanes follow the order

$$RI > RBr > RCl > RF,$$

in agreement with earlier infrared spectral results for *n*-butyl halides [91], while the enthalpy changes indicate the *opposite* order of basic strengths. The explanation suggested (ascribed to H. J. Bernstein) is that $\Delta\nu$ measures only the weakening of the bond PhO–H, whereas ΔH° measures the *overall* energy change accompanying the formation of the H bonded complex PhOH...XR and the simultaneous weakening of the PhO–H and X–R bonds. The data of table 8 show the alkyl halides to be decidedly weaker electron donors than *n*-butyl ether.

Table 8. *Thermodynamic properties and spectral shifts in hydrogen bonding of phenol to alkyl halides* (CCl_4, *25°*)[a]

Electron Donor, RX	$\Delta\nu$	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$
	(cm^{-1})	*kcal/mole*	*kcal/mole*	*cal/deg mole*
Fluorocyclohexane	53	3.1	1.31	6.1
Chlorocyclohexane	66	2.2	0.87	4.5
Bromocyclohexane	82	2.0	0.85	4.0
Iodocyclohexane	86	1.7	0.82	3.0
n-Butyl ether	278	6.0	2.45	11.8

[a] From West and co-workers [90].

Reference:

[90] R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, J. Am. Chem. Soc. **84**, 3221 (1962).

Infrared results of Jones and Watkinson for hydrogen bonding of phenol to *n*-heptyl halides (table 9) [92] show the same trends in $\Delta\nu$ and ΔH as in the work of West and co-workers, although the spectral shifts and enthalpy changes are smaller. The authors call attention to the probability that "free" phenol molecules are hydrogen bonded to the solvent (tetrachloroethylene), and they suggest that greater inductive electron release from cyclohexyl to halogen than from *n*-heptyl may account for the larger enthalpy changes observed by West and co-workers (compare tables 8 and 9).

Table 9. *Values of* ΔH *and* $\Delta\nu$ *for hydrogen bonding of 0.01* M *phenol to* n-*heptyl halides* ($CCl_2=CCl_2$, *25°*)[a]

Halide (1 M)	$\Delta\nu$	$-\Delta H$
	cm^{-1}	*kcal/mole*
$C_7H_{15}F$[b]	28.4	2.54
$C_7H_{15}F$	39.7	2.13
$C_7H_{15}Cl$	58.7	1.65
$C_7H_{15}Br$	69.2	1.57
$C_7H_{15}I$	71	1.25

[a] From Jones and Watkinson [92]. For bonding to PhOH with the exception noted.

[b] Bonded to PhOD.

Reference:

[92] D. A. K. Jones and J. G. Watkinson, J. Chem. Soc., p. 2366 (1964).

Table 10 shows results obtained by Jones and Watkinson [92] using a constant electron donor (*n*-heptyl fluoride) and several substituted phenols as proton donors. This experiment yielded a fairly good linear correlation of $\Delta\nu$ and ΔH values.

Table 10. *Values of* ΔH *and* $\Delta\nu$ *for hydrogen bonding of* m- *and* p-*substituted phenols to* n-*heptyl fluoride* ($CCl_2=CCl_2$, *25°*)[a]

Substituent in PhOH	$\Delta\nu$	$-\Delta H$
	cm^{-1}	*kcal/mole*
p-OMe	36.6	1.98
m-OMe	40.4	2.19
p-F	41.9	2.15
p-Cl	44.6	2.26
p-Br	45.4	2.31
p-I	46.4	2.43
m-NO_2	53.5	2.89
p-NO_2	59.4	3.31

[a] From Jones and Watkinson [92].

Reference:

[92] D. A. K. Jones and J. G. Watkinson, J. Chem. Soc., p. 2366 (1964).

The comparative ΔH values for formation of *n*-$C_7H_{15}F$...DOPh and *n*-$C_7H_{15}F$...HOPh (see table 9) indicate that the deuterium bond is stronger than the hydrogen bond, in agreement with previous evidence [92].

Krueger and Mettee [93] have measured frequency shifts and formation constants for numerous methanol-base adducts in carbon tetrachloride. Like the other workers cited [90–92] they concluded that shifts in O–H stretching frequencies upon hydrogen bond formation are not a measure of the overall bond strength.

b. Carbon tetrachloride. Infrared data are thought to indicate that proton donors such as methanol, pyrrole, and phenol [94, 95] form weak bonds to chlorine in carbon tetrachloride as a result of the tendency of X–H dipoles to "[seek] out an appropriately charged polar group . . . with which to associate." Although the carbon tetrachloride molecule has zero dipole moment, the $Cl^{-}–C^{+}$ bond has polar character [95]. In other words, carbon tetrachloride is not the completely inert medium it was formerly assumed to be.

3.4.4. Carbon Tetrachloride as an Electron Acceptor

About 30 years ago Earp and Glasstone, following up previous indications of molecular compound formation between carbon tetrachloride and ethers, made dielectric polarization measurements of the following systems [96–97]: Carbon tetrachloride mixed with ethyl ether, isopropyl ether, dioxane, acetone, or quinoline; carbon tetrabromide mixed with ethyl or isopropyl ether; hexachloroethane mixed with ethyl ether. The results in all cases indicated a weak tendency for 1 : 1 association, and for some systems approximate association constants were obtained. The authors considered that the union was a *chemical* one, with oxygen or nitrogen functioning as an electron donor.

Recent work has led to analogous conclusions. From calorimetric and cryoscopic data, Goates and co-workers [98] deduced that benzene and carbon tetrachloride form a 1 : 1 addition compound, with the approximate heat of association −3.5 kcal/mole. They suggested that formation of this complex may arise from π-bonding between the aromatic ring and the empty 3-*d* level of chlorine. For the corresponding *p*-xylene-carbon tetrachloride complex the heat of association is about −6.3 kcal/mole. Subsequently, Anderson and Prausnitz [99], using ultraviolet spectrophotometry, determined association constants for the 1 : 1 complex of carbon tetrachloride with benzene and also with mesitylene (in *n*-hexane). The association constant calculated for the complex formed with benzene is about 0.01 (liter/mole, 25°), and for the complex with mesitylene it is about 0.1. Anderson and Prausnitz attribute this complex formation to charge transfer, with the aromatic compound probably acting as the electron donor. However, Person [99a] has questioned the validity of the low K values obtained.

Sharpe and Walker observed that the dipole moments of most amines are higher in carbon tetrachloride than in benzene, and concluded that this indicated interaction of the amines with carbon tetrachloride [100]. On the assumption that interaction can be inferred when the increment exceeds 0.04 Debye unit, they concluded that ethyl ether and butyl ether also interact with carbon tetrachloride. In *their* view, also, the ether is the electron donor. On the basis of their own work and a review of work by others, they believe that tertiary amine oxides, esters, phosphines, and sulfides are additional substances which interact with carbon tetrachloride.

McKinnon and Williamson's recent heat of mixing studies [100a] indicate strong interaction of carbon tetrachloride with dioxane, while Whetsel and Kagarise's infrared data [101] are indicative of a weak specific interaction between carbon tetrachloride and cyclohexanone.

3.4.5. C–H Containing Compounds as Proton Donors

The ability of hydrogen in C–H containing solvents like chloroform and phenylacetylene to become bonded to electron donor groups was referred to in the beginning part of this section (also note table 5 and fig. 6).

Organic chemists have long known that C–H containing compounds with "negative" groups adjacent to the carbon possess exceptionally "active" or "labile" hydrogen. It has also been realized for more than 35 years [96, 97] that acetone and ether form crystalline compounds with chloroform, and that anomalies in the behavior of their liquid mixtures with chloroform indicate intermolecular association. It now seems highly logical to attribute such phenomena to hydrogen bond formation.

a. Chloroform and related solvents. Nevertheless, when Glasstone and Earp first interpreted the dielectric polarization behavior of mixtures of haloforms (or related C–H containing compounds) with acetone, ethers, or quinoline on the basis of hydrogen bonding, some skepticism was expressed about the ability of hydrogen in a C–H bond to play the part of a proton donor [96, 97]. Soon, however, a vast assortment of confirmatory evidence was obtained. Part of this was reviewed briefly by Pimentel and McClellan [102], and some of the recent work has been mentioned in further studies using nuclear magnetic resonance spectroscopy [88] and infrared spectroscopy [104]. The following is a *partial* list of techniques which, in addition to the two techniques just mentioned, have been used in studying interactions of chloroform with various bases: Dielectric polarization, freezing point diagrams, heats of mixing, the parachor, solubilities, and vapor pressure measurements [88, 102–104]. Pimentel and McClellan concluded their review by remarking: ". . . The evidence in favor of association of chloroform with bases is conclusive. The evidence that this association is of the H bonding type is substantial . . . ."

One of the strong indications that hydrogen bonding must occur in the association of bases with chloroform or other C–H containing molecules comes from the comprehensive solubility studies of Zellhoefer, Copley, and Marvel. For example, they found that the solvent capacities of halomethanes for basic molecules follow the order

$$CH_3X < CH_2X_2 < CHX_3 >> CX_4,$$

where X = Cl or F. The many solutes tested included ethers, thioethers, esters, ketones, and primary and tertiary amines. The failure of alcohols to associate with chloroform was attributed to their strong tendency toward intermolecular *self*-association [105, 106]. The order given above is exactly that predicted on postulating that C–H hydrogen is involved in the bonding and that its activity is progressively enhanced on continued replacement of methane hydrogens by halogen. Heats of mixing data [107] show bromine to be a little less effective than chlorine in promoting activity of C–H hydrogen. The phenyl group also appears to have less activating effect than chlorine.

Infrared spectroscopy has been a particularly favored method for studying hydrogen bonding by chloroform and related C–H containing compounds [101, 102–104, 108–112]. Besides adding strong support to earlier deductions from other kinds of data (dielectric polarization, solubilities, heats of mixing, etc.), it has contributed supplementary conclusions.

For example, in a comparative study of hydrogen bonding of chloroform, *sym.*-tetrachloroethane, or pentachloroethane (diluted with *n*-heptane) to phosphorus oxychloride, triethyl phosphate, and tri-*n*-butylphosphine oxide [111], the order of hydrogen bonding found for the three phosphoryl compounds tested was

$$n\text{-}Bu_3PO > (EtO)_3PO > POCl_3,$$

in harmony with Kosolapoff and McCullough's previous conclusions from heats of mixing data [113]. The comparative hydrogen bonding ability found for the three halohydrocarbons was

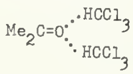
$$CHCl_3 > CHCl_2CCl_3 > CHCl_2CHCl_2.$$

A few years ago Kearns suggested [114] that, besides the 1 : 1 complexes like $Me_2C{=}O\ldots HCCl_3$ previously assumed to exist, 1 : 2 association can also occur, giving a complex of the general type indicated by (I).

$$Me_2C{=}O\ldots HCCl_2Cl\ldots HCCl_3$$

(I)

By assuming occurrence of 1 : 2 association, certain "excess" free energy and heats of mixing data can be accounted for. Whetsel and Kagarise, from infrared studies of the association of acetone or cyclohexanone with chloroform (diluted with cyclohexane) [101], agree that both 1 : 1 and 1 : 2 complexes are probably formed, but prefer Lascombe's formula (II) [115] for the 1 : 2 complex. In Lascombe's formula *both* molecules of chloroform are hydrogen bonded to the carbonyl group. Lowering the temperature from +27° to −55° produced spectral effects which were consistent with the inferences drawn from changes in concentration. For the 1 : 1 association of cyclohexanone with chloroform Whetsel and Kagarise calculated $K = 1.2 \pm 0.3$ (liter/mole, 30°). The association constant for acetone-chloroform complexing was the same within the experimental uncertainty. This value is about 10 times greater than earlier estimates. For the 1 : 2 association they estimated $K = 0.2$.



$$Me_2C{=}O\genfrac{}{}{0pt}{}{\cdot\cdot\,HCCl_3}{\cdot\cdot\,HCCl_3}$$

(II)

Whetsel and Lady [112] recently studied the complexing of chloroform with cyclohexylamine, aniline, and several aniline derivatives (in cyclohexane). In the case of most ring-substituted anilines, log K values for amine-chloroform association were found to be linearly related to pK_a values for the amines in water. Examples of equilibrium constants and heats of reaction obtained by Whetsel and Lady are given in table 11, which also contains results for other associations involving chloroform. Results in which $K_{\text{assocn.}}$ is given in mole fraction^{-1} units are presented separately in table 12. (As the data in these tables are shown mainly to permit general conclusions and comparisons, details about conditions of measurement and estimates of precision and accuracy given in the original papers have been omitted.)

As more is learned about intermolecular reactions, some of these values may need revision. During the past decade the self-association (dimerization) of chloroform has been discussed and studied considerably. On the basis of our preceding discussion self-association would certainly be expected, and there are numerous experimental reasons [121, 122] for accepting its existence as demonstrated. The dimerization constant 0.013 (liter/mole, 25°) has been obtained [116] from NMR data (see tables 11 and 12). Base-haloform association constants that have been calculated without taking chloroform dimerization into account, and also possible 1:2 association, are very likely somewhat in error.

As mentioned earlier in section 3.4, chloroform is thought to bond weakly to benzene, and still more weakly to carbon tetrachloride (see table 11).

Comparative K values for association of acetone with haloforms, like heats of mixing data [107], indicate that chlorine is more effective than bromine in activating the C–H hydrogen (see tables 11 and 12). Bromine in turn has a greater activating effect than iodine. The activating effects of fluorine and bromine appear to be about equally great (table 12).

Huggins and Carpenter [123] have deduced from NMR data that silicochloroform, $SiHCl_3$, is a slightly weaker proton donor than chloroform.

b. Acetylenic hydrocarbons. Hydrogen bonding of acetylene and related hydrocarbons to electron donors has been a topic of growing interest in the past 25 years. Such bonding was predictable from

TABLE 11. *Equilibrium constants and heats of reaction for base-haloform associations* [a]

Proton Donor	Electron Donor	Temp.	Method	$K_{assocn.}$	$-\Delta H$	Reference
		°C		*liter/mole*	*kcal/mole*	
$CHCl_3$	CCl_4	....	NMR	0.01	....	[88]
$CHCl_3$	$CHCl_3$	25	NMR	0.013	....	[116]
$CHCl_3$	C_6H_6	25	NMR	0.11	2.0	[88]
$CHCl_3$	$PhNH_2$	25	IR	0.51	1.7	[112]
$CHCl_3$	Et_3N	25	NMR	0.51	....	[88]
$CDCl_3$	Et_3N	....	IR	[b] 0.36	....	[118]
$CHCl_3$	Me_2CO	30	IR	1.2	....	[101]
$CDCl_3$	Me_2CO	31	IR	[c] 0.90	3.5	[117]
$CDCl_2Br$	Me_2CO	31	IR	[c] 0.80	3.3	[117]
$CDBr_3$	Me_2CO	31	IR	[c] 0.45	2.7	[117]
$CHCl_3$	$C_6H_{11}NH_2$	25	IR	1.10	3.6	[112]

[a] Except as noted otherwise, the mixtures were diluted with cyclohexane.
[b] No diluent.
[c] *n*-Hexane was used as diluent.

REFERENCES:

[88] C. J. Creswell and A. L. Allred, J. Phys. Chem. **66,** 1469 (1962).
[101] K. B. Whetsel and R. E. Kagarise, Spectrochim. Acta **18,** 329 (1962).
[112] K. B. Whetsel and J. H. Lady, J. Phys. Chem. **68,** 1010 (1964).
[116] C. F. Jumper, M. T. Emerson, and B. B. Howard, J. Chem. Phys. **35,** 1911 (1961).
[117] R. E. Kagarise, Spectrochim. Acta **19,** 629 (1963).
[118] G. M. Barrow and E. A. Yerger, J. Am. Chem. Soc. **76,** 5247 (1954).

TABLE 12. *Equilibrium constants and thermodynamic constants for base-haloform associations (cyclohexane, 25°)* [a]

Proton Donor	Electron Donor	$K_{assocn.}$ (m.f.)$^{-1}$	$-\Delta H$	$-\Delta S$	Reference
			(kcal/ mole)	*(cal/mole deg)*	
$CHCl_3$	CCl_4	0.1	....	....	[116]
$CHCl_3$	$CHCl_3$	0.16	....	....	[116]
$CHCl_3$	C_6H_6	1.06	1.97	6.5	[88]
$CHCl_3$	Et_3N	4.2	4.15	11.0	[88]
CHF_3	THF [b]	4.57	2.4	5.2	[119]
CHF_3	THF	4.77	2.59	5.59	[c] [120]
CDF_3	THF	4.95	2.73	5.97	[c] [120]
$CHCl_3$	THF	5.78	3.6	8.6	[119]
$CHBr_3$	THF	4.81	2.6	5.6	[119]
CHI_3	THF	4.64	1.6	2.3	[119]

[a] By *proton* NMR spectroscopy except as noted otherwise.
[b] Tetrahydrofuran.
[c] By *fluorine* NMR spectroscopy.

REFERENCES:

[88] C. J. Creswell and A. L. Allred, J. Phys. Chem. **66,** 1469 (1962).
[116] C. F. Jumper, M. T. Emerson, and B. B. Howard, J. Chem. Phys. **35,** 1911 (1961).
[119] C. J. Creswell and A. L. Allred, J. Am. Chem. Soc. **85,** 1723 (1963).
[120] C. J. Creswell and A. L. Allred, J. Am. Chem. Soc. **84,** 3966 (1962).

the labile nature of C–H hydrogen in these compounds. Copley and Holley [124] measured the solubility of acetylene in numerous organic solvents, and, in harmony with expectations, found its solubilities in ethers, esters, and ketones to be greatly in excess of those predicted by Raoult's law. They also found, from heats of mixing data, that phenylacetylene (ethynylbenzene) forms 1:1 complexes with *N,N*-dimethylacetamide, ethyl ether, acetone, cyclohexylamine, and methyl acetate. It will be recalled that acetylene is very soluble in acetone and has customarily been transported as an acetone solution, for safe handling [125].

Shortly after Copley and Holley's work, Stanford and Gordy [126] obtained supporting evidence of hydrogen bonding from infrared spectra of phenylacetylene mixed with oxygen- or nitrogen-containing solvents (acetone, dioxane, triethyl phosphate, *N,N*-dimethylacetamide, pyridine, and related bases). Recent investigations, principally by infrared spectroscopy and/or NMR spectroscopy, have yielded much additional evidence of C–H...O and C–H...N formation in acetylene and related compounds, as well as evidence of C–H bonding to other *n*- or *π*-electron donors. Most of the work, though of general interest, is not closely pertinent to our topic, and only a few examples will be mentioned. Some of the additional work is reviewed in references cited [104, 127–30].

Brand and co-workers [127] found that in general the comparative infrared spectral behavior of acetylene derivatives correlates well with their chemical reactivities. They noted also that gas-liquid chromatography supplies evidence for hydrogen bonding—whenever hydrogen bonding to the stationary phase can occur, the retention time of an acetylene derivative is substantially increased. For 1:1 association of phenylacetylene with ethyl ether they computed $K_{\text{assocn.}} = 1.1$ (mole fraction units, CCl_4, 29°), $\Delta H = -1.4$ kcal/mole, and $\Delta S = -4.5$ cal/mole deg.

Kreevoy and co-workers [128], applying both IR and NMR spectroscopy, estimated for the phenylacetylene-pyridine 1:1 complex an association constant in the range 0.1–0.2 (liter/mole, CCl_4).

In view of the *π*-electron donor character of acetylene derivatives, mentioned earlier (sec. 3.4.2), a tendency toward self-association is to be expected in C–H containing acetylenes. Brand and co-workers found such evidence [127] in the infrared spectra of all compounds which they studied in the liquid state—for example, *n*-hexylacetylene (1-octyne), phenylacetylene, and ethyl propiolate (propynoic acid ethyl ester). Josien and co-workers [129] demonstrated self-association of 1-heptyne and 1-deutero-1-heptyne (in CCl_4) by infrared spectroscopy, as well as association of these two hydrocarbons with carbon disulfide, ethers, ketones, and aromatic hydrocarbons. Like other proton donors, acetylenes associate more strongly with aromatic hydrocarbons as the latter increase in basic character.

West and Kraihanzel's more recently published infrared investigations [130] included a fuller study of the basic properties of acetylenes and the self-association of "terminal" acetylenes. They pointed out that acetylene derivatives such as phenylacetylene and propargyl halides have more than one electron donor center—the acetylene bond and also *π*-electrons of the aromatic ring and *n*-electrons on the halogen atoms. West and Kraihanzel found that self-association of 1-alkynes is very incomplete, even in the pure liquids, and so has only a slight effect on the macroscopic physical properties.

c. Other studies of C–H *containing solvents.* Shatenshtein (ref. [25], sec. III) has discussed the behavior of hydrocarbons as acids in types of reactions with which this review is not concerned, such as the formation of organometallic compounds and hydrogen isotope exchange reactions with bases.

Recently Allerhand and Schleyer published a comprehensive survey, based on infrared spectroscopy, of the ability of C–H groups to serve as proton donors in hydrogen bonding [104]. Their results were obtained using two strong proton acceptors—pyridine-d_5 and methylsulfoxide-d_6 (in carbon tetrachloride). Among their conclusions are the following:

(1) A marked spectral shift is definite evidence for hydrogen bonding; the absence of a detectable band shift or alteration in band intensity means that hydrogen bonding, although not necessarily absent, is unimportant.

(2) The capacity of a C–H group to act as a proton donor in hydrogen bonding varies with the carbon hybridization,

$$C(sp)\text{–}H > C(sp^2)\text{–}H > C(sp^3)\text{–}H,$$

and increases with the number of adjacent electron-withdrawing groups.

(3) More than one electron-withdrawing group must be attached to an sp^3-hybridized carbon for any C–H hydrogens to participate in hydrogen bonding.

(4) When three or more chlorines are attached to the benzene ring the aromatic protons become labile enough for bonding to strong proton acceptors. As an example, *sym.*-trichlorobenzene bonds to pyridine.

(5) The relative proton donor capacities of the haloforms is

$$CHBr_3 > CHI_3 > CHCl_3.$$

(This conclusion is in disagreement with results cited in sec. 3.4.5a, in which the reference base was acetone or tetrahydrofuran.)

(6) Methyl groups do not hydrogen bond, and neither do C–H groups in alkyl chains, aldehydes, formates, or formamides.

(7) C–H groups can have a very wide range of proton donor abilities. Spectral shifts range to well over 100 cm^{-1}.

3.4.6. Chemical Reactivity of Halogenated Hydrocarbons

In the use of halogenated hydrocarbons as "inert" solvents, their chemical reactivity has sometimes been overlooked. *Chloroform* is well known to react with atmospheric oxygen when kept in colorless glass containers [131]. Carbonyl chloride (phosgene) and hydrogen chloride are products. Before its employment as an aprotic solvent, the ethanol (0.5–1%) added to chloroform as a stabilizer must, of course, be removed [131]. *Dichloromethane* behaves similarly to chloroform [131]. In the writer's laboratory, *1,2-dichloroethane* (*ethylene chloride*) of high commercial grade has been found to acquire a pronounced acidic reaction within a few days when stored in a colorless glass container in diffuse daylight, but no acidic reaction is observed after prolonged storage in an amber glass bottle. Formation of acid is detected conveniently by adding a benzene solution of an indicator base such as methyl yellow.

Müller and Ehrmann [132] exposed several halogenated hydrocarbons to radiation from a mercury vapor lamp in the presence of dry nitrogen or oxygen. With nitrogen, no change was observed, but with oxygen, reaction occurred, one product being hydrogen chloride. The other principal products identified are listed in table 13.

Table 13. *Products formed on irradiating halogenated hydrocarbons in the presence of dry oxygen* [a]

Compound Irradiated	Main Product
1,2-Dichloroethane	Monochloroacetic acid
sym.-Tetrachloroethane	Dichloroacetyl chloride
Pentachloroethane	Trichloroacetyl chloride
Trichloroethylene	Dichloroacetyl chloride
Tetrachloroethylene	Trichloroacetyl chloride
Chlorobenzene	No change
Benzyl chloride	Benzoic acid
1,1-Dichlorotoluene	Benzoyl chloride

[a] From Müller and Ehrmann [132].

Because of the considerable use of *carbon tetrachloride* as a solvent in infrared spectroscopy, evidence of its reactivity with nitrogen bases warrants special mention. Several workers have observed its reaction with triethylamine at room temperature [133–136]. Protection from daylight retards the reaction. Joesten and Drago [137], when studying the association of triethylamine with phenol in carbon tetrachloride, minimized the concentration of free amine in contact with carbon tetrachloride by first mixing the amine with the phenol and then adding the solvent.

Reference:

[132] E. Müller and K. Ehrmann, Chem. Ber. **69B**, 2207 (1936).

Stevenson and Coppinger [136] studied the reaction of triethylamine with several tetrahalogen derivatives of methane, and concluded that the order of reactivity of the halo-derivatives is

$$CBr_4 > CBrCl_3 > CCl_4 > CFCl_3.$$

They believe that 1:1 amine-halide association occurs first, with subsequent formation of amine hydrohalide and chloroform. Reaction also occurs in mixtures diluted with isooctane. Di-*n*-propylamine and tri-*n*-propylamine were found to react similarly with carbon tetrachloride.

Reaction of piperidine with carbon tetrachloride has also been observed [138, 139]. The reaction was at first thought to be catalyzed by copper in a chromium-plated brass hypodermic needle [138], but later observers of the reaction [139] claimed that copper is dissolved, and therefore is not a catalyst for the reaction. Still others [155, 157] have commented on the reactivity of amines with carbon tetrachloride.

In checking claims that *chloroform* likewise reacts with triethylamine, Williams [140] concluded that purified chloroform is "almost unreactive," the seeming reactivity of chloroform B.P. being due to impurities (mainly to CH_2BrCl). These conclusions were supported by Foster [134].

Sadek and Fuoss reported unexpected reactivity of carbon tetrachloride with ethanol [65]. Mixtures of the two solvents showed much higher conductance than either of the separate liquids, and after several hours the conductance had more than doubled. Methanol is a great deal less reactive with carbon tetrachloride. Mass-spectrometric examination of products formed by irradiating a mixture of carbon tetrachloride and ethanol indicated that hydrogen chloride and carbon monoxide are among the compounds formed. Phosgene may be an intermediate product.

3.4.7. "Dipolar Aprotic" Solvents

Parker [141] has devoted considerable study to the behavior of a group of solvents which he characterizes as "dipolar aprotic" solvents. These are defined as "solvents with dielectric constants > 15, which . . . cannot donate suitably labile hydrogen atoms to form strong hydrogen bonds with an appropriate species." The following are examples: Acetone, acetonitrile, benzonitrile, dimethylacetamide, dimethylformamide, methyl sulfoxide, nitrobenzene, nitromethane, and sulfolane (tetramethylenesulfone). These solvents have dipole moments in the range 2.7–4.7 [141, 142] and dielectric constants in the approximate range 21–46.5. On referring to table 3 (sec. 3.3) it will be noted that solvents such as these were assigned to *Brønsted's fourth class*. "Dipolar aprotic" solvents, like the aprotic solvents just discussed, are not *completely* lacking in acid-base properties even though they do not display strong tendencies toward hydrogen bond formation. As will be seen in section 4, the limited hydrogen bonding capacities of solvents of Brønsted's fourth and eighth classes causes hydrogen bonding of solutes to become much more apparent than in aqueous and alcoholic solutions.

Current investigations, in which dipolar aprotic solvents are being much used, have led to a revival of interest in varied kinds of evidence that some solvents of this group may form dimers, as well as weak 1:1 complexes with other dipolar aprotic solvents. Such complex formation is believed to be due predominantly to antiparallel, electrostatic, multipolar interactions involving localized polar groups rather than entire molecules [143–145]. Some years ago Højendahl [146] postulated an interaction of the sort to account for the variation of the polarization of nitrobenzene in benzene solutions as a function of its concentration. The variation could be accounted for fairly well in the dilute range of concentrations on assuming that part of the nitrobenzene molecules associate in pairs with opposed dipoles, the resultant moment being zero.

The postulate of specific interactions between neighboring molecules is not always needed in accounting for "static" dielectric constants of polar liquids. Buckley and Maryott [147] modified the Onsager-Kirkwood theory of the static dielectric constant of polar liquids [148, 149] by considering the influence of molecular shape, and found that on treating some molecules as prolate spheroids and others as oblate spheroids the "deviation factor," G, became unity or very nearly so, over a wide range of temperature, signifying agreement of theory and experiment. Such cases included benzonitrile, propionitrile, chlorobenzene, ethyl bromide, ethyl ether, methyl ethyl ketone, and nitromethane. It was not necessary to postulate specific molecular interactions or dipole associations. In the case of nitrobenzene, however, the assumption of association seems needed. (Hydrogen bonded liquids were excluded from consideration.)

Nitromethane, another dipolar aprotic solvent, is widely thought to be self-associated. The de Maines and co-workers [150] have itemized many types of experiments which indicate self-association of nitromethane in the pure liquid and when diluted with inert solvents. From ultraviolet absorption data they calculated closely similar dimerization constants for carbon tetrachloride and n-heptane solutions (105.1 and 104.2, respectively, liter/moles, 20°). The respective values found for ΔH (kcal/mole) and ΔS (cal/mole deg) were -0.34 and -12.8.

3.4.8. Concluding Discussion of Solvents

The investigations summarized in the preceding paragraphs show convincingly that practically all so-called "inert" solvents display measurable acid-base character when examined (in suitable environments) by very sensitive modern techniques, thus extending prior chemical evidence and conclusions from older physical measuring techniques.

Although hydrogen bonding is by no means the only factor involved in solute-solvent interactions (for example, see Williams' and Hallam's reviews of infrared studies of molecular interactions [151, 152]), there seems clear evidence that very commonly it is a major factor. Bellamy and co-workers [95] (see table 14) showed that the frequency shifts of the N–H stretching mode of pyrrole (serving as reference proton donor) in 20 solvents of varied character increase progressively from n-hexane, one of the most inert solvents, to pyridine, a well-recognized hydrogen bond former with proton donors. It can be seen by inspection that the frequency shifts ($\Delta\nu/\nu \times 10^3$) are *not* linearly related to the dielectric constants of the solvents.

Extending earlier work by Gordy with numerous basic solvents and different proton donors (HCl, MeOD, D_2O) [153], Bellamy and co-workers compared the frequency shifts of the N–H stretching mode of pyrrole with corresponding frequency shifts for other proton donors in solvents ranging from inert to recognized proton acceptors. Part of the results obtained by (or cited by) Bellamy and

TABLE 14. *Relative frequency shifts ($\Delta\nu/\nu \times 10^3$) in hydrogen bonding of pyrrole to organic solvents* [a]

Solvent (ϵ)	$\Delta\nu/\nu \times 10^3$ (N–H)	Solvent (ϵ)	$\Delta\nu/\nu \times 10^3$ (N–H)
n-Hexane (1.9)	6.8	Benzene (2.3)	20.4
Carbon tetrachloride (2.2)	8.5	Nitrobenzene (34.8)	22.9
Chloroform (4.8)	12.5	Mesitylene (2.3)	25.8
Carbon disulfide (2.6)	13.9	Acetonitrile (37.5)	30.6
Chlorobenzene (5.6)	14.7	Ethyl acetate (6.0)	34.6
sym.-Tetrachloroethane (8.2 [b])	15.6	Acetone (20.7)	39.6
Bromobenzene (5.4 [b])	16.4	Cyclohexanone (18.3)	47.3
sym.-Tetrabromoethane (7.0 [b])	17.6	Dioxane (2.2)	50.2
1,2-Dichloroethane (10.2)	18.4	Ethyl ether (4.3)	50.4
Nitromethane (35.9)	19.8	Pyridine (12.3)	88.1

[a] Referred to the vapor state. Excerpts from table 1 of Bellamy and co-workers [95].

[b] From ref. [35].

REFERENCES:

[95] L. J. Bellamy, H. E. Hallam, and R. L. Williams, Trans. Faraday Soc. **54,** 1120 (1958).

[35] A. A. Maryott and E. R. Smith, Table of Dielectric Constants of Pure Liquids, NBS Circ. 514, Aug. 10, 1951.

co-workers are shown in figure 7. Clearly, the shifts for the four different proton donors indicated (pyrrole, HBr, MeOD, $B_{10}H_{14}$) are linearly related, to a good approximation, even though the proton donors vary considerably in donor capacity. This result led the authors to observe [95]: "It would seem that the nature of any complex formed due to the association of, say, pyrrole with benzene is essentially similar to that formed by any of the other solutes with the same solvent. This suggests that hydrogen bonding . . . is the major factor involved in all cases."

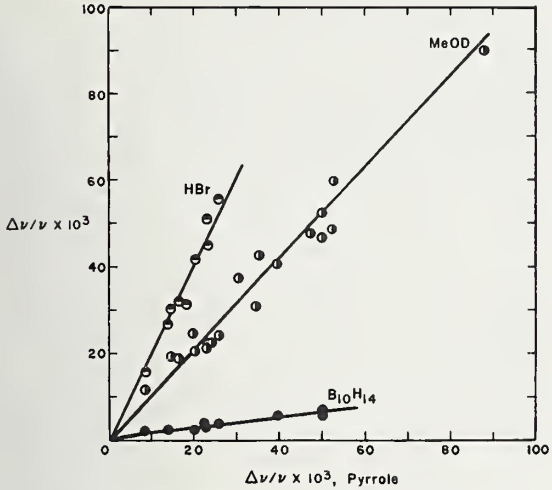


FIGURE 7. *Frequency shifts of the* HBr, MeOD, *and* $B_{10}H_{14}$ *stretching modes in a variety of solvents, compared with the corresponding frequency shifts of the* NH *stretching mode of pyrrole.*

Based on data obtained or cited by L. J. Bellamy and co-workers [95].

One of the main purposes of section 3 has been to show that most of the aprotic solvents are not truly inert, but show proton donor-acceptor behavior, thus affecting quantitative relationships observed in studying interactions between stronger acids and bases. When this is borne in mind, the aprotic solvents are admirably suitable media for ascertaining differentiating kinds of acid-base behavior that are masked in amphiprotic and other active solvents. In years to come they should find much more extended use in analysis and other chemical applications.

For the most part, the remainder of the discussion will be concerned with much stronger proton donor-acceptor reactions, involving compounds generally thought of as acids and bases because they are measurably ionized in water.

4. The Role of Hydrogen Bonding in Aprotic Media

We have come to the central theme of this discussion, namely, the varied types of hydrogen bonding which determine overall acid-base behavior in aprotic solvents.

Hydrogen bonding plays a major role in all types of solvents. It is responsible for the most characteristic properties of water as a solvent—for example, its high dielectric constant, its "leveling effects" on dissolved acids and bases, and the formation of "iceberg" structures about inert solutes—and a widening recognition of its importance is responsible for recent intensified interest and new approaches in the study of aqueous behavior.

Hydrogen bonding is equally important in aprotic solvents. In section 3.4 it was shown that even these solvents, although frequently referred to as "inert," display significant and differing hydrogen bonding tendencies. However, in these solvents the interactions of principal interest are the much stronger interactions between dissolved species. To comprehend acid-base behavior in aprotic solvents one must become acquainted with different types of intermolecular hydrogen bonding reactions that are likely to be occurring simultaneously, as well as with the relative strengths of such interactions.

Intramolecular hydrogen bonding (chelation) assumes greater importance in aprotic solvents than in leveling solvents. Among the *intermolecular* hydrogen bonding reactions of particular importance are self-association of acids, bases, and salts, formation of hydrogen-bonded ion pairs, and the formation of conjugate and heteroconjugate ions. The objective of this section is, first, to assemble experimental evidence about various kinds of hydrogen bonding interactions, obtained by many procedures, such as cryoscopy and ebullioscopy, conductance, electric polarization measurements, and absorption spectroscopy. The section will then be concluded with a brief discussion of theoretical aspects of hydrogen bonding in aprotic solvents.

4.1. Self-Association of Nitrogen-Containing Bases

Self-association through formation of NH...N bonds is now known to occur rather widely among heterocyclic bases, aromatic amines, and also aliphatic amines, both in the liquid and solid states and also as concentrated solutions in inert solvents. Compounds not having a hydrogen atom attached to nitrogen—for example, triethylamine and pyridine—do not, of course, undergo such self-association.

Like types of hydrogen bonding that were discussed earlier, NH...N formation was inferred some years ago from such evidence as solubility behavior and cryoscopic or ebullioscopic data, with later substantiation by newer techniques like dielectric polarization, infrared spectroscopy, and NMR spectroscopy. The NH...N bond seems to be comparatively weak—weaker, for example, than the OH...O bonds formed by aggregation of alcohol molecules. Occasional failures to detect its formation have been ascribed to use of too dilute solutions, too limited a concentration range, or instruments of insufficient sensitivity. In some cases, NH is considered to become bonded to a π-electron system.

Studies of NH...N formation have followed the common pattern of first obtaining varied qualitative evidence, with succeeding attempts to determine association and thermodynamic constants. Investigations are now in the second stage. The small association constants are experimentally difficult to determine, for such reasons as sensitivity of the bases towards atmospheric moisture (which may affect the extent of aggregation), susceptibility to oxidation, and reaction with solvents like carbon tetrachloride. The magnitude of the association constant will be somewhat affected by the degree of inertness of the aprotic solvent selected. The association constants obtained also depend on assumptions made with regard to the composition of the hydrogen-bonded aggregates (that is, whether they are dimers, trimers, tetramers, mixed species, etc.) and their structure (linear or cyclic). Consequently, the association constants determined in different laboratories are often not in close agreement. Comparison of results is impeded somewhat because the choice of concentration units varies with the areas of interest of investigators, some of whom prefer mole fraction units, while others prefer molar or molal units. The symbols K_c, K_m, and K_x (or K_N) are generally used to designate equilibrium constants in molar, molal, and mole-fractional units, respectively. In *dilute solutions*, the following relations are approximately correct for *association* reactions [78, 170]:

$$K_c = K_m / d_4^t \text{ of solvent,} \tag{26}$$

$$K_c = K_x \text{ (mol. wt. of solvent)/(1000 } d_4^t\text{, solvent).} \tag{27}$$

(It will be realized, of course, that the reciprocals of these conversion factors must be applied to *dissociation* constants [32].)

Most authors now refer to the various self-aggregates as "multimers" [153a] or as "*n*-mers," avoiding the term "polymers" because of its different significance. "Oligomer" is another new term, applied when *n* has a small value [169–171].

4.1.1. Aliphatic Amines

Not surprisingly, tertiary aliphatic amines, which cannot form NH...N bonds, often show strikingly different behavior from that of primary and secondary amines. Marvel and coworkers [107] noted, for example, that the heat of mixing of dimethylcyclohexylamine with chloroform is much higher (approx. 1.2 kcal/mole, 3°) than that of cyclohexylamine (0.8 kcal) or *n*-butylamine (0.7 kcal), and suggested that the low values for the primary aliphatic amines may be due to N–H...N association. In later studies, Lambert and Strong [154] measured the second virial coefficients of ammonia and primary, secondary, and tertiary methyl- and ethylamines (as vapors, 20 to 130 °C), and interpreted the results as showing dimerization to occur with all of the compounds except tertiary methyl- and ethylamine. From Raman and infrared spectral data for pyrrolidine over a wide temperature range, Evans and Wahr [155] concluded that gaseous pyrrolidine is monomeric, but most, if not all, molecules of liquid pyrrolidine (25°) are associated by N–H...N bonds, while there is partial association in carbon tetrachloride solutions. (Pyrrolidine was observed to react slowly with carbon tetrachloride; compare sec. 3.4.6.) Linnell and co-workers [156] determined the dimerization constant of pyrrolidine in carbon tetrachloride from infrared data, obtaining the approximate value 0.89 (liter/mole). Feeney and Sutcliffe [157] studied *n*-mer formation of mono- and diethylamine, isobutylamine, and ammonia (CCl_4) by NMR spectroscopy, while Bystrov and Lezina [158], also applying NMR, investigated N–H...N formation in the following bases (CCl_4): Methyl- and dimethylamine, ethyleneimine, trimethyleneimine, pyrrolidine, piperidine, and hexamethyleneimine.

Wolff and co-workers have performed very detailed studies of hydrogen bonding by primary aliphatic amines, employing Raman spectroscopy [159], vapor pressure measurements [160, 161], and infrared spectroscopy [162, 163]. The following primary amines, dissolved in aliphatic hydrocarbon solvents, were included in the investigations: Methyl, ethyl, *n*-propyl, *n*-hexyl, and *n*-decyl.

From Raman spectroscopy they concluded that on the assumption that the amino nitrogen is sp^3-hybridized the most probable structures are ones in which only one hydrogen of the amino group forms a hydrogen bond, the other remaining free. Infrared data (−110 to +190°) supported this conclusion for amines in the liquid state, but in crystallized methylamine the results seemed to indicate that both hydrogens of the amino group take part in hydrogen bonding. For carbon tetrachloride solutions the existence of the monomer and of cyclic dimers and trimers was deduced. The mean association energy of methylamine (CCl_4) was calculated to be about 2 kcal/mole (within the limits of error), in agreement with the result obtained from vapor pressure measurements (mostly, −55 to +20°) of the system methylamine-*n*-hexane. The same mean energy of association was found for the other amines studied. At low temperatures and high amine concentrations, besides NH...N bonds, C–H...N bonds are also thought to form.

Vapor pressure data led Wolff and associates to the conclusion that at room temperature and a methylamine mole fraction of < 0.15, the associated particles consist of monomers, dimers, trimers, and tetramers. Representative data which they obtained are shown in tables 15 and 16. Table 15 compares association constants obtained for methyl-, ethyl-, and *n*-propylamine (*n*-hexane, −20 to +20°,

TABLE 15. *Comparative association constants of primary aliphatic amines from vapor pressure data* (*n-hexane, mole fraction units*)[a]

Amine	t, °C	$K_{1,2}$	$K_{2,3}$	$K_{3,4}$
$MeNH_2$	+20	[b] 1.52	2.56	3.85
	0	1.99	3.46	5.17
	−20	2.67	4.72	7.04
$EtNH_2$	+20	1.17	2.06	3.13
	0	1.55	2.74	4.12
	−20	2.02	3.62	5.41
n-$PrNH_2$	+20	1.00	1.89	2.86
	0	1.31	2.37	3.56
	−20	1.92	3.38	5.04

[a] Selected from results of Wolff and co-workers [161].
[b] $K_{1,2}$ (liter/mole) = 0.198.

REFERENCE:

[161] H. Wolff, A. Höpfner, and H.-M. Höpfner, Ber. Bunsenges. Physik. Chem. **68**, 410 (1964).

mole fraction units). The constants were computed for stepwise conversion of monomer to the dimer, trimer, and tetramer. The following conclusions were drawn: (1) Under similar conditions, primary amines are less associated than alcohols; (2) for each amine, the equilibrium constants for dimer, trimer, and tetramer formation are different, and increase in the order named. (This means that the associations cannot be described as "associations derived by repeatable steps," an assumption often made in studying *n*-mer formation.); (3) with increasing carbon content, the amines become less highly associated; (4) with decreasing temperatures, all association constants show the expected increases; (5) the heats of formation for the different reactions are not measurably different (all are ~ −2 kcal/mole).

Table 16 indicates how the chain length of the solvent affects the K values for *n*-mer formation from methylamine. The results shown are representative of those obtained with ethyl- and propylamine. It is noteworthy that when $K_{\text{assocn.}}$ values are expressed in mole fraction units, they show a decrease with increasing chain length of the solvent, whereas $K_{\text{assocn.}}$ values in molar concentration units show the opposite trend (see footnotes to table 16).

4.1.2. Aromatic Amines

Solubility determinations [105] and infrared data [164–166] furnished part of the early evidence for NH...N formation by aniline. Recent results, obtained mainly by spectroscopy (IR, UV, and NMR), have yielded conflicting conclusions, but again, those favoring NH...N formation as the explanation for associative tendencies offer the more convincing arguments.

TABLE 16. *Effect of diluent and temperature on self-association of methylamine* (*mole fraction units*)

Diluent	t, °C	$K_{1,2}$	$K_{2,3}$	$K_{3,4}$
n-Butane	+15	[b] 1.93	3.33	4.96
	0	2.33	4.08	6.08
	−20	3.06	5.45	8.13
	−40	3.88	7.04	10.5
n-Hexane	+20	[c] 1.52	2.56	3.85
	0	1.99	3.46	5.17
	−20	2.67	4.72	7.04
	−40	3.68	6.62	9.86
n-Nonane	+20	[d] 1.28	1.92	2.88
	0	1.68	2.75	4.12
	−20	2.32	3.98	5.93
	−40	3.28	5.80	8.63

[a] Table 4 of Wolff and co-workers (abridged) [161]; from vapor pressure data.
[b] K (liter/mole) = 0.190.
[c] K (liter/mole) = 0.198.
[d] K (liter/mole) = 0.230.

REFERENCE:

[161] H. Wolf, A. Höpfner, and H.-M. Höpfner, Ber. Bunsenges. Physik. Chem. **68**, 410 (1964).

Examples of other aromatic amines for which NH...N formation has been postulated are: *o*- and *p*-Toluidine, *o*- and *m*-chloroaniline, diphenylamine, α-naphthylamine, and *N*-methyl- and *N*-ethylaniline [165–166]. Intermolecular NH...N formation is not expected, of course, nor observed [165] in the case of *ortho*-substituted aromatic amines like *o*-nitroaniline and methyl anthranilate, for which there is very abundant, well-known evidence of intramolecular hydrogen bonding (chelation). Moreover, steric factors are important in NH...N formation, as in all other known types of hydrogen bonding.

Whetsel and co-workers [167] measured the near-infrared N–H absorption bands of aniline and a few other primary aromatic amines in several solvents (C_6H_{12}, CCl_4, $CHCl_3$, CS_2, C_6H_6, MeCN) at various concentrations, and observed an appreciable effect of concentration and solvent on the positions and intensities of the bands. The bearing of these results on qualitative and quantitative analyses of aromatic amines by near-infrared spectroscopy was pointed out. More detailed studies have since been undertaken to elucidate the molecular interactions which cause the spectral shifts. A recent paper by Lady and Whetsel [168] reports intensive studies of the first overtone N–H symmetric stretching band of aniline (C_6H_{12}, 10 to 70°). The data were analyzed by different methods, including graphical methods of Rossotti and co-workers [169–171]. For concentrations up to 4 *M*, the results are consistent with the postulate that monomer coexists with hydrogen bonded dimer and (cyclic) tetramer. A similar model is thought to be valid for *m*-toluidine and *m*-chloroaniline, also. Up to 0.2 *M*, a simple model involving only dimerization holds fairly well for aniline.

The heats of formation found for aniline dimer and tetramer are about −1.6 and −7.7 kcal/mole, respectively. The corresponding association constants, which are somewhat more uncertain, are about 0.2 and 3–4 liter/mole [168]. Dimerization constants of about 0.3 and 0.15 (cyclohexane, liter/mole) have been estimated for *N*-methyl- and *N*-ethylaniline, respectively.

Dearden [172] investigated the self-association of aniline (C_6H_{12}) by ultraviolet spectroscopy. In analyzing the data, he assumed that all associated species have the same molar absorptivities (which he considers to be not strictly true), and also assumed that *either* dimer, trimer, *or* stepwise multimer formation takes place; the respective constants obtained are about 2 liter/mole, 80 (liter/mole)^2, and 2.7 liter/mole.

It should be borne in mind that bases like aniline, which are sufficiently good proton donors for self-association, are readily hydrogen bonded to other basic species. As an example, Few and Smith found (in agreement with earlier Russian work) [173] that the apparent molar polarization of aniline and methylaniline at infinite dilution is much greater in dioxane than in benzene, while with dimethylaniline, the difference is much smaller; these results were attributed to bonding of amino hydrogen to oxygen of dioxane, with resulting modification of the charge distribution. In more recent work, Dodd and Stephenson [174] have studied N–H infrared frequency shifts of amines in solvents like acetone and pyridine, attributing the shifts to hydrogen bonding, with the aromatic amine serving as the proton donor. Many other possibilities for hydrogen bonding between primary or secondary aromatic amino groups and other basic groups are readily imagined. The interacting groups may, of course, be present in the same or different molecules.

4.1.3. Amidines, Guanidines, and Miscellaneous Heterocyclic Bases

Self-association through N–H...N formation has been studied most extensively for bases of the types listed in table 17. The references cited in the table are mostly to recent papers; some of these review earlier work.

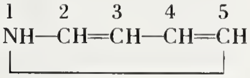
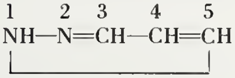
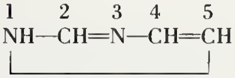
Pyrrole (III) as a proton donor in hydrogen bonding was mentioned earlier (see tables 5 and 14, fig. 7, and related discussion). Happe concluded (NMR data, cyclohexane) [178] that pyrrole forms a dimer in which the NH of one ring is bonded to π-electrons of a second ring. He estimated $K_{1,2}=4.3$ (m.f.)$^{-1}$ (which is equivalent to about 0.46 liter/mole), assuming either an open dimer (with one free NH) or a closed ("cyclic") dimer (no free NH). This value of $K_{1,2}$ corresponds to about 1 percent dimerization in 0.01 *M* solution. The solutions examined were considered dilute enough to exclude formation of significant amounts of higher multimers. Lumbroso reported (IR data, CCl_4, 21°) [180] a $K_{1,2}$ value of about 0.2 liter/mole, assuming a cyclic structure. Dielectric polarization measurements yielded the following approximate values (believed to be underestimates): 0.14 (C_6H_{12}); 0.09 (CCl_4). In benzene or dioxane, the dimerization constant was estimated to be about 0.06, a value considered unreliable because both solvents are basic enough for hydrogen bonding to pyrrole. Lumbroso shares Happe's view that in the dimer NH is bonded to π-electrons of a second ring, but favors the closed structure because it accounts best for the dielectric polarization data, even though hydrogen bonds would be linear in open dimers, bent in closed dimers.

Several workers have studied the 1:1 association of pyrrole with other bases (for example, pyridine, triethylamine, dioxane) [176–180]. The most probable value of $K_{\text{assocn.}}$ (liter/mole) for the pyrrole-pyridine complex seems to be in the range 2.5 to 2.7 [176–179]. A recently obtained value for ΔH of association is −3.2 kcal/mole (25°, CCl_4, IR data) [179]. The hydrogen bond in this complex is probably of the N–H...N type, though some bonding to the π-electrons of pyridine is considered possible [178].

Formation of NH...N bonds by *pyrazole* (IV) and some of its alkyl or aryl derivatives in aprotic solvents (C_6H_6, CCl_4, $CHCl_3$, and others) was first studied cryoscopically [181], then by infrared [171, 182] and NMR [183] spectroscopy. Details of the carefully analyzed results will be found in the papers cited. It would appear that in solutions of pyrazole in aprotic solvents (CCl_4, $CHCl_3$, CH_2Cl_2, CS_2, C_6H_6), at stoichiometric concentrations $\leqslant 1$ *M*, the monomer, cyclic dimer, and cyclic trimer coexist. The cyclic trimer seems to have a practically strainless structure. Derivatives such as 3,5-dialkylpyrazoles show similar behavior. The extent of association is much greater than in the case of pyrrole. Saturated solutions appear to contain significant amounts of multimers up to the decamer. Vinogradov and Kilpatrick [182] found that 3,5-dimethylpyrazole is much less self-associated in benzene than in carbon tetrachloride; this result is predictable, of course, from the ability of benzene to compete as a proton acceptor (see sec. 3.4.1).

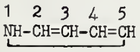
Hunter and Marriott, on determining the molecular weights of substituted *amidines* (V) and *imidazoles* (VI) (which can be regarded as cyclic amidines) in naphthalene over a range of concentration, concluded that members of these two classes have pronounced tendencies toward self-association by NH...N formation [184]. In accord with their expectations, compounds without an NH group (as, for example, 1,2-dimethylbenzimidazole) are not associated. Moreover, they observed that imidazoles have much lower melting points if the 1-position is substituted, indicating weaker intermolecular forces. From similar measurements, Roberts [185] concluded that *N,N'*-diphenylformamidine

TABLE 17. *Structures of some self-associating bases*

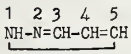
Class of base	General structure	Formula number	References
Pyrrole		(III)	[165, 166, 175–180]
Pyrazole		(IV)	[171, 181–183]
Amidine	$\overset{1}{\mathrm{R_2N}}{-}\overset{2}{\mathrm{C(R)}}{=}\mathrm{NR}$	(V)	[181, 184, 185]
Imidazole		(VI)	[169, 171, 181, 184, 186–188]
Guanidine	$\overset{1}{\mathrm{R_2N}}{-}\overset{2}{\mathrm{C}}({=}\overset{3}{\mathrm{NR}}){-}\mathrm{NR_2}$	(VII)	[181, 184]

REFERENCES:

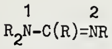
[165] W. Gordy and S. C. Stanford, J. Am. Chem. Soc. **62**, 497 (1940).
[166] N. Fuson, M.-L. Josien, R. L. Powell, and E. Utterback, J. Chem. Phys. **20**, 145 (1952).
[169] F. J. C. Rossotti and H. Rossotti, J. Phys. Chem. **65**, 926, 930, 1376 (1961).
[171] D. M. W. Anderson, J. L. Duncan, and F. J. C. Rossotti, J. Chem. Soc., p. 140, 4201, 2165 (1961).
[175] N. Fuson and M.-L. Josien, J. Chem. Phys. **20**, 1043 (1952).
[176] S. N. Vinogradov and R. H. Linnell, J. Chem. Phys. **23**, 93 (1955).
[177] N. Fuson, P. Pineau, and M.-L. Josien, J. Chim. Phys. **55**, 454 (1958).
[178] J. A. Happe, J. Phys. Chem. **65**, 72 (1961).
[179] H. J. Wimette and R. H. Linnell, J. Phys. Chem. **66**, 546 (1962).
[180] H. Lumbroso, J. Chim. Phys. **61**, 132 (1964).
[181] N. E. White and M. Kilpatrick, J. Phys. Chem. **59**, 1044 (1955).
[182] S. N. Vinogradov and M. Kilpatrick, J. Phys. Chem. **68**, 181 (1964).
[183] V. F. Bystrov, I. I. Grandberg, and G. I. Sharova, Opt. Spectry. (USSR) (English Transl.) **17**, 31 (1964).
[184] L. Hunter and J. A. Marriott, J. Chem. Soc., p. 777 (1941).
[185] R. M. Roberts, J. Am. Chem. Soc. **72**, 3608 (1950).
[186] D. G. O'Sullivan, J. Chem. Soc., p. 3278 (1960).
[187] H. Zimmermann, Z. Elektrochem. **65**, 821 (1961).
[188] N. Joop and H. Zimmermann, Z. Elektrochem. **66**, 440, 541 (1962).



(III)

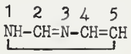


(IV)

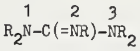


$\overset{1}{\mathrm{R_2N}}{-}\overset{2}{\mathrm{C(R)}}{=}\mathrm{NR}$

(V)



(VI)



$\overset{1}{\mathrm{R_2N}}{-}\overset{2}{\mathrm{C}}(=\overset{3}{\mathrm{NR}}){-}\mathrm{NR_2}$

(VII)

(PhNH–CH=NPh) is extensively associated in benzene at 6° and appreciably associated in naphthalene at 80°. White and Kilpatrick [181] also studied the association of this compound in benzene cryoscopically, deduced that a cyclic dimer is formed, and calculated the dimerization constant $K_{1,2}$, to be about 69 (kg of solvent/mole).

Self-association of amidines, though initially Hunter and Marriott's main interest, might have escaped recognition if the much more highly associated cyclic analogs, the imidazoles, had not been included in the investigations. As these authors pointed out, the pronounced associative tendencies of the imidazoles are probably due to their more acid character. Amidines are among the strongest organic bases. As their structure (V) indicates, the cation formed on proton addition (at the N–2 position) will be stabilized by resonance. However, simple amidines like diphenylformamidine and -acetamidine, though obtainable commercially and of potential interest as reference bases, have not been very widely studied. Tri-*N*-substituted amidines, not now commerically offered, should not be measurably associated, and thus might prove to be especially valuable reference bases for nonaqueous solutions.

Self-association of imidazoles, and also of the closely related benzimidazoles, by N–H...N formation has received considerable attention. Hunter and Marriott studied more than 30 bases of this type, finding that 1-alkyl- or 1-aryl-substituted compounds have normal molecular weights in naphthalene, while the results obtained for all compounds *unsubstituted* in the 1-position indicate extensive self-association. A later, more complete analysis of cryoscopic data (C_6H_6) for 2-*n*-butylbenzimidazole [181] indicated very extensive linear association; this conclusion has been supported by infrared data for various imidazole derivatives [169, 171, 186–188].

Anderson and associates [171] investigated the nature of oligomers of imidazole (CCl_4). They found that significant concentrations of all oligomers up to the dodecamer are present in saturated solutions, but pointed out that imidazole, in contrast to pyrazole (which, as previously mentioned, forms cyclic dimers and trimers), cannot form cyclic oligomers smaller than the decamer, for steric reasons. The linear association of imidazoles is presumed to be stabilized by resonance. It was found [171] that the hydrogen bonding equilibria of imidazole (CCl_4, $18 \pm 1°$) can be represented quantitatively by dimerization, with $K_{1,2} = 234 \pm 15$ liter/mole, and subsequent stepwise N–H...N formation, with $K_{\mathrm{assocn.}}$ (for each step) $= 760 \pm 20$ liter/mole.

Zimmermann and Joop [187, 188], who have been interested especially in theoretical aspects of NH...N bonding in imidazole and methylimidazole, have carefully reviewed and extended the available information on this topic. Their results, from varied experimental data (x-ray, IR, Raman, NMR, isotope effects, dipole moments), support the other evidence of extensive linear association.

Self-association of *1,3-diphenylguanidine* (VIII) has been observed cryoscopically, first in naphthalene (~80°) [184] and later in benzene (~5.5°, 0.005–0.1 molal) [181]. 1,2,3-Triphenylguanidine

$$\overset{1}{\mathrm{PhNH}}-\mathrm{C}(=\overset{2}{\mathrm{NH}})-\overset{3}{\mathrm{NHPh}}$$

(VIII)

and 1,1,2,3-tetraphenylguanidine seem to be unassociated in liquid naphthalene [184]. White and Kilpatrick concluded from their cryoscopic data for diphenylguanidine in benzene [181] that a linear dimer and a cyclic trimer form successively, with the association constants (molal units) $K_{1,2} = \sim 53$ and $K_{1,3} = \sim 290$ or 350 (according to the method used for calculation). The structures which they suggested for the dimer and trimer would be formed by hydrogen bonding of the type

$$\mathrm{PhNH{-}C(NH_2){=}N(Ph)\ldots H{-}NH{-}C({-}NHPh){=}NHPh}$$

This type of N–H...N formation can be thought of as arising from a hypothetical tautomeric form of diphenylguanidine (IX), in which $-NH_2$ is the

$$\overset{1}{\mathrm{PhNH}}-\mathrm{C}(=\overset{3}{\mathrm{NPh}})-\overset{2}{\mathrm{NH_2}}$$

(IX)

proton donor group, and =NPh the proton acceptor. It seems more reasonable for PhNH– to serve as the proton donor, and =NH as the proton acceptor. Considering the scientific and industrial usefulness of this compound and some other substituted guanidines, further studies of their associative behavior are very desirable. An additional need is for compounds such as (X), for example, 1,3-diphenyl-2-methylguanidine, to be made easily available for determinations of their behavior and properties.

$$\overset{1}{\mathrm{PhNH}}-\mathrm{C}(=\overset{2}{\mathrm{NR}})-\overset{3}{\mathrm{NHPh}}$$

(X)

The main purpose of the foregoing brief review has been to present evidence that N–H...N bonding, once believed to be non-existent, is of rather common occurrence. Though comparatively weak, such bonding must be taken into consideration in interpreting data and planning the most favorable conditions for experimental studies. Its occurrence seems especially likely when steric factors do not interfere and the structures formed are stabilized by resonance.

4.2. Self-Association of Acids

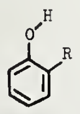
Self-association of acids through formation of hydrogen bonds of the type O–H...O – sometimes forming linear aggregates and sometimes, cyclic structures – is one of the most extensively studied and best known examples of hydrogen bonding, though much of the work is widely scattered through the literature. The first evidence of self-association of acids in aprotic solvents came from molecular weight determinations and distribution ratio data [189]; later this was confirmed and augmented by numerous other kinds of physical and chemical data.

The most familiar examples of self-associating acids are carboxylic acids, which have been studied in the vapor, liquid, and solid states, as well as in aprotic and more active solvents. In a limited number of cases, monomer $\rightleftharpoons$ dimer equilibrium constants in aprotic solvents have been obtained, and also related thermodynamic constants. Phenols, nitric acid, sulfonic acids, and phosphoric acid esters of the general formulas $(RO)P(O)(OH)_2$ and $(RO)_2P(O)OH$, where R may be an alkyl or an aryl group, have been found to display analogous associative tendencies, as would be expected on structural grounds.

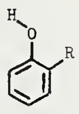
4.2.1. Phenols

The associative behavior of phenols in aprotic solvents is a subject of importance, for some of the most important reference materials for aprotic solvents are derived from phenol. For example, picric acid (2,4,6-trinitrophenol) is strong enough to serve as a standard acid in titrations [14]. Methylpicric acid (trinitro-*m*-cresol) [20], dinitrophenols [16], mononitrophenols, and various related compounds, which are weaker than picric acid, are valuable (or potentially valuable) acid-base indicators and reference acids for measuring the relative strengths of bases. Another very important group of phenolic compounds is the sulfonephthalein family of indicators—for example, bromophenol blue (3′,3″,5′,5″-tetrabromo*phenolsulfonephthalein*) [29]. Still another phenolic indicator of considerable interest is bromophthalein magenta E (3′,3″,5′,5″-tetrabromo*phenolphthalein ethyl ester*) [14].

Phenol is a much stronger acid ($pK_a = 10$) than aliphatic alcohols. Its proton donor capacity, as well as other chemical and physical properties, are well accounted for by the resonance hypothesis [190–191], according to which phenol is a resonance hybrid of Kekulé and quinoid structures. As a result of this resonance, the C–O bond has partial double-bond character, and the benzene ring and OH group tend to lie in the same plane. This planar structure leads to geometrical isomerism in *ortho*-substituted phenols (see formulas XI and XII).


(cis)

(XI)


(trans)

(XII)

However, in phenol itself and symmetrical 2,6-disubstituted phenols, the *cis* and *trans* isomers are equivalent. Self-associating tendencies are influenced by the nature of any substituents *ortho* to the OH group.

The relative donor capacities of phenols in hydrogen bond formation are expected, of course, to parallel their capacities for proton transfer to a base, and thus to increase as pK_a ($-\log K_a$) values diminish.

a. Self-association of phenol in aprotic solvents. Table 18 is a compilation of equilibrium constants for self-association of phenol in several aprotic solvents, obtained by different methods over a period of 30 years. It is evident that most of the investigators represented have favored the assumption of a monomer-dimer equilibrium at the lowest concentrations studied. However, Saunders and Hyne [196, 199] consider a six-membered cyclic trimer to be a likely structure, and think that their data (for 0.01–5 M solutions) are best represented by a monomer-trimer equilibrium. Furthermore, they believe that the NMR data of Huggins and coworkers [195] were not obtained at low enough concentrations for application of the "limiting slope" method used in calculating their $K_{1,2}$ value. Saunders and Hyne do not dispute the existence of a monomer-dimer equilibrium in solutions too dilute for measurement by present NMR techniques. In agreement with most workers, they think it likely that after the first few steps in multimerization the successive constants approach a limit or vary uniformly.

Coggeshall and Saier [194], who based their calculations (for solutions about 0.06–0.95 M) on the assumption of different values for $K_{1,2}$ and $K_{n,n+1}$, found that various alcohols and alkylphenols have constants of the same general magnitude.

Davison [200] determined $K_{1,2}$ values for *o*- and *p*-cresol and for *m*- and *p*-nitrophenol in benzene cryoscopically (~ 5 °C). The relative values follow the same order as the acidities, that is, $o\text{-Me} = p\text{-Me} < m\text{-NO}_2 \ll p\text{-NO}_2$. Other phenols for which monomer-dimer constants have been calculated include *m*-cresol (C_6H_{12}) [172], *p*-cresol (C_6H_{12}, CCl_4) [172, 198] and 4-chlorophenol [198].

Interactions of phenol with various aprotic solvents which were referred to earlier (sec. 3.4) offer a ready explanation for any small solvent effects on its self-association. Philbrick [192] attributed the comparatively low self-association of phenol in nitrobenzene (table 18) to its association with the solvent in the manner PhOH...ON(O)Ph. The distribution method which he used for obtaining dimerization constants is now known to lead to erroneous results in many cases because of the water carried into the organic layer. In some instances, there is increased association, and in others, decreased association.

Still another factor which affects association constants is temperature control. As would be expected, the extent of association decreases with rising temperature, and vice versa. Considering the various factors mentioned, the values in table 18 seem in reasonably good agreement when expressed in the same concentration units, but additional systematic study is clearly desirable.

b. Hindered phenols. The discovery of hindered phenols by Stillson and co-workers [201] has in-

TABLE 18. *Equilibrium constants for self-association of phenol in various aprotic solvents* [a]

Solvent	Temp.	Method [b]	$K_{1,2}$ [c]	$K_{1,3}$ [d]	$K_{n,n+1}$ [e]	Reference
	(°C)					
C_6H_6	25	D	0.575	……………	……………	[192]
$C_6H_5CH_3$	25	D	0.843	……………	……………	[192]
C_6H_5Cl	25	D	0.648	……………	……………	[192]
$C_6H_5NO_2$	25	D	0.196	……………	……………	[192]
C_6H_6	25	VPL	[f] 0.570	……………	……………	[193]
CCl_4	……………	IR	……………	……………	2.26	[193a]
CCl_4	Room	IR	1.39	……………	2.94	[194]
CCl_4	28	NMR	[g] 13 ± 7	……………	……………	[195]
CCl_4	21	NMR	……………	4.78	……………	[196]
CCl_4	Room	UV	[h] 2–5	……………	……………	[197]
n-C_6H_{14}	Room	UV	[h] 4.5	……………	……………	[197]
CCl_4	30	IR	[i] 7.22	……………	……………	[198]
C_6H_{12}	Room	UV	1.28	15.4	1.45	[172]

[a] Experiments are listed in chronological order. They did not all cover the same concentration range.

[b] D, distribution between aq. and org. layers; VPL, vapor pressure lowering; other symbols refer to familiar methods of absorption spectroscopy.

[c] For the reaction $2\ PhOH \rightleftharpoons (PhOH)_2$; liter/mole unless otherwise indicated.

[d] For the reaction $3\ PhOH \rightleftharpoons (PhOH)_3$; liter²/mole².

[e] For the reaction $(PhOH)_n + PhOH \rightleftharpoons (PhOH)_{n+1}$; molar units.

[f] $\Delta H \approx -2.4$ kcal/mole.

[g] (Mole fraction)$^{-1}$; 5 percent by vol. of cyclohexane was present as reference solute.

[h] Provisional values.

[i] (Mole fraction)$^{-1}$; $\Delta H = -5.1$ kcal/mole. The dimer is the predominant multimer up to about 0.2 *M*.

REFERENCES

[192] F. A. Philbrick, J. Am. Chem. Soc. **56**, 2581 (1934).

[193] E. N. Lassettre and R. G. Dickinson, J. Am. Chem. Soc. **61**, 54 (1939).

[193a] H. Kempter and R. Mecke, Z. Physik. Chem. **B46**, 229 (1940).

[194] N. D. Coggeshall and E. L. Saier, J. Am. Chem. Soc. **73**, 5414 (1951).

[195] C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, J. Phys. Chem. **60**, 1311 (1956).

[196] M. Saunders and J. B. Hyne, J. Chem. Phys. **29**, 1319 (1958); **31**, 270 (1959).

[197] M. Ito, J. Mol. Spectry. **4**, 125 (1960).

[198] M. M. Maguire and R. West, Spectrochim. Acta **17**, 369 (1961).

[172] J. C. Dearden, Can. J. Chem. **41**, 2683 (1963).

spired numerous studies of their spectroscopic (IR, UV, NMR) behavior [194, 202–213]. These phenols, which contain a bulky group (most commonly, *t*-Bu) in the 2- and 6-positions, do not give the conventional chemical tests and reactions of phenols. In pursuing their study by IR spectroscopy, Coggeshall devised (see table 19) [202] a useful classification of phenols as "unhindered," "partially hindered," or "hindered" on the basis of the shifts of the phenolic OH band on self-association (CCl_4). Since it is generally agreed that shifts of the O–H stretching frequency measure the extent of hydrogen bonding interactions, the very small shifts observed (table 19) for the chemically inactive (hindered) phenols furnish a direct indication that bulky *ortho*-groups obstruct hydrogen bonding. It has been found, as anticipated, that in some partially hindered phenols self-association does not seem to proceed beyond the dimer stage, while in hindered phenols, even dimerization does not occur.

Coggeshall's infrared data have been confirmed and extended by other workers [204, 205, 207–11]. Although 3- and 5-alkyl groups have no direct steric effect on reactions of phenolic OH, they reinforce

Table 19. *Classification of* ortho-*alkylphenols according to infrared spectral shifts observed on self-association* (CCl_4)[a]

Nature of Alkyl Substituent in		$\Delta\lambda$, μ	Classification of the phenol
2-Position	6-Position		
None or small	None or small	> 0.15	Unhindered.
Large	None or small	0.04–0.15	Partially hindered.
Large	Large	0.04	Hindered.

[a] From Coggeshall [202].

Reference:

[202] N. D. Coggeshall, J. Am. Chem. Soc. **69**, 1620 (1947).

the hindering effect of alkyl groups in the 2- and 6-positions. As an example, in the classification scheme of Sears and Kitchen [204], the relative "hydrogen bonding indexes" range from 0 (for complete hindrance, as in 2,6-*tt*-octyl-4-methylphenol) to 1 (for no hindrance, as in phenol); on this scale, the indexes for 2,6-dimethyl-, 2,4,6-trimethyl-, 2,3,6-trimethyl-, and 2,3,5,6-tetramethylphenols fall off in the sequence 0.33, 0.29, 0.20, and 0.14. This is an example of what has been called the "buttressing effect" [214]. The 3- and 5-methyl groups are presumed to force the 2- and 6-methyl groups closer to OH, thereby enhancing their hindering effects on OH.

Although the buttressing effects seem to be well established, it should not be forgotten that methyl (and other alkyl) substitutions tend to inhibit association because they reduce slightly the proton donor ability of phenol, as shown, for example, by the aqueous *pK* values for the cresols [215]. Hunter has emphasized an additional reason for not attributing chemical unreactivity and abnormal spectral behavior in 2,6-dialkyl-phenols entirely to physical obstruction of the approach of phenolic OH to other reactive groups [206]. In his view, bulky *ortho* substituents can prevent the OH group from achieving planarity with the benzene ring, thus inhibiting the resonance which makes phenols so much more strongly acidic than alcohols; in consequence, hindered phenols are "reduced to the status of tertiary alcohols." His opinion is not shared by Puttnam [209] or by Bellamy and Williams [210], who consider the OH group in hindered phenols to be largely coplanar with the ring. From studying effects of numerous proton acceptor solvents on the infrared spectra of hindered and unhindered phenols, Bellamy and Williams concluded that association of OH with other reactive groups, which occurs very rapidly in the case of phenol, is retarded when bulky groups are placed adjacent to OH, because collisions suitably oriented for association are then less frequent.

Puttnam's recent reexamination and extension of some of the earlier IR work on phenols, using a higher resolution spectrometer [209], yielded conclusions which agree very substantially with those from earlier studies. His principal conclusions with respect to alkyl-substituted phenols may be summed up as follows:

(1) In all phenols, the OH group is coplanar with the aromatic ring.

(2) A *single* alkyl (R–) substitution—other than *t*-Bu—adjacent to the OH group has only a slight effect on hydrogen bond formation.

(3) R groups in both the 2- and 6-positions cause a reduction in hydrogen bond formation. However, for R's other than *t*-Bu, a small amount of higher multimers tends to coexist with the monomer and dimer.

(4) The hindering effect of *ortho* R's increases with increasing branching. Phenols containing *t*-Bu in both *ortho* positions exist practically exclusively in the monomeric form.

These conclusions agree very well with the association constants for some hindered and partially hindered phenols (CCl_4) which are collected in table 20.

Table 20. *Association constants of some hindered and partially hindered phenols* (CCl_4, *room temp.*)[a]

Substituents present			Method	$K_{1,2}$ [b]	$K_{n,n+1}$ [b, c]
2–	4–	6–			
....	....	....	IR	1.39	2.94
....	*t*-Bu	....	IR	1.72	2.94
s-Bu	....	....	IR	1.00	0.72
t-Bu	....	....	IR	1.54	
t-Bu	Me	....	IR	0.96	
t-Bu	*t*-Bu	....	IR	1.04	
i-Pr	....	....	NMR	1.7	
i-Pr	....	*i*-Pr	NMR	1.3	
t-Bu	....	....	NMR	1.0	
t-Bu	....	Me	NMR	≤ 0.05	
t-Bu	....	*t*-Bu	NMR	[d]≤ 0.05	

[a] No substituents were in the 3- or 5-positions. IR results are from Coggeshall and Saier [194]; in the original article, the numerical values given corresponded to *dissociation* constants. NMR results are from Somers and Gutowsky [212].

[b] For the reaction $2\ PhOH \rightleftharpoons (PhOH)_2$, where PhOH signifies the substituted phenol. Concn. units: IR results, liter/mole; NMR, (mole fraction)$^{-1}$.

[c] For the reaction $(PhOH)_n + PhOH \rightleftharpoons (PhOH)_{n+1}$.

[d] Bellamy and Williams [210] concluded (IR data) that this compound is a monomer even when undiluted.

To explain why phenols containing halogen or methoxy in the 2-position have *two* infrared absorption bands in place of the single band observed for monomeric phenol and symmetrical 2,6-disubstituted phenols [216], Pauling postulated the existence of *cis*- and *trans*-isomers (XI and XII) [190]. Double bands were not observed for thymol and *o*-cresol [216]. However, Puttnam [209] detected two absorption bands for 2-*t*-butylphenol, and concluded that the configuration is mainly *trans*-; he also detected two bands for 2-methyl-6-*t*-butylphenol. Ingold [211] has concluded (IR frequencies and intensities) that 2-alkylphenols exist in the *cis*- and *trans*-configurations both in solution and in the vapor state.

c. Intramolecular hydrogen bonding in phenols [190, 206, 209, 216–24]. Chelate ring formation by hydrogen bonding is too well known a phenomenon to require detailed treatment. *Ortho*-nitro- and *ortho*-halophenols are among the best known examples of chelated structures, the tendency toward chelation being especially strong in *o*-nitrophenols because of resonance as well as favorable geometry. The hydroxy and methoxy groups are other proton-acceptor groups with recognized capacities to form stable rings by bonding to phenolic hydrogen. In general, 6-membered rings are the most stable, though 5- and 7-membered rings also occur. Obviously, *intra*molecular hydrogen bonding must occur at the expense of *inter*molecular hydrogen bonding.

Chelate ring formation stabilizes a phenol molecule in the *cis*-configuration (XI). Jaffé has pointed out that the entropy change on intramolecular hydrogen bond formation in molecules such as *o*-chlorophenol is practically negligible, because of the favorable geometry, and ΔH and ΔG are essentially equal. Apparently this is one reason why very weak intramolecular hydrogen bonds can form in preference to much stronger intermolecular bonds, even in highly polar solvents [225].

Infrared spectroscopy has contributed the largest volume of systematic knowledge about inter- and intramolecular hydrogen bonding by phenols. Commonly, though not exclusively, the studies of bonding involve observations and interpretations of changes in frequency and/or intensity of the O–H stretching vibration in the 3-micron region of the spectrum, which occur on changes of solvent or on various substitutions in the phenol molecule. It has already been mentioned that the more acidic the phenol, the more likely it is to become hydrogen bonded to electron donors. The stronger the hydrogen bond formed, the greater the change in frequency and intensity. This is illustrated (for changes in frequency) by the data in table 21, which are from work by Ingraham, Corse, and co-workers [226]. These authors found that the spectral shifts are linearly related to the Hammett σ values [227] by the following equation:

$$\nu=\nu_0+\rho_\nu\sigma. \tag{28}$$

In eq 28 ν_0 and ν are the respective frequencies of the unsubstituted and the *m*- or *p*-substituted phenol; σ and ρ are, respectively, the Hammett substituent and reaction constants. Puttnam [209] found that the frequency shifts for phenols with one *ortho*-substituent are similarly linearly related to Hammett σ values, *provided* the frequencies used are those for the *trans*-isomers.

TABLE 21. *Hydroxyl frequencies* (cm^{-1}) *of some 3- and 4-substituted phenols in* CCl_4 *and* C_2Cl_4 [a]

Substituent	CCl_4	C_2Cl_4
4-MeO	3615.6	3616.0
4-OH	....	3615.6
4-*t*-Bu	3612.1	3609.7
4-Me	3612.8	3611.7
3,5-Me_2	3611.7	3609.7
3-Me	3611.3	3610.1
None	3610.1	3610.1
4-Ph	3609.3	3607.4
3-OH	3610.1	3608.9
4-Cl	3608.5	3607.0
4-Br	3607.4	3606.2
3-NO_2	3599.9	3597.6
4-NO_2	3594.5	3591.1

[a] Excerpts from Table I of Ingraham, Corse, and co-workers [226].

REFERENCE:

[226] L. L. Ingraham, J. Corse, G. F. Bailey, and F. Stitt, J. Am. Chem. Soc. **74**, 2297 (1952).

In intermolecular hydrogen bonding, the infrared OH frequencies shift with dilution, as hydrogen-bonded species give place to the monomeric form. Intramolecular hydrogen bonding can be recognized by the constancy of frequencies on dilution.

Intermolecular hydrogen bonding of phenol to π-electron donors such as aromatic and unsaturated aliphatic hydrocarbons was discussed earlier (see tables 5 and 7). As would be anticipated, intramolecular bonding of similar types has been detected—for example, in *o*-phenylphenol [216] and *o*-allylphenol [223].

o-Hydroxybenzonitrile (*o*-cyanophenol) is incapable of forming a chelate ring because of unfavorable geometry—the –OH and –CN groups are too far apart. Consequently, it resembles its *m*- and *p*-isomers in chemical and physical behavior [228, 206, 220].

Table 22 contains examples of results obtained by Baker and Shulgin [223] in measuring the OH frequency shifts produced by various *ortho* substitutions in the phenol molecule. From their data they concluded that the strengths of intramolecular hydrogen bonds between OH and *ortho* groups increase generally in the order:

$$F < O < Cl < Br < I < S < {=}O < N.$$

The increase in $\Delta\nu$ from 346 cm^{-1} for *o*-nitrophenol to 437 cm^{-1} for 2-nitro-3,5-dimethylphenol was explained as a buttressing effect which increases the strength of the hydrogen bond. The decrease to 82 cm^{-1} for 2-nitro-3,4,6-trichlorophenol was attributed to a steric interaction large enough to

TABLE 22. *IR frequency shifts of phenols on hydrogen bonding to* ortho-*substituent groups* (CCl_4, *0.7–0.0007* M)[a]

Substituents and their position					$\Delta\nu$, O—H,
2-	3-	4-	5-	6-	
					(*cm*$^{-1}$)
F					18
OMe					52
OMe				OMe	56
Cl					61
CH_2=$CHCH_2$					63
Cl		Cl			63
Cl		Cl	Cl		67
Br					78
Cl		NO_2			83
Br		Br			83
CH_2Cl		NO_2			85
I					105
Me_2N					244
Me_2N	Me		Me		329
NO_2					346
NO_2		NO_2			388
NO_2	Me		Me		437
NO_2	Cl	Cl		Cl	[b]82

[a] Excerpts from Table II, Baker and Shulgin [223].

[b] Attributed to K. Bradley.

REFERENCE:

[223] A. W. Baker and A. T. Shulgin, J. Am. Chem. Soc. **80**, 5358 (1958).

displace the nitro group from the plane of the ring, thereby lengthening the distance between OH and NO_2 and reducing the electron donor capacity of the NO_2 group, with a consequent weakening of the intramolecular hydrogen bond. Later, Baker and Kaeding [222] revised the relative order of the four *o*-halophenols as follows:

$$I < F < Br < Cl.$$

They based the new order on spectral data obtained for six 2,6-halophenols having different halogen atoms in the 2- and 6-positions. The authors' revised explanation, which will not be repeated here, takes into account repulsive energy due to overlapping of the halogen atoms' lone pair orbitals and the O–H bonding orbital. It is noteworthy that solutions (in hexachloro-1,3-butadiene) of the *unsymmetrical* 2,6-dihalophenols exhibited a *pair* of absorption bands.

In an early estimate, based on the ratio of the areas of the IR absorption bands (CCl_4), Pauling [190] concluded that the *cis* and *trans* forms of *o*-chlorophenol are present in the ratio 10/1. Baker [221], using exhaustively purified materials, has arrived at the following *cis*/*trans* ratios for *o*-halophenols:

o-Cl, 56/1; *o*-Br, 38/1; *o*-I, 13.5/1.

Allan and Reeves, from the chemical shift parameter in NMR spectroscopy [229], have arrived at the same *cis*/*trans* ratios for *o*-chloro- and *o*-bromophenols (CS_2 solutions, 25°), and a slightly different value (19/1) for *o*-iodophenol. (In the calculations, solvation of the *trans*-form was considered to be negligible.) In agreement with Baker [221], the enthalpy of *cis-trans* isomerism was found to be 2–3 kcal/mole. Like others, Allan and Reeves find no evidence of an intramolecular hydrogen bond in *o*-fluorophenol; the attractive force maintaining it in the *cis* configuration is considered to be electrostatic in nature, because the fluorine radius is too small for bonding to phenolic hydrogen.

In studying temperature effects on hydrogen bonding, Finch and Lippincott [230] observed that the higher frequency band for *o*-chlorophenol (that is, the band corresponding to the *intra*molecularly bonded OH frequency) remained constant both in position and intensity in the temperature range 2–25 °C while, in contrast, the *inter*molecularly bonded OH frequency decreased 36 cm^{-1} when the temperature dropped from 27 to −3 °C. The absorption curves (for CCl_4 solutions, concentration not stated) are shown in figure 8. The changes in frequency and intensity of absorption for the *trans* form are in the direction expected on lowering the temperature, because of increased intermolecular hydrogen bonding.

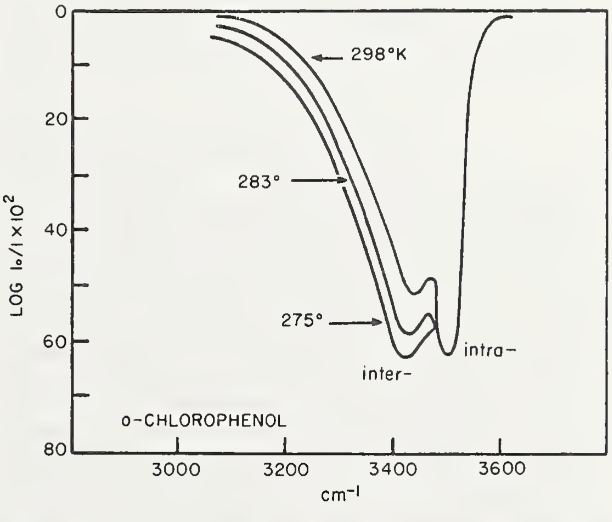


FIGURE 8. *Infrared absorption bands of intermolecularly and intramolecularly bonded* OH *in o-chlorophenol* (CCl_4) *at three temperatures; it will be seen that the position and intensity of the "inter-" band vary with temperature, whereas position and intensity of the "intra-" band remain constant.*

Reproduced from J. N. Finch and E. R. Lippincott, J. Phys. Chem. **61**, 894 (1957), with the permission of the authors and publisher. (Ref. No. 230.)

There have been numerous other IR investigations of *o*-halophenols, including several very recent studies [231–233]. Brown and co-workers [231], who are interested in the comparative biological effects of various *ortho*halophenols, have been investigating systematically electronic, steric, and solvent effects on the position and intensity of the O–H stretching absorptions in numerous *ortho*-bromophenols possessing additional substituent groups. Such studies have potential value to those employing IR spectroscopy in analyses, as well as to those interested in developing additional, or better, acid-base indicators.

The numerous conclusions of Brown and co-workers include the following:

(1) A methyl group in the 6-position of an *o*-bromophenol causes the molecule to exist solely in the chelated conformation.

(2) The phenol group in *o*-bromophenols shows a preference for intramolecular OH...Br formation over intermolecular bonding to ether (OH...OEt$_2$).

(3) Examination of *o*-bromophenol in CCl$_4$ and MeCN, singly and mixed, indicates that the dielectric constant of the solvent is of minor importance.

There is disagreement about the relative abilities of the four halogens to become bonded to *ortho*-OH. Thus, Bourassa-Bataille and co-workers [232], from measuring the IR spectra of the four *o*-halophenols in CCl$_4$-Et$_2$O mixtures, decided on the relative order,

$$F < I < Br < Cl,$$

while Jones and Watkinson [233] decided on the relative order (CCl$_2$=CCl$_2$ solutions)

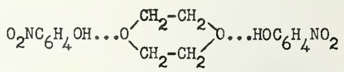
$$I < Cl < Br.$$

Both of these series disagree in part with the order deduced by Baker and Kaeding (see above).

Information about associative tendencies in phenols is needed for the proper selection of phenolic indicators for quantitative spectral studies. In view of the preceding discussion, 2,6-dibromophenols would be expected to be monomeric in solvents like benzene, and their spectral behavior should not be complicated by *cis-trans* isomerism. For such reasons, Davis and Schuhmann [14], when performing spectrophotometric acid-base studies in benzene with the phenolic indicator, bromophthalein magenta E (which can be thought of as a substituted 2,6-dibromophenol), considered it justifiable to treat it as a monomeric species. In actuality, no deviation from Beer's law was detected in the concentration range employed (1.6×10^{-5} to 3×10^{-4} *M*).

Effects of additional substituents on the strength of the intramolecular hydrogen bond in *o*-nitrophenol is another subject of continuing interest. The investigations frequently include studies of the persistence of the chelate structure when various polar solvents are added to the aprotic medium. Some of the earlier evidence was reviewed briefly by Davis [16]. The work cited and additional results of Davis indicate that in aprotic solvents strong intramolecular hydrogen bonds form in *o*-nitrophenol itself and in the dinitrophenols which contain an *o*-nitro group (that is, the 2,4-, 2,5-, and 2,6-isomers).

Baker and Shulgin's work [223] on IR spectral effects of substitutions in *o*-nitrophenol was mentioned a little earlier (see table 22). In another recent study, Dearden and Forbes [235] obtained ultraviolet absorbance data for *o*-nitrophenol and also made comparisons with the *m*- and *p*-isomers. The chelate structure of *o*-nitrophenol was found to persist on changing the solvent from cyclohexane to ether or ethanol—only very minor shifts occurred in the positions of the absorption bands. Ultraviolet shifts (expressed in wave numbers) were found to parallel approximately IR results previously reported. Von Keussler and Rossmy [234] and Cardinaud [236] have studied the comparative behavior of some phenols and deuterophenols, and discussed theoretical implications of the results. From comparisons of the IR spectral behavior of the three nitrophenols (CCl$_4$), Cardinaud deduced that both *o*-NO$_2$C$_6$H$_4$OH and *o*-NO$_2$C$_6$H$_4$OD exist only as the *cis*, chelated form; there was no trace of a band for free OH or OD. The absorption of the chelated form was not perturbed significantly by addition of dioxane. He suggests that *p*-nitrophenol tends to form dimers by "head-to-tail" association in which both nitro groups are bonded to an OH group. In contrast, he considers that *m*-nitrophenol behaves analogously to phenol, forming noncyclic aggregates. The solubility of both *m*- and *p*-nitrophenol in CCl$_4$ is too little for aggregation to proceed beyond the dimer. Dioxane greatly enhances the solubility of *p*-nitrophenol in CCl$_4$, and is thought to associate with it in the manner,



$$O_2NC_6H_4OH\ldots O\begin{matrix} / CH_2{-}CH_2 \backslash \\ \backslash CH_2{-}CH_2 / \end{matrix}O\ldots HOC_6H_4NO_2$$

Nyquist [237] has studied the absorption of various *ortho*-substituted phenols in the γ(O–H) (out-of-plane) frequency region. As indicated in other studies, a large substituent in the 6-position of *o*-nitrophenol seems to enhance the strength of the intramolecular hydrogen bond by bending the OH group closer to NO$_2$.

The conclusions from spectroscopic studies of nitrophenols merit wide dissemination. If nitrophenols are to continue playing an important role as acid-base indicators and reference acids in nonaqueous and aqueous solutions, there will be need for increased consideration of factors which affect their proton donor ability and spectral behavior. For example, it seems doubtful that 2,4-dinitrophenol, which has been used as a reference acid in a considerable volume of work in nonaqueous solvents, for studying the comparative strengths of nitrogen-containing bases, is the most suitable indicator obtainable.

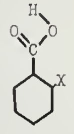
d. The Deuterium Isotope Effect in Phenols. Effects of replacing hydrogen by deuterium are discussed briefly in section 4.2.6.

4.2.2. Carboxylic Acids

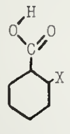
a. General discussion. It has long been known that carboxylic acids, both aliphatic and aromatic, have a pronounced tendency to dimerize, in the vapor state as well as in aprotic solvents. In fact, from some of the early studies, using relatively concentrated solutions (about 0.01 *m* and stronger), it was concluded that only double molecules were present [247]. Later work with more dilute solutions revealed the existence of a monomer-dimer equilibrium, and attempts were made to evaluate equilibrium constants.

Possible formation of aggregates higher than the dimeric form has not been excluded, and the formation of trimers, in particular, has sometimes been considered. However, the monomer and dimer are commonly regarded as being the predominant species in aprotic solvents. Generally, dimeric carboxylic acids are assumed to be cyclic, though occasionally it is suggested that part of the molecules are "open."

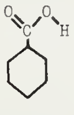
A large proportion of the investigations have included benzoic acid. Formulas indicating the three most likely conformations of the monomeric acid are shown below (XIIIa, XIIIb, and XIV). Configurations (XIIIa) and (XIIIb) are identical in benzoic acid itself, but are nonidentical in unsymmetrically substituted benzoic acids. Infrared evidence supports (XIII) [238–241]. Mansel Davies [242] indicates a hydrogen bond between the carbonyl groups; however, the two oxygens are not considered to be equivalent. When the carboxyl proton can become bonded to an *ortho* substituent, as in *o*-methoxybenzoic acid (XV) or *o*-hydroxybenzoic (salicylic) acid, configuration (XIV) is favored.



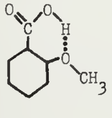
(XIIIa)



(XIIIb)

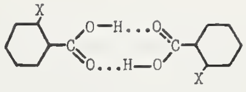


(XIV)

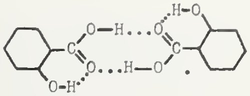


(XV)

The accepted structure for most carboxylic acid dimers is indicated by (XVI); the O–H...O bonds are considered to be linear. This has sometimes led to the conclusion that hydrogen bonds must always be linear, but there are many known cases of "bent" hydrogen bonds, notably in the case of intramolecular hydrogen bonding. A well-known example is dimeric salicylic acid (XVII), in which there is simultaneous intra- and intermolecular hydrogen bonding [190b]. Schneider, in considering the requirements for a stable hydrogen bond, X–H...Y, to form between a proton donor group XH and an electron donor group Y, concluded that hydrogen bonding will be strongest when the direction of the lone pair orbital of Y and the direction of the hydrogen bond are collinear [243]. The only requirement for XH is that the charge distribution of its orbital must leave the proton sufficiently exposed. These requirements are well met in the dimerization of carboxylic acids.



(XVI)



(XVII)

The groups composing (XVI) are considered to lie essentially in the same plane, and it is apparent that conformational isomerism can be looked for in the dimers of unsymmetrically substituted benzoic acids. For example, Brooks and co-workers [244] have discussed conformational isomerism in the dimer of *o*-methoxybenzoic acid.

The chelate structure of salicylic acid, stabilized by resonance, is thought to persist in the salicylate ion. Branch and Yabroff [245] proposed this as an explanation of the unexpectedly great strength of salicylic acid in water, and subsequently Baker [246] offered an analogous explanation (involving a doubly chelated mesomeric structure) for the still greater strength of 2,6-dihydroxybenzoic acid in aqueous solutions. Such chelate structures should be at least equally stable in aprotic solvents. In accord with this expectation, Davis and Hetzer [32] found both salicylic acid and *p*-orsellinic (2,6-dihydroxy-4-methylbenzoic) acid to behave as strong acids in benzene by the criterion of their tendencies to associate with diphenylguanidine.

b. Dimerization constants. Probably no equilibrium process has been studied by a greater variety of physical methods than the monomer-dimer equilibrium of carboxylic acids (eq 29).

$$2\,\mathrm{RCOOH} \rightleftharpoons (\mathrm{RCOOH})_2. \qquad (29)$$

The following examples, selected mainly from recent work which yielded equilibrium constants as well as qualitative evidence, illustrate the diversified approaches: *Cryoscopy* [247, 248], *ebullioscopy* at atmospheric pressure [249] and at reduced pressures [250], *isopiestic* data [251, 252] *acid catalysis* of the inversion of menthone [253], *spectroscopy* in the *visible* region [254, 254a], *dielectric polarization* data [255–258, 267b], *distribution* between immiscible solvents [259–260], *heat of dilution* data [261], *ultrasonic absorption* [262, 263], *infrared absorption* [249, 264–267], and *ultraviolet absorption* [268, 269]. *NMR spectroscopy* [270] has also been applied in studying carboxylic acid dimerization; but no association constants appear to have been reported so far.

Useful summaries of attempts to measure the self-association of carboxylic acids were included in papers by LeFèvre and Vine [255] and Allen and

Caldin [250b], covering literature up to about 1953.

The equilibrium constant for dimerization (eq 29) is most commonly symbolized by $K_{1,2}$ (or K_{12}). The rather confusing practice in some of the earlier literature of referring to the reciprocal of the dimerization constant, $K_{2,1}$ (which corresponds to the process $(RCOOH)_2 \rightleftharpoons 2\ RCOOH$), as the "dimerization constant" has been largely discontinued. An alternative symbol, K_d, has been used at times for the dimerization constant, but is increasingly applied, instead, to distribution of acids between aqueous and aprotic solvents.

The distribution method for determining $K_{1,2}$ values was widely used in the past but has been criticized increasingly on the ground that dimerization tendencies cannot be assessed accurately in wet solvents. Some 30 years ago, Fredenhagen [272] observed that cryoscopic results for solutions of organic acids dissolved in benzene which had not been carefully dried did not indicate the expected double molecule formation until the molar concentration of the acid exceeded that of the water present in the benzene. In similar experiments Bell and Arnold [247] studied the cryoscopic behavior of trichloroacetic acid in dry benzene and in an equimolar mixture with water in benzene. The results indicated that a hydrate of the composition $CCl_3COOH \cdot H_2O$ forms in wet benzene in preference to the acid dimer. Wenograd and Spurr [260] determined the dimerization of several aliphatic acids in both dry and wet carbon tetrachloride, by infrared spectroscopy and distribution data, respectively. Their results indicated that the values obtained by the distribution method do not apply to acid association in the dry solvent. Christian and coworkers [273] have strongly criticized the distribution method, adding the following statement: "We also wish to emphasize that the presence of tiny amounts of dissolved water can lead to erroneous results in the case of other methods for determining association constants for carboxylic acids. In fact, we suspect that a major reason for the lack of agreement between various literature values of association constants of carboxylic acids in solution is that small, variable amounts of dissolved water have been present in most of the systems investigated." Their work indicated that acetic acid, like trichloroacetic acid [247], forms the monomer monohydrate in preference to the anhydrous dimer when dissolved in wet benzene.

TABLE 23. *Log* $K_{1,2}$ *values for miscellaneous carboxylic acids* (CCl_4, *25°*)

Acid	pK_a, Water [a]	Log $K_{1,2}$ (liter/mole)[b]		Reference
		Dry solvent (IR)	Wet solvent (D)	
Benzoic	4.20	3.37	....	[267a]
Trichloroacetic	0.64	2.43	....	[267]
		2.72	....	[264]
Dichloroacetic	1.26	3.04	....	[264]
Chloroacetic	2.86	3.20	....	[264]
Phenylacetic	4.31	3.29	2.91	[260]
Acetic	4.76	3.60	....	[264]
		3.38	....	[260]
		3.30	2.51	[267, 259]
		3.24	....	[266]
Valeric	4.84	3.44	3.20	[260]
Propionic	4.87	3.39	2.85; 2.65	[260, 259]
Caproic	....	3.27	2.99	[260]
Lauric	....	3.29	....	[260]

[a] pK_a values are from the compilation by Robinson and Stokes [271].

[b] IR, infrared spectroscopy; D, distribution between immiscible solvents.

REFERENCES:

[259] M. Davies, P. Jones, D. Patnaik, and E. A. Moelwyn-Hughes, J. Chem. Soc., p. 1249 (1951).

[260] (a) J. Wenograd and R. A. Spurr, J. Am. Chem. Soc. **79**, 5844 (1957); (b) J. Wenograd, Dissertation Abstr. **16**, 38 (1956).

[264] J. T. Harris, Jr. and M. E. Hobbs, J. Am. Chem. Soc. **76**, 1419 (1954).

[266] J. J. Lindberg and C. Majani, Suomen Kemistilehti B **37**, 21 (1964).

[267] H. E. Affsprung, S. D. Christian, and A. M. Melnick, Spectrochim, Acta **20**, 285 (1964).

[267a] Y. I'Haya and T. Shibuya, Bull. Chem. Soc. Japan **38**, 1144 (1965).

[271] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2d ed. Academic Press, New York, 1959.

Of the many dimerization constants which have been determined, relatively few are on a comparable basis. Differing aprotic solvents have been used—benzene, toluene, chlorobenzene, cyclohexane, heptane, carbon tetrachloride, chloroform, and others—and temperatures of measurement have varied from the freezing point to the boiling point of the solvent. However, the most recent measurements have been made either at (or near) 25° or at a series of temperatures which permit the calculation of values for 25°. Table 23 contains results obtained for benzoic acid and some aliphatic acids in carbon tetrachloride solutions (25°) during the past 10 to 15 years. The comparative tendencies for dimerization are expressed as log $K_{1,2}$ values for presumably water-free solutions (see 3d column). In some cases log $K_{1,2}$ values were also obtained for water-containing solutions (column 4). The latter values are all distinctly lower than those for "dry" carbon tetrachloride solutions, supporting the view that hydrogen bonding to water reduces the extent of self-association through hydrogen bond formation. In the two cases (trichloroacetic and acetic acids) where two or more log $K_{1,2}$ values are available, the agreement is not good. However, two generalizations appear justifiable: (1) In comparing the log $K_{1,2}$ values for carbon tetrachloride solutions with the corresponding tendencies for ionic dissociation in water—see pK_a ($-\log K_a$)

values in column 2 — it seems evident that the weaker the acid in water, the greater the tendency for self-association in carbon tetrachloride. (2) The pK_a values cover a greater numerical range than the log $K_{1,2}$ values.

A greater range of log $K_{1,2}$ values is available for benzene solutions of benzoic and substituted benzoic acids; see table 24, column 4. As mentioned in the footnotes to this table, calculations were made where needed to convert the log $K_{1,2}$ values

TABLE 24. *Comparative values of* pK_a, log K'', *and* log $K_{1,2}$ *for some carboxylic acids (25°)*

Acid	pK_a, Water [a]	Log K'', Benzene [b]	Log $K_{1,2}$, Benzene [c]	Method [d]	Reference
		(*liter/mole*)	(*liter/mole*)		
Trichloroacetic	0.64	....	1.38	P	[255]
			1.23–1.40 (20°)	CAT	[253]
o-Nitrobenzoic	2.17	7.44	1.92	I	[252]
Phenylpropiolic	[e]2.2	....	1.95	E	[250]
o-Bromobenzoic	2.85	6.17	2.52	P	[258]
			2.41	I	[252]
o-Iodobenzoic	2.86	6.22	2.51	P	[258]
			2.44	I	[252]
o-Chlorobenzoic	2.94	6.08	2.43	E	[250]
			2.37	P	[258]
			2.41	I	[252]
o-Fluorobenzoic	3.27	5.77	2.48	P	[258]
			2.68	I	[252]
m-Bromobenzoic	3.81	6.06	2.62	I	[252]
m-Chlorobenzoic	3.83	6.06	2.62	I	[252]
m-Iodobenzoic	3.85	6.05	2.61	E	[250]
			2.68	I	[252]
m-Fluorobenzoic	3.86	5.94	2.65	IR	[252]
o-Toluic	3.91	4.94	2.63	I	[251a]
p-Bromobenzoic	3.97	5.86	2.82	I	[252]
p-Iodobenzoic	3.98	5.85	2.74	I	[252]
p-Chlorobenzoic	3.98	5.82	2.83	I	[252]
p-Fluorobenzoic	4.14	5.61	2.78	IR	[252]
Benzoic	4.20	5.26;	2.79	I	[251a]
		[f]5.32	2.75	E	[250]
			2.84	P	[258]
			2.82	I	[252]
			2.80	U	[263]
m-Toluic	4.27	5.13	2.86	I	[251a]
p-Toluic	4.37	5.03	3.38	E	[250]
p-Methoxybenzoic	4.47	4.92	2.75	E	[250]
o-Methoxybenzoic	4.09	3.7	0.59	I	[252]

[a] From compilations in [32] and [271].

[b] Log K'' values are for association of the carboxylic acid with diphenylguanidine; see Davis and Hetzer [32].

[c] Values are cited in chronological order. Some of the values for 25° were obtained by interpolation or extrapolation in a plot of log K versus $1000/T$. Log $K_{1,2}$ values originally given in molal or mole-fraction units were converted to molar units by applying eq 26 or 27 (see sec. 4.1.1).

[d] P, dielectric polarization; CAT, catalytic method; I, isopiestic; E, ebullioscopic; IR, infrared.

[e] R. A. Robinson, provisional value.

[f] See Davis and Paabo, ref. [15].

REFERENCES:

[250] G. Allen and E. F. Caldin, (a) Trans. Faraday Soc. **49**, 895 (1953); (b) Quart. Rev. (London) **7**, 255 (1953).

[251a] F. T. Wall and F. W. Banes, J. Am. Chem. Soc. **67**, 898 (1945).

[252] H. Dunken and G. Jäger, Z. Chem. **3**, 432 (1963).

[253] A. Weissberger, J. Am. Chem. Soc. **65**, 102 (1943).

[255] R. J. W. LeFèvre and H. Vine, J. Chem. Soc., p. 1795 (1938).

[258] K. Palm and H. Dunken, Z. Physik. Chem. (Leipzig) **217**, 248 (1961).

[263] W. Maier, J. Chim. Phys. **61**, 239 (1964).

[271] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2d ed. (Academic Press, Inc., New York, N.Y., 1959).

to the same concentration units (liter/mole) and temperature (25°). The agreement among multiple values obtained by different methods is better than in the examples shown in table 23; for example, see the various log $K_{1,2}$ values obtained for *o*-chlorobenzoic, *m*-iodobenzoic, and benzoic acids. The trend towards increased self-association in the aprotic solvent with decreasing ionization (increasing pK_a value) in water which was noted in the preceding table is more strongly evident.

The relative tendencies for the acids to dimerize in benzene may also be compared with their acidic strengths in benzene; these are indicated by the log K'' values (column 3), which measure the relative affinities of the acids for the base diphenylguanidine (see eqs 15–16, section 2.3). The log K'' values were shown earlier [32] to parallel the tendencies for ionization of the acids in water—that is, the greater the ionization of the acid in water, the greater its capacity for association with diphenylguanidine to form hydrogen-bonded ion pairs. The data in table 24 reveal that acids with the greatest tendencies toward self-association combine the least readily with diphenylguanidine.

The correlation of strong self-associative tendencies in aprotic solvents with reduced manifestations of acidic behavior in water was previously evident to others, even on the basis of much more limited evidence [255, 253, 257b, 248, 250]. Barton and Kraus [248] observed that log $K_{1,2}$ values for benzoic, *o*-bromobenzoic, cinnamic, and phenylpropiolic acids in benzene (at about 5.5°) are approximately linearly related to the pK_a values for water solutions (25°), but 2-phenylpropionic (hydrocinnamic) acid exhibited a puzzling failure to conform to this relationship. Subsequent work of Allen and Caldin [250] supplied an explanation for the deviating behavior of 2-phenylpropionic acid. On examining a larger body of data they discovered that carboxylic acids can be subdivided roughly into two groups: (1) Acids in which the —COOH group is conjugated with the side chain (benzoic, substituted benzoic, cinnamic, crotonic, and phenylpropiolic acids); (2) acids in which —COOH is *not* conjugated with the side chain (aliphatic acids, including phenylacetic and 2-phenylpropionic acids). The acids of group (1) seem to be more highly dimerized than those of group (2).

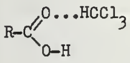
In comparing the isomeric toluic and monohalobenzoic acids (table 24) it will be observed that the extent of dimerization increases in the order $o- < m- < p-$. The dimerization constant of *p*-toluic acid seems unexpectedly large. No explanation has been offered for this. Interestingly, a dimerization constant for 2,4-dimethylbenzoic acid in benzene which was determined indirectly by Davis and Paabo [254a] proved to be almost identical with the value reported for *o*-toluic acid [251a]. The indirect method used (which was applied earlier to benzoic acid [254], giving log $K_{1,2} = 2.72$) consists of measuring the absorbance at 540 nanometers (mμ) of various mixtures of diphenylguanidine, bromophthalein magenta E (3′,3″,5′,5″-tetrabromophenolphthalein ethyl ester), and a carboxylic acid in benzene, then calculating both the equilibrium constant for 1:1 association of the carboxylic acid with diphenylguanidine and the dimerization constant of the carboxylic acid by fitting various assumed values of $K_{1,2}$ to the data.

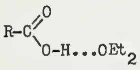
Results of I'Haya and Shibuya [267a] in a very recent investigation of the dimerization of benzoic acid in carbon tetrachloride and in chloroform support their claim that measurements of the integrated intensities of absorption bands give better values than peak intensity measurements. The data used were for the carbonyl stretching-vibration bands of the monomeric and dimeric forms of benzoic acid. Averaging the results for 14 solutions in *carbon tetrachloride* having stoichiometric concentrations in the range 0.0003–0.073 *M* they obtained log $K_{1,2}(\sim 25°) = 3.37$, the R.S.D. (relative standard deviation) of the values of $K_{1,2}$ being 8.3 percent. For *chloroform* solutions (15 mixtures, 0.00013–0.076 *M*) they obtained log $K_{1,2} = 2.60$, R.S.D. for $K_{1,2}$ being 7.3 percent. The dimerization constants, unlike results from earlier investigations (see ref. 267a, literature cited), did not exhibit a concentration dependence.

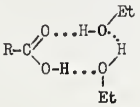
From dielectric polarization data for *cyclohexane* solutions Thyrion and Decroocq [267b] have obtained the following values of log $K_{1,2}$ (25°): CH_3COOH, 4.32; $CHCl_2COOH$, 3.48; CCl_3COOH (10 solutions, 0.0042–0.051 *M*, R.S.D. for $K_{1,2}$ 7.6%), 3.18; CF_3COOH (10 solutions, 0.0045–0.06 *M*, R.S.D. of $K_{1,2}$ values 11.2%), 2.51. Values of pK_a for the first three acids are given in table 23, and work of Henne and Fox [267c] indicates that pK for trifluoroacetic acid is ~ 0.19. Thus, it is evident that the same kind of parallelism noted earlier holds for this series of acids—that is, the stronger the acid in water the less the tendency toward dimerization. It will be noted that the dimerization constants for the first three acids in cyclohexane are substantially greater than corresponding values for carbon tetrachloride solutions (table 23)—much closer agreement would have seemed reasonable.

c. Hetero-association. As exemplified in recent work by Affsprung and associates [267], mixtures of carboxylic acids exhibit the expected tendency to form "hetero"-dimers as well as "homo"-dimers. From IR data these authors determined $K_{1,2}$ for both *acetic* and *trichloroacetic* acids, and also $K_{\text{assocn.}}$ for the *hetero*-association, using solutions in which the two acids were present in equimolal concentrations. When reduced to *molar* units (CCl_4, 25°) the log K values found for the three associative processes, in the order mentioned, are 3.30, 2.43, and 3.65, indicating that the hetero-dimer is formed in preference to the homo-dimers. Although this result should not be attributed solely to statistical factors, it is worth noting that in systems containing two monomeric acids, A and A′, in equal concentration, random collisions of A with A′ are more probable than collisions of A with A or of A′ with A′.

d. Solvent effects on dimerization. In the light of present-day knowledge one would expect carboxylic acids to associate with solvents that are capable of forming hydrogen-bonded complexes, at the expense of self-association. Employing either their electron donor capacity or proton donor capacity, or both, carboxylic acids are capable of forming complexes of the types illustrated below (XVIII–XX).


(XVIII)

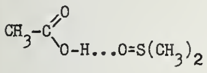

(XIX)

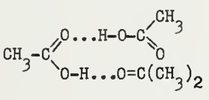

(XX)

π-Electron donors may be included among the solvents expected to form complexes of type (XIX).

The effects of different *aprotic* solvents on the extent of dimerization seem to be completely consistent with expectations based on our previous comparisons of these solvents (section 3.4). Thus, trichloroacetic acid (compare tables 23 and 24) appears to be less dimerized in benzene, a π-electron donor, than in carbon tetrachloride. Analogously, other carboxylic acids have been found to be less dimerized in benzene than in heptane [256] or in carbon tetrachloride [274]. Brooks and co-workers [244], who studied the dimerization of benzoic acid in *n*-hexane, carbon tetrachloride, carbon disulfide, and chloroform (IR spectra, equimolar solutions), found that these solvents produced an increased monomer-dimer ratio in the sequence named.

It is appropriate to say a few words about the effects of polar solvents, in view of their frequent admixture with aprotic solvents. Brooks and associates [244] found that benzoic acid is not measurably dimerized in acetonitrile, even at fairly high concentrations (1 *M*). Lindberg and Majani [266], who were interested in the association of acetic acid with methyl sulfoxide, concluded (IR spectra) that both 1:1 and 2:1 association occur. The structures postulated are shown below (XXI, XXII):


(XXI)


(XXII)

In acetic acid-methyl sulfoxide mixtures diluted with carbon tetrachloride, log *K* for the formation of (XXI) appears to be about 2.58 (liter/mole, 25°).

The importance of such studies, as contributions to increased understanding of solvent effects on acid-base behavior, as well as for correct interpretations of absorption spectra, is easily appreciated. In two very recent investigations of interactions of carboxylic acids with varied solvents, Lascombe and associates [275] and Collings and Morgan [276] have examined solvent-produced shifts of the carbonyl stretching frequency of the acids in the region 1700–1800 cm^{-1}. The comprehensive investigations by Lascombe et al. dealt with acetic acid (CH_3COOH and CH_3COOD) and also propionic, butyric, caproic, and benzoic acids in some 20 to 30 different solvents of the three types represented in (XVIII–XX). The spectra of acetic acid-butanol mixtures were interpreted as indicating the presence of three species—a 1:1 aggregate, RCOOH...O(H)R (compare XIX), and two species of the composition $RCOOH \cdot 2BuOH$. One of these is assigned a structure analogous to (XX), and the other is presumed to have the same structure except that the two alcohol molecules are not connected by a hydrogen bond.

Carboxylic acid-solvent interactions have also been studied recently by means of ultraviolet spectroscopy [268, 269, 277, 278]. In an investigation of this type, Forbes and Knight [278] concluded that benzoic, *p*-toluic, salicylic, and *p*-hydroxybenzoic acid are more prone to dimerize than to associate with ethyl ether in cyclohexane solutions. However, the acids are thought to be monomeric in 100 percent ether.

In discussing the determination of dimerization constants by the distribution method (sec. 4.2.2b) it was emphasized that carboxylic acids seem prone to associate with water molecules in aprotic solvents at the partial expense of dimerization. However, the dimeric structure is believed to persist to some extent in aqueous solutions, and to account for anomalous deviations in the behavior of carboxylic acids at low concentrations where the Debye-Hückel theory should be applicable [279–281]. MacDougall and Blumer [279] calculated that $K_{1,2}$ for acetic acid in water is 0.185 (liter/mole, 25°), and Katchalsky and associates [280] deduced a closely similar value (0.16); they also computed several other dimerization constants, ranging from 0.04 for formic acid to 0.75 for benzoic acid. Davies and Griffiths [281], while agreeing that acetic acid is appreciably dimerized in water, arrived at a somewhat different association constant. In this connection it is noteworthy that the acids found to be the most highly dimerized in benzene or carbon tetrachloride (tables 23 and 24) are the ones least ionized in water. It is also of interest that benzoic acid seems to be more highly dimerized than acetic acid both in water and in aprotic solvents.

e. Chelated acids. As noted above (sec. 4.2.2a), *ortho*-hydroxybenzoic (salicylic) acid and related acids seem to be strengthened by chelate ring formation. In contrast, intramolecular hydrogen bonding in *o*-methoxybenzoic acid (XV) will obviously reduce the extent of its involvement as a proton donor in intermolecular reactions. Both infrared [282, 283, 244, 252] and ultraviolet [269] spectral data indicate the presence of chelated *o*-methoxybenzoic acid in solvents like carbon tetrachloride and cyclohexane. It would also be inferred from the comparatively low value (0.59) for log $K_{1,2}$ found for *o*-methoxybenzoic acid in benzene (see table 24) that the acid is largely in the monomeric, intramolecularly hydrogen-bonded form. The abnormally high dipole moments of related naphthoic acids (for example, 1-methoxy-2-naphthoic and 3-methoxy-

2-naphthoic acids) have likewise [284] been explained in terms of chelation. In accord with all these findings, Davis and Hetzer [32] observed that in benzene solution *o*-methoxybenzoic acid associates much less readily with diphenylguanidine than do most other benzoic acids. Chelation of *o*-methoxybenzoic acid is not evident in solvents which can become hydrogen bonded to the -OMe group, like water, alcohols, and dioxane-water [32]. It is also reduced in extent by the addition of ethyl ether to carbon tetrachloride solutions [244].

Intramolecular hydrogen bonding has also been postulated for the *ortho*-halobenzoic acids, which seem anomalously weak both in ethanol [285] and in benzene [32]. However, infrared studies lately reported [244, 252] were interpreted as signifying absence of intramolecular hydrogen bonding. The monomeric acids exhibit two absorption peaks (as do also the corresponding esters) in carbon tetrachloride and chloroform solutions; these have been attributed to the presence of the two conformational isomers (compare XIIIa and XIIIb) because all four *o*-halobenzoic acids show only single, closely similar monomeric *hydroxyl* bands. We have noted above, however, that carbon tetrachloride and chloroform are not completely inert solvents (sec. 3.4.3b and 3.4.5a), and it does not seem certain that the conclusions can be generalized to all aprotic solvents.

The strong evidence of intramolecular hydrogen bonding found for *o*-nitrophenol does not appear in the spectral [252] or chemical [32] behavior of *o*-nitrobenzoic acid, in which chelation is not geometrically favored.

f. Thermodynamic constants. Comparative thermodynamic data for the monomer-dimer equilibrium of carboxylic acids are available in a limited number of cases [250–252, 263]. Table 25 contains a com-

TABLE 25. *Thermodynamic constants for the monomer-dimer equilibrium of some carboxylic acids (liter/mole, benzene, 25°)*[a]

Acid	Method [b]	$-\Delta G^\circ$	$-\Delta H$	$-\Delta S^\circ$	$\Delta H/0.298\Delta S$	Reference
		kcal/mole	*kcal/mole*	*cal/deg mole*		
Benzoic	I	3.81	8.42	15.5	1.8	[251a]
Benzoic	E	3.76	7.70	13.2	1.95	[250a]
Benzoic	P	3.84	9.29	18.3	1.7	[252]
o-Bromobenzoic	P	3.29	8.14	16.3	1.7	[252]
o-Chlorobenzoic	E	3.31	8.31	16.8	1.7	[250a]
o-Chlorobenzoic	P	3.29	8.12	16.2	1.7	[252]
o-Fluorobenzoic	P	3.66	9.65	20.1	1.6	[252]
o-Iodobenzoic	P	3.33	8.77	18.2	1.6	[252]
o-Methoxybenzoic	P	0.80	2.06	4.25	1.6	[252]
o-Nitrobenzoic	P	2.62	7.50	16.4	1.5	[252]
o-Toluic	I	3.58	8.39	16.1	1.7	[251a]
m-Bromobenzoic	P	3.58	9.06	18.4	1.65	[252]
m-Chlorobenzoic	P	3.57	8.92	17.9	1.7	[252]
m-Fluorobenzoic	IR	3.62	8.47	16.3	1.75	[252]
m-Iodobenzoic	E	3.57	7.65	13.7	1.9	[250a]
m-Iodobenzoic	P	3.65	9.32	19.0	1.6	[252]
m-Toluic	I	3.91	9.26	17.9	1.7	[251a]
p-Bromobenzoic	P	3.84	9.35	18.5	1.7	[252]
p-Chlorobenzoic	P	3.86	9.36	18.5	1.7	[252]
p-Fluorobenzoic	IR	3.79	9.33	18.6	1.7	[252]
p-Iodobenzoic	P	3.74	9.23	18.4	1.7	[252]
p-Methoxybenzoic	E	3.74	6.57	9.5	2.3	[250a]
p-Toluic	E	4.61	8.72	13.8	2.1	[250a]
Phenylpropiolic	E	4.03	8.75	15.2	1.9	[250a]

[a] Where necessary, values for 25° were obtained by interpolation or extrapolation in a plot of log $K_{1,2}$ versus $1000/T$. Part of the log $K_{1,2}$ values, originally given in mole fraction units, were converted to molar units by applying eq 27 (see Sec. 4.1.1). Thermodynamic constants were calculated, when necessary, by conventional methods.

[b] I, isopiestic; P, dielectric polarization; E, ebullioscopic, IR, infrared.

REFERENCES:

[250a] G. Allen and E. F. Caldin, Trans. Faraday Soc. **49**, 895 (1953).
[251a] F. T. Wall and F. W. Banes, J. Am. Chem. Soc. **67**, 898 (1945).
[252] H. Dunken and G. Jäger, Z. Chem. **3**, 432 (1963).

pilation of values for phenylpropiolic acid and a series of benzoic acid derivatives; several methods of measurement are represented [250a, 251a, 252]. Table 26 contains thermodynamic constants for the monomer-dimer equilibrium of benzoic acid in several solvents, derived from ultrasonic absorption data [263]. The values for benzoic acid in benzene, together with the results cited in table 25, provide four independent measurements by different methods. The constants have all been converted (when needed) to the same (molar) units of concentration (see eq 27). For reasons given earlier (sec. 4.2.2b), data obtained by the distribution method have not been included.

Table 26. *Thermodynamic constants for the monomer-dimer equilibrium of benzoic acid in different solvents (liter/mole, 25°)*[a]

Solvent	$-\Delta G$	$-\Delta H$	$-\Delta S$	$\Delta H/0.298\ \Delta S$
	kcal/mole	*kcal/mole*	*cal/deg mole*	
Cyclohexane	6.07	13.7	25.6	1.8
Carbon tetrachloride	5.69	13.6	26.4	1.7
Chlorobenzene	4.45	10.1	19.0	1.8
Toluene	4.00	9.6	19.0	1.7
Benzene	3.82	8.6	16.1	1.8
Chloroform	3.60	9.3	19.3	1.6

[a] Converted from K_x to K_c units by means of eq 27 (see sec. 4.1.1). Thermodynamic constants were calculated by conventional procedures. From results of Maier and associates [263].

Reference:

[263] W. Maier, J. Chim. Phys. **61**, 239 (1964).

The following points may be noted in table 25: (1) All of the thermodynamic constants are negative in sign; (2) values of $-\Delta H$ are mostly in the range 8–9.4 kcal/mole; (3) $-\Delta S$ values are mostly in the range 13–20 cal/deg mole; (4) the ratio $\Delta H/T\Delta S$, where $T=298$ °K, is 1.7 for about half the cases listed, the range of values being 1.5–2.3. *o*-Methoxybenzoic acid conforms well to the last generalization. There is likewise an approximately linear relation between ΔG and ΔH. It should be remembered, of course, that these acids have closely similar structures. From comparing the four sets of values for benzoic acid (see also *m*-iodobenzoic acid) it is apparent that the reproducibility attained in such measurements is not yet great enough for significance to be attached to deviating cases.

In an earlier paper [33] Davis and Hetzer commented on the approximate constancy of the ratio $\Delta H/0.298\ \Delta S$ for a smaller group of benzoic acids. Still earlier, signs of a linear correlation of ΔH and ΔS (based on a very limited amount of data) and the theoretical basis of such a correlation were discussed by Allen and Caldin [250b].

The approximate constancy of the ratio $\Delta H/0.298\ \Delta S$ upon changing the solvent is indicated by the data of table 26. The numerical values of ΔH and ΔS are noticeably greater for benzoic acid when in the two solvents cyclohexane and carbon tetrachloride than in the aromatic solvents or chloroform—they are closer to the values pertaining to dimerization in the vapor phase [250b, 263]. These results are consistent with the evidence, previously mentioned, of tendencies for association of carboxylic acids with aromatic solvents and chloroform.

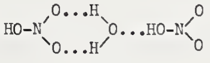
g. Possible equilibrium between open-chain and cyclic dimers. Although the possible presence of a dimer containing only one hydrogen bond is recognized, as noted in the introductory discussion of carboxylic acids, dimeric carboxylic acids are usually assumed to be predominantly in the cyclic form when dissolved in aprotic solvents, and calculations of dimerization constants have commonly been made under this assumption. Not long ago [286] Bellamy and associates raised the question again, calling attention to the previous suggestion by Fénéant [287] that the breadth of the ν_s band of carboxylic acids may result in part from the presence of a mixture of cyclic and open-chain dimers. In Bellamy's view, this subject merits further study.

h. Thiolobenzoic acid. Thiolobenzoic acid, PhC(=O)SH, studied by infrared (CCl_4), ultraviolet (C_6H_{12}), and NMR spectroscopy (C_6H_6), as well as cryoscopically (C_6H_6), has been found to exhibit inappreciable tendency toward dimerization [288]. According to evidence summarized by Pimentel and McClellan [102], the —SH group is a relatively poor proton donor, although instances of hydrogen bonding have been observed with strong electron donors.

4.2.3. Nitric Acid

Self-association of nitric acid in aprotic solvents has been inferred from data for its distribution between concentrated aqueous solutions and aprotic solvents such as benzene, toluene, kerosene, and chloroform. This work originated in the need for interpreting data obtained in extracting strongly acidic materials from aqueous solutions into aprotic solvents by the aid of basic substances like dialkyl hydrogen phosphates and tri-*n*-octylamine [289–291].

In the work of Hardy and associates [289] infrared absorption curves for the extracts in aprotic solvents indicated strongly the presence of a dimeric form as the predominant species, possibly in the form of a monohydrate. The structure favored by the authors is (XXIII). The solvents used in the



(XXIII)

infrared studies were benzene, carbon tetrachloride, cyclohexane, *n*-dodecane, kerosene, and toluene. Larger aggregates are considered likely to form in very highly concentrated solutions.

Verstegen [290] determined dimerization constants for nitric acid in benzene, *o*-dichlorobenzene, and chloroform. His own results and those of other workers are shown in table 27. It should be borne in mind that all of these values are for *wet* solvents. Why *o*-dichlorobenzene occupies its relative position in table 27 is not clear, but the relative order of the other solvents is in harmony with our preceding discussion of aprotic solvents.

TABLE 27. *Dimerization constants for nitric acid in wet aprotic solvents*[a]

Solvent	Log $K_{1,2}$	Reference
	(Liter/mole)	
Kerosene	3.60	[289]
Benzene	3.09	[290]
Toluene	2.77	[289]
Xylene	2.48	[291]
o-Dichlorobenzene	2.00	[290]
Chloroform	1.70	[290]

[a] From Verstegen's compilation of his own and published results, all obtained by distribution measurements [290].

REFERENCES:

[289] C. J. Hardy, B. F. Greenfield, and D. Scargill, J. Chem. Soc., p. 90 (1961).

[290] J. M. P. J. Verstegen, J. Inorg. Nucl. Chem. **26**, 1085 (1964).

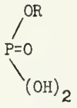
[291] U. Bertocci and G. Rolandi, J. Inorg. Nucl. Chem. **23**, 323 (1961).

Attention should be called to a communication by Högfeldt [292], who has investigated the distribution of nitric acid between water and several aromatic hydrocarbon solvents [293]. Högfeldt disagrees with deductions of Hardy and associates [289] and of Verstegen [290] in regard to dimer formation in the organic layer. In his opinion the method used for determining water in the organic phase is not accurate enough to warrant such definite conclusions. He has suggested an alternative formulation of the distribution reaction [292, 293].

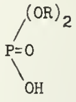
4.2.4. Phosphorus-Containing Organic Acids

The practical importance which phosphorus-containing organic acids attained within the past 20 years in solvent-extraction processes created a need for information about their states of aggregation in various organic solvents. These processes involve distribution of the acids between aqueous and organic layers.

The phosphorus-containing acids chiefly used up to now in the extraction processes are derived from orthophosphoric acid by partial esterification, as indicated in (XXIV) and (XXV).



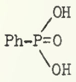
(XXIV)



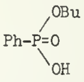
(XXV)

Commonly used examples of (XXIV) are *n*-butyl (dihydrogen) phosphate and phenyl (dihydrogen) phosphate (sometimes referred to, respectively, as "butylphosphoric acid" and "phenylphosphoric acid"). Examples of (XXV) are di-*n*-butyl (hydrogen) phosphate and diphenyl (hydrogen) phosphate (occasionally called "dibutylphosphoric" and "diphenylphosphoric" acids).

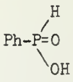
Acids with alkyl or aryl attached directly to phosphorus are less well known, and their nomenclature has not been firmly established. Examples are: Benzenephosphonic (phenylphosphonic) acid (XXVI), butyl benzenephosphonate (XXVII), and benzenephosphonous (phenylphosphinic) acid (XXVIII). Phosphonous acids may have *two* R groups attached to P, as in (XXIX).



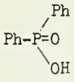
(XXVI)



(XXVII)



(XXVIII)



(XXIX)

Infrared surveys have shown that acids of these six types, all of which contain the P(=O)OH or $P(=O)(OH)_2$ grouping, have a very strong tendency when in solvents like carbon tetrachloride and carbon disulfide to form aggregates containing O–H...O bonds [294, 295]. This conclusion has been reinforced by studies employing additional measuring techniques (notably distribution and cryoscopy) [296–311].

a. Nature of aggregates formed. There seems to be agreement on the following points:

(1) Acids with the grouping P(=O)OH usually form dimers in aprotic solvents, resembling carboxylic acids. The dimers are thought to have a cyclic structure analogous to that of carboxylic acid dimers (XVI). Acids of types (XXV), (XXVII), and (XXIX) are included in this category. (XXVIII) is an exception; according to Kosolapoff and Powell [309] it forms trimeric aggregates (cryoscopy in benzene and naphthalene); these are thought likely to be cyclic.

(2) Acids containing the grouping $P(=O)(OH)_2$ form linear aggregates of magnitude varying with concentration and temperature. Types (XXIV) and (XXVI) belong to this category.

(3) The tendency of phosphorus-containing organic acids to form aggregates is very great—it exceeds that of carboxylic acids.

b. Solvent effects. Like carboxylic acids, phosphorus-containing acids can form aggregates with solvents having proton donor capacity (for example, $CHCl_3$), electron donor capacity (ethers, ketones, etc.), or both (water, alcohols); compare section 4.2.2b, formulas (XVIII–XX). Any such aggregate formation naturally reduces the extent of self-association.

While studying the distribution of di-*n*-butyl phosphate between water and organic solvents, Dyrssen [296] observed that it has an appreciable tendency to associate with tributyl phosphate (which is well-known for its electron donor capacity—for example, see Davis and Schuhmann [14]). Peppard, Ferraro, and Mason have made several studies of solvent effects on the self-association of acids of types (XXIV), (XXV), and (XXVII), by cryoscopy, infrared spectroscopy, isopiestic measurements, and, most recently, by NMR spectroscopy [299–301]. From isopiestic data [300] they reached the following conclusions: "In general, the monobasic acids are dimers in solvents such as *n*-hexane, cyclohexane, benzene and carbon tetrachloride; monomers in methyl alcohol; and intermediate in chloroform and acetone." In studying solutions of 2-ethylhexyl (dihydrogen) phosphate they deduced the presence of large aggregates (of molecular weight 8–14.5 times the formula weight) in *n*-hexane and cyclohexane, hexamers in benzene and carbon tetrachloride, dimers in acetone, and monomers in methanol [300]. Acetic acid is another solvent in which the acids appear to be predominantly monomeric [299]. In this connection, it seems pertinent to note that Davis and Hetzer [313] found that diphenyl phosphate, which is strongly acidic in water, acts as a weak acid in glacial acetic acid; heteroassociation of the solute and solvent was suggested as an explanation (see footnote 15 of ref. 313).

Further examples of solvent effects will be noted in the next section.

c. Monomer-dimer equilibrium constants. A very limited number of log $K_{1,2}$ values, obtained from extraction experiments, are available for dialkyl and diaryl phosphates; quantitative evidence does not seem to have been obtained for the other classes of organophosphorus acids.

Table 28 presents log $K_{1,2}$ values for di-*n*-butyl phosphate in 10 wet organic solvents and in water; these were obtained by Dyrssen and coworkers [296, 297] or by Hardy and associates [303, 304]. Although the conditions which had to be employed were far from ideal, expected trends in solvent effects are discernible. For example, dimerization appears to be less extensive in π-electron donor solvents (toluene, benzene) than in aliphatic hydrocarbons or carbon tetrachloride, and still less extensive in *n*-electron donors (isopropyl ether, methyl isobutyl ketone). As expected, the dimer/monomer ratio is lowest in water and methyl isobutyl carbinol. Ferraro and Peppard's recently reported study [302] of the dimerization of some dialkyl and diaryl phosphates in carbon tetrachloride (dry and wet, 25°), using NMR spectroscopy, shows clearly the interference with the dimerization process which water produces (see their fig. 3). They calculated for log $K_{1,2}$ (liter/mole) the approximate value 3.18, which is much lower than the values obtained by the distribution method (see table 28), but close to the value reported for chloroacetic acid (see table 23). If water acts merely as a competitor in hydrogen bond formation, a *higher* value would have been expected for dry CCl_4 solutions. Further consideration of the role of water is obviously needed. (Note the following discussion of sulfinic and sulfonic acids.) The value of $-\Delta H$ (kcal/mole) per hydrogen bond was estimated as being 5.5–5.8—this is smaller than Maier's value (6.8) for benzoic acid in CCl_4 [263] (see table 26).

TABLE 28. *Solvent effects on the dimerization of di-n-butyl phosphate in various (wet) organic solvents (25°)*[a]

Organic solvent	Mineral acid in aqueous layer	Log $K_{1,2}$	Reference
		liter/mole	
n-Hexane	0.1 *M* HNO_3	6.87	[297]
Kerosene	1 *M* HNO_3	5.78	[303]
Carbon tetrachloride	0.1 *M* HNO_3	6.49	[297]
	1 *M* HNO_3	5.33	[303]
Toluene	1 *M* HNO_3	5.09	[304]
Benzene	1 *M* HNO_3	4.88	[303]
Chloroform	0.1 *M* (Na, H)ClO_4	4.48	[296]
	0.1 *M* HNO_3	4.61	[297]
	0.1 *M* $HClO_4$	4.21	[303]
	1 *M* $HClO_4$	4.36	[303]
Nitrobenzene	1 *M* HNO_3	3.55	[303]
Isopropyl ether	0.1 *M* HNO_3	2.29	[297]
Methyl isobutyl ketone	0.1 *M* (Na, H)ClO_4	1.19	[296]
Water[b]	None	1.11	[296]
Methyl isobutyl carbinol	0.1 *M* HNO_3	<-1	[297]

[a] Based on data from distribution experiments.

[b] Saturated solution of di-*n*-butyl phosphate.

REFERENCES:

[296] D. Dyrssen, Acta Chem. Scand. **11**, 1771 (1957).

[297] D. Dyrssen and L. D. Hay, Acta Chem. Scand. **14**, 1091 (1960).

[303] C. J. Hardy and D. Scargill, J. Inorg. Nucl. Chem. **11**, 128 (1959).

[304] B. F. Greenfield and C. J. Hardy, J. Inorg. Nucl. Chem. **21**, 359 (1961).

Krašovec and Jan [307] have compared the log $K_{1,2}$ (wet chloroform) and pK_a (water) values of several diaryl phosphates, using the distribution method; see table 29. As in the case of the carboxylic acids listed in tables 23 and 24, the acids having the lowest acidic strength in water appear to possess

TABLE 29. *Dimerization constants (wet chloroform) and* pK_a *values (water) of some diaryl and dialkyl phosphates* (R_2HPO_4) [a]

Identity of R	Log $K_{1,2}$	pK_a	Reference
	liter/mole		
p-Chlorophenyl	3.44	0.20	[307]
Phenyl	3.76	0.26	[307]
Benzyl	3.90	0.70	[307]
2-Naphthyl	4.02	0.74	[307]
p-Tolyl	4.24	0.40	[307]
Ethyl (25°)	4.46	0.73	[298]
n-Butyl (25°)	4.48	1.00	[296]

[a] Both sets of values were calculated from distribution data; $t = 20$ °C except as indicated otherwise.

REFERENCES:

[296] D. Dyrssen, Acta Chem. Scand. **11**, 1771 (1957).
[298] D. Dyrssen, S. Ekberg, and D. H. Liem, Acta Chem. Scand. **18**, 135 (1964).
[307] F. Krašovec and J. Jan, Croat. Chem. Acta **35**, 183 (1963).

the greatest capacity for self-association. Di-*p*-tolyl phosphate (like *p*-toluic acid) seems to behave anomalously.

Ashby and Kosolapoff [310] determined the apparent molecular weights of the three isomeric tolylphosphonic acids—see (XXVI)—cryoscopically and ebullioscopically, using (when solubilities permitted) the solvents acetone, camphor, naphthalene, and water. The extent of aggregation of the isomers appears to increase in the order *ortho* < *meta* < *para*.

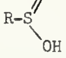
Additional findings are discussed in the references cited.

4.2.5. Sulfinic and Sulfonic Acids

a. Sulfinic acids, R–S(=O)OH. Self-association of sulfinic acids has been studied in benzene, carbon tetrachloride, and nitrobenzene.

Wright [314] determined the extent of association of several carboxylic acids and of several sulfinic acids (benzene-, *p*-toluene, 1- and 2-naphthalenesulfinic acids) cryoscopically in benzene and nitrobenzene, and found the sulfinic acids to be more highly associated than the carboxylic acids—apparently they form trimers and hexamers. The association of both carboxylic and sulfinic acids was found to be greater when water was present.

Detoni and Hadži [315] studied by IR and UV spectroscopy the association of benzene-, *p*-toluene-, 2-naphthalene-, and *o*-methoxybenzenesulfinic acids in carbon tetrachloride, both dry and moist. Of various suggested structures for these acids they favor (XXX). They concluded that benzenesulfinic acid forms aggregates greater than the dimer and, in agreement with Wright, found that this acid is much more highly associated in wet than in dry solvent. For carboxylic acids the opposite seems to be true (see table 23).



(XXX)

b. Sulfonic acids, R–SO_2OH. Kehiaian and Nenitzescu's ebulliometric measurements [316, 317] of anhydrous benzene solutions of benzenesulfonic acid led to the conclusion that this acid does not dimerize, but instead forms higher aggregates. The association constants ($K_{n,\,n+1}$) for the different steps are held to be the same, and values found at the temperatures 52.6, 65.2, and 80.1 (°C) are, respectively, 10.9, 8.75, and 6.95 (molal units); the extrapolated value for 25° is 18.4. This is equivalent (see eq 26) to log $K_{n,\,n+1}$ (liter/mole) = 1.21. The values found for ΔH (kcal/mole) and ΔS (cal/deg mole) are −3.7 and −6.8, respectively.

4.2.6. *tert.*-Butyl Hydroperoxide and Deuteroperoxide. Deuterium Isotope Effects on Hydrogen Bonding by Brønsted Acids

Recently published investigations of Walling and Heaton [318] have provided information about the self-association and other hydrogen-bonding behavior of *t*-butyl hydroperoxide and *t*-butyl deuteroperoxide in carbon tetrachloride. Their results, which are summarized in table 30, are based on IR and distribution data. These results indicate that *t*-butyl *hydro*peroxide dimerizes more readily than *t*-butyl *deutero*peroxide; a cyclic structure (XXXI)

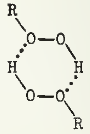
TABLE 30. *Log* K, ΔH, *and* ΔS *for some complex-forming reactions of t*-BuOOH *and t*-BuOOD (CCl_4) [a]

Complex formed	Log $K_{\text{assocn.}}$		$-\Delta H$	$-\Delta S$
	30°	70°		
			kcal/mole	*cal/deg mole*
t-BuOOH + PhCH=CH_2	−0.57	−0.77	2.39	10.5
t-BuOOH + C_6H_6	−0.82	−0.96	1.58	9.0
t-BuOOH + *o*-$C_6H_4Cl_2$	−0.82	−0.89	0.74	6.2
t-BuOOH + PhCl	–	−1.00	–	–
(*t*-BuOOH)$_2$	+0.28	−0.22	5.95	18.4
t-BuOOD + PhCH=CH_2	−0.08	−0.30	2.7	9
t-BuOOD + C_6H_6	—	−0.60	—	—
(*t*-BuOOD)$_2$	+0.22	−0.19	4.9	15

[a] Results obtained by Walling and Heaton (IR spectroscopy) [318].

REFERENCE:

[318] C. Walling and L. Heaton, J. Am. Chem. Soc. **87**, 48 (1965).



(XXXI)

is postulated for these dimers. In contrast, the deuteroperoxide seems to be more reactive than the hydroperoxide in associating with benzene and styrene. Walling and Heaton have called attention to analogous cases.

For example, in IR studies of Plourde and West [319], it was found that the *enthalpy* of *self*-association is greater for phenol-*h* than for phenol-*d*, whereas in other associations with bases the enthalpy of reaction is greater for phenol-*d* than for phenol-*h*; see table 31. (Also see table 9.) These studies showed, moreover, that the *free energy* of association with bases is almost the same for phenol-*h* and phenol-*d*, since a greater enthalpy change is almost balanced by a greater entropy change. The *intramolecular* deuterium bond was found to be slightly stronger than the hydrogen bond in *o*-chlorophenol and *o*-phenylphenol, and much stronger in *o*-iodophenol. In explanation of the results it was suggested that "relatively weak" hydrogen bonds (not necessarily all hydrogen bonds) are stronger in the case of deuterium because the "lower zero point vibrational energy of OD . . . makes the OD bond shorter than the OH, allowing closer approach of the base and greater interaction. . . . The reversal in the isotope effects [in the self-association reaction] may be due to increased basicity of the oxygen in phenol-*h*."

TABLE 31. *Enthalpy changes for some complex-forming reactions of phenol-*h *and phenol-*d [a]

Electron donor	$-\Delta H$, kcal/mole Proton donor	
	PhOH	PhOD
Benzene	1.84	2.18
Ethyl Acetate	4.81	5.07
Tetrahydrofuran	5.55	5.86
n-Butyl Ether	6.00	6.17
Phenol-*h*	4.53	—
Phenol-*d*	—	4.24

[a] Results of G. R. Plourde, from IR measurements [319]; solvent and concentration units are not specified.

REFERENCE:

[319] G. R. Plourde, Dissertation Abstr. **22**, 1400 (1962).

The relative strengths of hydrogen and deuterium bonds have also been compared in trifluoroacetic acid. Taylor and Templeman's investigations of CF_3COOH and CF_3COOD in the vapor phase [320] indicated that the hydrogen bond formed in self-association is somewhat stronger than the deuterium bond. Similarly, data of Maryott and associates [257a] indicate that acetic acid-*h* is more dimerized than acetic acid-*d* in benzene (30°). On the other hand, Creswell and Allred [120] found in NMR studies that fluoroform-*d* bonds more readily than fluoroform-*h* to tetrahydrofuran.

4.3. Hydrogen-Bonded Ion Pairs

In our preliminary discussion of acid-base reactions in aprotic solvents (sec. 2) it was emphasized that such reactions should be formulated as *association reactions*, in a manner illustrated by eq 30,

$$\underset{\text{base}}{B} + \underset{\text{acid}}{HA} \rightleftharpoons \underset{\text{salt}}{BHA}, \tag{30}$$

in which the organic base B is generally an aliphatic amine or derivative of guanidine, or else one of the weaker bases related to aniline or to pyridine. Salts of the class BHA are often said to consist of "ion pairs," as expressed by the structure BH^+A^-. However, this is an incomplete designation in a number of cases where, as we shall presently see, there is substantial evidence of *cation-to-anion hydrogen bonding*. It is desirable to recognize the occurrence of such bonding by using the term "*hydrogen-bonded ion pairs*," symbolically represented by $BH^+ \ldots A^-$.

Cation-to-anion hydrogen bonding in *incompletely substituted* ammonium salts (R_3NHA, R_2NH_2A, RNH_3A) is a very plausible explanation for certain pronounced differences in their behavior and that of *completely substituted* ammonium salts (R_4NA) when dissolved in aprotic solvents. Differentiating behavior has been discovered, for example, in measurements of such properties as conductance, dielectric polarization, and spectral absorption. Varied experimental evidence will be presented, mainly pertaining to solutions in aprotic solvents, although deductions from studies of hydrogen bonding in crystalline solids will also be included. It will also prove valuable to include examples of experiments in which *dipolar aprotic* solvents (e.g., nitrobenzene) were used. As we saw earlier, dipolar aprotic solvents can be assigned to Brønsted's "class 4," that is, solvents of comparatively high dielectric constant but weak proton-donor and proton-acceptor capabilities. Like the aprotic solvents, dipolar aprotic solvents have scarcely any masking effect on differentiating acid-base behavior.

Contrasts in the behavior of completely substituted ammonium salts as distinguished from incompletely substituted ammonium salts were first discovered more than 50 years ago [322]. Additional kinds of differentiating behavior have been discovered in the past 20 years in comparative studies of acid-base reactions yielding tertiary ammonium salts and those yielding secondary or primary ammonium salts. It will be shown that such additional examples can be explained satisfactorily in terms of hydrogen bonding reactions that are only possible in salts having *more than one proton* attached to the ammonium nitrogen.

4.3.1. Conductance

Extended understanding of acid-base behavior in aprotic solvents has been one of the important byproducts of investigations of the conductance of salts in nonaqueous solvents—in particular, the classic investigations associated with such names as Walden, Kraus, and Fuoss.

a. Walden's work. Walden's electrochemical investigations of binary salts in numerous nonaqueous solvents extended over more than 20 years. In these studies, which were summarized in the Baker lectures for 1927–1928 [322], the anions represented were mainly perchlorate, picrate, and halides; and primary, secondary, tertiary, and quaternary ammonium ions were among the principal cations represented.

Walden was very much struck by his discovery that some of the binary salts known to be equally strong in aqueous, methanolic, or ethanolic solutions (using conductivity as the measure of strength) can be subdivided into strong and weak electrolytes in acetone. In further work he found that tetraalkylammonium halides and picrates are strong electrolytes in nonaqueous solvents like acetone or ethylene chloride, as well as in water, methanol, and ethanol. In contrast, mono-, di-, and trialkylammonium halides and picrates, although strong electrolytes in water and the alcohols, become weak or only moderately strong electrolytes in acetone, benzene, and halogenated hydrocarbons.

Walden concluded that the strength of a binary salt depends both on the nature of the cation and the nature of the anion, but the former exerts the greater effect. In fact, he said: "The differences between the tetra-alkylated ammonium salts (particularly the chlorides) on the one hand, and the di- and tri-alkylated salts on the other, are so large that it would indeed be permissible to speak of them as entirely different electrolytes. . . ." The following series was given as expressing the relationships among these salts with respect to conductivity and percentage dissociation at equivalent dilutions:

tetra- > tri-(mono-) > di-alkylated ammonium salt.

His corresponding series for anions (in salts containing the same cation) is:

$$\mathrm{Pi}^- > \mathrm{ClO}_4^- > \mathrm{I}^- > \mathrm{NO}_3^- > \mathrm{Br}^- > \mathrm{Cl}^-.$$

In subsequent work Walden and Birr found that nitromethane is an additional differentiating solvent [323].

In a different type of investigation Walden and his associates compared the mobilities of isomeric substituted ammonium ions in different solvents [322, 324]. For example, Walden and Birr measured the mobilities of three isomeric cations—tetramethylammonium, diethylammonium, and mono-*n*-butylammonium—in water and in acetonitrile [324]. All three ions were found to have approximately the same mobility in acetonitrile, but not in water. Instead, the mobilities decrease in the following order:

tetramethylammonium > diethylammonium > butylammonium.

Walden and Birr inferred that the dissimilar mobilities of the isomeric cations in water result from different degrees of solvation—the tetramethylammonium ion being probably unhydrated; diethylammonium ion, partly hydrated; and monobutylammonium ion, more completely hydrated. The similar mobilities in acetonitrile were thought to indicate that the three cations are not solvated to any extent in this solvent.

b. Wynne-Jones' postulate. Wynne-Jones seems to have been the first person to suggest that the marked reduction in the conductivities of incompletely substituted ammonium salts in non-hydroxylic solvents, which his own experimental work showed to occur in nitrobenzene as well as in the solvents used by Walden, may be explained on the assumption of hydrogen bonding of anions to cations [325]. To indicate such bonding in a trialkylammonium chloride he wrote its structure as $\mathrm{R_3N{:}H{:}Cl}$, applying the concept of bicovalent hydrogen, used at that time to explain hydrogen bonding, and saying that the assumption of such bonding can account for the low conductivities of incompletely alkylated ammonium salts in non-hydroxylic solvents, as well as for the necessity of adding a hydroxylic solvent to assist ionization and for the effects of different solvents on ionic mobilities that had been observed by Walden and co-workers. He reasoned that when a salt can exist in a non-ionic (hydrogen-bonded) form its separation into cations and anions will be assisted when the solvent can interact with the partly substituted ammonium ion, thus separating it from the anion, as indicated by eq 31:

$$\mathrm{R_3N{:}H{:}Cl} + \mathrm{S}\ \text{(a hydroxylic solvent molecule)} \rightleftharpoons \mathrm{R_3N{:}H{:}S^+} + \mathrm{Cl^-}. \qquad (31)$$

Additional molecules of solvent can become hydrogen bonded to mono- and dialkylammonium ions. This suggestion, with the structures of hydrated cations now written more specifically—for example, $\mathrm{R_3NH^+ \ldots OH_2}$—has become widely accepted, as it explains other phenomena besides the promotion of ionic conductance by hydroxylic solvents and differences in the mobilities of isomeric cations in such solvents.

In harmony with Walden's findings, Wynne-Jones observed that the hydrochlorides of bases like piperidine, dipropylamine, and diphenylguanidine are extremely weak electrolytes in nitrobenzene. (In partial disagreement with Walden, he concluded that the perchlorates of the bases studied are more highly conducting than the picrates in nitrobenzene.)

Wynne-Jones also noted the differing behavior of *incompletely substituted ammonium salts* in five solvents of *closely similar dielectric constants.* In three of these solvents (acetone, acetonitrile, nitrobenzene) the salts are only weak electrolytes, even though in the other two solvents (methanol, ethanol) they are strong electrolytes.

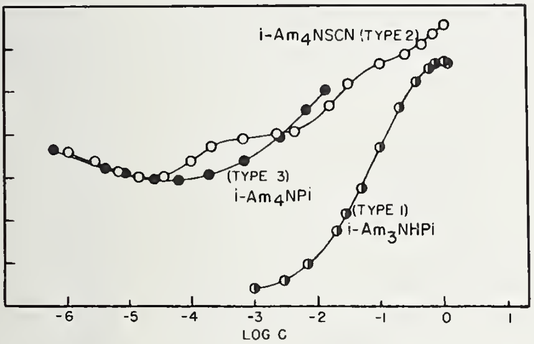


Figure 9. *Conductance plots for three different types of salts in benzene.*

Reproduced with minor changes from C. A. Kraus, J. Chem. Educ. **35**, 324 (1958), with the permission of the author and the publisher. (Ref. No. 329.)

c. Investigations of Kraus, Fuoss, and associates [24, 326–336]. Striking differences in the conductance behavior of completely and incompletely substituted ammonium salts were also observed by C. A. Kraus and R. M. Fuoss and their co-workers in the course of extensive investigations of "properties of electrolytic solutions." Kraus concluded [329] that electrolytes in benzene solution show three types of behavior, which are illustrated by the three conductance curves of figure 9. These curves were obtained by plotting the logarithm of the equivalent conductance against the logarithm of the (molar) concentration. At concentrations less than about 1 *M* each curve of figure 9 shows at least one minimum. The minima at the lowest concentrations studied are attributed to overlapping reactions involving such species as "ion pairs," "simple ions," and "triple ions." Thus, representing any uni-univalent salt by the formula MX, the following equilibria are supposed to coexist:

$$M^+X^- \rightleftharpoons M^+ + X^- \qquad (32)$$

$$M^+X^- + M^+ \rightleftharpoons M^+X^-M^+ \qquad (33a)$$

$$X^- + M^+X^- \rightleftharpoons X^-M^+X^-. \qquad (33b)$$

Equation 32 indicates an equilibrium between ion pairs and simple ions, the corresponding equilibrium constant being referred to as the "ion-pair dissociation constant." Equations 33a and 33b indicate the formation of positively or negatively charged triple ions by association of ion pairs with simple ions. At high concentrations more complex aggregates may be formed.

Here, we are interested only in the equilibrium represented by eq 32, which is believed to account well for conductance behavior at very low concentrations—for example, for the tetraalkylammonium salts in the concentration range extending from about 10^{-5} to 10^{-6} *M*, where the conductance rises gradually from its minimum value. Experimental results which are not shown in figure 9 indicate an analogous gradual rise in the conductance of the tertiary ammonium picrate at very low concentrations. Kraus and Fuoss have devised procedures for calculating ion-pair dissociation constants, examples of which are given in tables 32 to 35.

In table 32 the ion-pair dissociation constants (expressed as *log K* values) of several quaternary ammonium picrates in benzene and five other organic solvents are compared with the constants for picrates with at least one hydrogen atom attached to the ammonium nitrogen. The table illustrates Kraus' two main reasons for considering, in agreement with Wynne-Jones, that cations and anions of partly substituted ammonium salts interact through non-Coulombic as well as through Coulombic forces:

(1) Ion-pair dissociation constants of *completely* substituted ammonium picrates are more than 1000-fold greater than those of *incompletely* substituted picrates, not only in benzene, chlorobenzene, and ethylene chloride (all with relatively low dielectric constants), but also in nitrobenzene ($\epsilon \sim 35$). The close similarity of the constants for the picrates having NH_4^+, $BuNH_3^+$, $Bu_2NH_2^+$, or Bu_3NH^+ as the cation is especially noteworthy [24, 327–329, 335].

(2) The enormous disparity in the ion-pair dissociation constants of ammonium picrate and tetraalkylammonium picrates almost disappears when pyridine is the solvent, though its dielectric constant is only about a third that of nitrobenzene. Such behavior is to be expected if we accept the view that the ammonium ion is hydrogen bonded to picrate in nitrobenzene solution, but to pyridine when the latter is the solvent [332]. The differences can be represented by the two structures $H_3NH^+ \ldots Pi^-$ and $H_3NH^+ \ldots Py$.

The last two salts listed in table 32 under the heading "Other Ammonium Salts" are *hydroxyammonium* picrates. That is, they are derived from tertiary amine oxides instead of from amines, and oxygen, rather than hydrogen, is directly attached to the ammonium nitrogen. The two examples given—Me_3NOHPi and $PhN(Me_2)OHPi$—seem to be about equally strong as electrolytes, having ion-pair dissociation constants about a tenth as great as those of ammonium picrate and partly alkylated ammonium picrates. As in the preceding cases, hydrogen bonding of cation to anion is an attractive and plausible explanation for the very low tendency toward ion-pair dissociation, as well as for the marked disparity in the dissociation constants of *methoxy*trimethylammonium and *hydroxy*trimethylammonium picrates.

Table 33 contains ion-pair dissociation constants which indicate a dependence of these values on the nature of the anion. Thus, in comparing values for pyridonium perchlorate and pyridonium picrate in ethylene chloride and in comparing values for butylammonium perchlorate and butylammonium picrate in nitrobenzene we observe the perchlorate to be

TABLE 32. *Log K for ion-pair dissociation of some quaternary and other ammonium picrates in several organic solvents (25°)* [a]

Solvent (ϵ)	Quaternary Ammonium Salts			Other Ammonium Salts		
	Cation [b]	Log *K*	Reference	Cation [b]	Log *K*	Reference
Benzene (2.27)	$i\text{-Am}_4\text{N}^+$	-17.05	[326]	$i\text{-Am}_3\text{NH}^+$	-20.60	[326]
Chlorobenzene (5.63)	Bu_4N^+	-7.73	[330]	Bu_3NH^+	-12.68	[330]
Ethylene chloride (10.23)	Bu_4N^+	-3.64	[331]	Bu_3NH^+	-7.68	[331]
Pyridine (12.3)	Me_4N^+	-3.17	[332]	NH_4^+	-3.55	[332]
	Bu_4N^+	-2.91	[332]	—	—	
Acetone (20.7)	Me_4N^+	-1.95	[333]	NH_4^+	-2.95	[333]
	Bu_4N^+	-1.65	[334]	—	—	
Nitrobenzene (34.8)	—	—		NH_4^+	-3.84	[24]
	—	—		BuNH_3^+	-3.83	[24]
	—	—		Bu_2NH_2^+	-3.81	[24]
	Bu_4N^+	[c] -0.7	[327]	Bu_3NH^+	-3.72	[24]
	Me_4N^+	-1.40	[335]	Me_3NH^+	-3.82	[335]
	PhN^+Me_3	-1.39	[335]	$\text{PhN(Me}_2\text{)H}^+$	-4.39	[24]
	$\text{Me}_3\text{N}^+\text{OMe}$	-1.60	[335]	Me_3NOH^+	-4.77	[24]
				$\text{PhN(Me}_2\text{)OH}^+$	-4.72	[24]

[a] Log *K* corresponds to the reaction $\text{R}_4\text{N}^+\text{Pi}^- \rightleftharpoons \text{R}_4\text{N}^+ + \text{Pi}^-$, where R may be alkyl, aryl, or hydrogen. Some of the *K* values have been rounded off from three significant figures. Concentrations are in molar units.

[b] Bu signifies *n*-butyl.

[c] Approximate value; the constant is too large for accurate determination.

REFERENCES:

[24] C. R. Witschonke and C. A. Kraus, J. Am. Chem. Soc. **69,** 2472 (1947).
[326] R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. **55,** 3614 (1933).
[327] C. A. Kraus, J. Phys. Chem. **43,** 231 (1939).
[330] R. L. McIntosh, D. J. Mead, and R. M. Fuoss, J. Am. Chem. Soc. **62,** 506 (1940).
[331] D. J. Mead, C. A. Kraus, and R. M. Fuoss, J. Am. Chem. Soc. **61,** 3257 (1939).
[332] D. S. Burgess and C. A. Kraus, J. Am. Chem. Soc. **70,** 706 (1948).
[333] M. J. McDowell and C. A. Kraus, J. Am. Chem. Soc. **73,** 3293 (1951).
[334] M. B. Reynolds and C. A. Kraus, J. Am. Chem. Soc. **70,** 1709 (1948).
[335] E. G. Taylor and C. A. Kraus, J. Am. Chem. Soc. **69,** 1731 (1947).

TABLE 33. *Ion-pair dissociation constants of some incompletely substituted ammonium salts containing different anions* [a]

Solvent (ϵ)	Cation	Anion	Log *K*	Reference
Benzene (2.27)	$i\text{-Am}_3\text{NH}^+$	Pi^-	-20.60	[326]
Toluene (2.38) [b]	Bu_3NH^+	Cl^-	-18.82	[336]
Ethylene chloride (10.23)	PyH^+ [c]	ClO_4^-	[d] -6.3	[327]
	PyH^+	Pi^-	[d] -7.4	[327]
Nitrobenzene (34.8)	BuNH_3^+	ClO_4^-	-2.60	[24]
	BuNH_3^+	Pi^-	-3.83	[24]
	Bu_3NH^+	Pi^-	-3.72	[24]
	Bu_3NH^+	I^-	-4.02	[24]

[a] Log *K* corresponds to the reaction $\text{BH}^+\text{A}^- \rightleftharpoons \text{BH}^+ + \text{A}^-$. Concentrations are in molar units, and $t = 25°$ unless otherwise indicated.

[b] At 35°.

[c] For convenience, pyridinium ion (PyH^+) is listed as being a substituted ammonium ion.

[d] Approximate value.

REFERENCES:

[24] C. R. Witschonke and C. A. Kraus, J. Am. Chem. Soc. **69,** 2472 (1947).
[327] C. A. Kraus, J. Phys. Chem. **43,** 231 (1939).
[336] V. Deitz and R. M. Fuoss, J. Am. Chem. Soc. **60,** 2394 (1938).

the more highly dissociated salt. Kraus regarded these examples as further evidence of non-Coulombic attraction between cation and anion, perchlorate ion being known to possess a weaker affinity for the proton than picrate ion [327, 328].

Part of the results obtained by Kraus and Witschonke in studying ion-pair dissociation of picrates in nitrobenzene [24] have already been shown in table 32. In additional measurements, summarized in table 34 (as log K values), they studied three picrates (anilinium, dimethylanilinium, and pyridinium) which undergo "acid-base dissociation" (eq 18) as well as ion-pair dissociation (eq 17). Acid-base *association* constants are given in the table in place of acid-base dissociation constants. Results for anilinium picrate in *acetonitrile*, obtained by French and Muggleton [337], are included. It should be noted that the acid-base association constants were inferred from the conductance values and the stoichiometry, not measured directly. This table indicates that acid-base behavior is likely to seem more complex in dipolar aprotic solvents than in aprotic solvents in which, as we have seen (table 32), ion-pair dissociations are an almost negligible accompaniment of acid-base association.

TABLE 34. *Values of log* K_{BHA} *and log* K_{BH^+,A^-} *for some picrates undergoing both acid-base dissociation and ion-pair dissociation* (25°) [a]

Solvent (ϵ)	Cation	Log K_{BHA}	Log K_{BH^+,A^-}	Reference
Nitrobenzene (34.8)	$PhNH_3^+$	2.10	−4.7	[24]
	$PhN(Me_2)H^+$	3.60	−4.39	
	PyH^+	4.79	−4.26	
Acetonitrile (36.2)	$PhNH_3^+$	2.63	−2.98	[337]

[a] Log K_{BHA} corresponds to the equilibrium $B + HA \rightleftharpoons BHA$, and log K_{BH^+,A^-} corresponds to the equilibrium $BHA \rightleftharpoons BH^+ + A^-$. Concentrations are in moles/liter.

REFERENCES:

[24] C. R. Witschonke and C. A. Kraus, J. Am. Chem. Soc. **69**, 2472 (1947).
[337] C. M. French and D. F. Muggleton, J. Chem. Soc., p. 2131 (1957).

TABLE 35. *Effects of bases on ion-pair dissociation constants of ammonium and partly substituted ammonium picrates in nitrobenzene* (25°) [a]

Cation	Base Added	Molarity of Base	Log K
NH_4^+	None	....	−3.84
	C_5H_5N	0.039	−3.63
Bu_3NH^+	None	....	−3.72
	C_5H_5N	0.036	−3.63
$PhN(Me_2)OH^+$	None	....	−4.70
	C_5H_5N	0.035	−3.31
Me_3NOH^+	None	....	−4.77
	H_2O	0.01	−4.65
	C_5H_5N	0.001	−4.45
	C_5H_5N	0.010	−3.92
	C_5H_5N	0.037	−3.48
	Et_3N	0.001	−3.30
	Et_3N	0.038	−3.06
	$C_5H_{10}NH$	0.001	−3.28
	$C_5H_{10}NH$	0.010	−2.97

[a] Condensed from results of C. R. Witschonke and C. A. Kraus, J. Am. Chem. Soc. **69**, 2472 (1947).

REFERENCE:

[24] C. R. Witschonke and C. A. Kraus, J. Am. Chem. Soc. **69**, 2472 (1947).

We noted in discussing table 32 that picrates of all types undergo ion-pair dissociation to about the same extent in the basic solvent pyridine and attributed this behavior to formation of cations of the type $BH^+ \ldots Py$. Any other base would be expected to perform analogously, to an extent dependent on its electron-donor ability. Kraus and Witschonke tested this assumption by adding pyridine to nitrobenzene solutions of four picrates which exhibit a strong tendency toward formation of hydrogen-bonded ion pairs, namely, NH_4Pi, Bu_3NHPi, $PhN(Me_2)OHPi$, and Me_3NOHPi (compare table 32) [24]. Water, triethylamine, and piperidine were also added, in varying amounts, to nitrobenzene solutions of Me_3NOHPi. Examples of results obtained are shown in table 35. As predicted, adding any one of these bases, which except for water have dielectric constants far lower than that of nitrobenzene (see table 2), produced increases in the extent of ion-pair formation. Effects were proportionate to the concentration of added base, and also paralleled the accepted order of electron-donor abilities of the bases.

d. Summary. In our brief review of conductance experiments by Walden, Wynne-Jones, Kraus, Fuoss, and their associates we have seen that all of the experiments indicate a strong tendency for hydrogen bond formation between cations and anions of salts that are produced by combining hydrogen acids with ammonia, amines, pyridine, or tertiary amine oxides. The principal evidence is:

(1) Such salts undergo far less ion-pair dissociation than their quaternary ammonium analogs in aprotic solvents and likewise in dipolar aprotic solvents;

(2) Insignificant differences in ion-pair dissociation are observed when the salts are transferred to a basic solvent such as pyridine or when a basic compound is added to their solutions in aprotic or dipolar aprotic solvents.

We are justified in concluding that nonpolar and dipolar aprotic solvents are differentiating solvents because they are deficient in proton donor-acceptor abilities. This similarity in the behavior of the two groups of solvents enables us to make predictions about acid-base behavior in nonpolar aprotic solvents by analogy with acid-base behavior in dipolar aprotic solvents—or vice versa—when direct experimental evidence is lacking.

Very little can be said about the extent of ionic dissociation of hydrogen acids dissolved in aprotic or dipolar aprotic solvents. In the earliest recorded experiments, Kablukoff studied the electrical conductivity of hydrogen chloride in carefully dried benzene, xylene, hexane, and ether [338]. He reported that addition of this acid produced very slight reductions in the resistance of the solvents. Such evidence of conductance is commonly attributed to minute traces of water or other basic impurities [339]. According to Kraus [327], hydrogen chloride dissolved in nitrobenzene is a very weak electrolyte, while perchloric acid is a rather strong electrolyte in the same solvent. La Mer and Downes [340] stated that addition of trichloroacetic acid to benzene does not change the conductivity, at least in amounts up to 0.04 M. Maryott [341] commented that acids or bases have almost negligibly low conductances in dilute benzene solutions.

We have stressed the minuteness of the tendency for trialkylammonium picrates and related salts to undergo ion-pair dissociation in benzene and similar solvents. However, it should be pointed out that acid-base titrations have been performed conductimetrically in benzene, by La Mer and Downes [340] and by Maryott [341]. Such titrations are possible because the conductance method is so sensitive that minute increases in ion concentrations accompanying salt formation are measurable. Moreover, the concentrations used in the titrations referred to were much larger than those at which simple ions are most likely to be formed, and triple ions or still larger aggregates were probably more prevalent. More will be said about triple ions in section 4.4.

4.3.2. Dielectric Constants

In the discussion of figure 9, which contains curves showing the conductance of salts dissolved in benzene as a function of concentration, it was stated that the shapes of the curves have been explained by Kraus and associates [329] in terms of equilibria between simple ions, ion pairs, and triple ions (eqs 32, 33a, and 33b). Our attention will continue to be focused on *ion pairs*. Some of the best direct evidence for the existence of this species comes from the dipole moments derived from dielectric constant data. Values of dipole moments of salts obtained by several investigators are given in tables 36 to 38.

The variation of the dielectric constant of salt solutions with concentration provides additional information about association or dissociation of dissolved molecules. For example, such curves have demonstrated differences in the aggregation of primary, secondary, and tertiary ammonium salts. Illustrative curves will be discussed in the following section (see fig. 10).

a. Dielectric polarization of substituted ammonium picrates and halides in benzene. Kraus and co-workers [342] demonstrated that quaternary and tertiary ammonium picrates and halides have large polar (dipole) moments in benzene solution. Subsequently, Maryott [23, 343] confirmed this finding and determined the dipole moments of additional salts, including some primary and secondary ammonium picrates. Results of both authors are shown in table 36. It is clear that the dipole moments of the salts are far larger than the moments of the component bases and acids, which are in the range 0–2 D (Debye unit). According to the more recent measurements (which are thought to be a little more accurate than the values first obtained), the dipole moments of partly alkylated ammonium picrates appear to be in the vicinity of 11–12 D, the dipole moments of *completely* alkylated ammonium picrates being several units higher. A similar difference is seen on comparing the moments for Bu_4NBr and Bu_3NHBr. These values are consistent with the assumption of ion pair formation. The lower moments of the incompletely alkylated salts indicate a closer association of cation and anion, in harmony with the postulate of hydrogen bonding [329].

Figure 10 was constructed by Maryott [343], from dielectric polarization data for several partly alkylated ammonium picrates, to compare effects of altering the concentration of the solute and also changing the solvent from benzene to dioxane. In this figure the increment $\Delta\epsilon/N_2$ is plotted against N_2. In all cases, $\Delta\epsilon/N_2$ is quite high at low solute content. When *dioxane* is the solvent $\Delta\epsilon/N_2$ changes very little during a 10-fold increase in N_2. The same is true for benzene containing tributylammonium picrate, in agreement with results of Kraus and associates [328, 342] for triamyl- and tributylammonium picrates and tributylammonium chloride, bromide, and iodide. The interpretation given [342, 343] is that the molecular state of these tertiary ammonium salts is not affected by changes of concentration.

A decided drop of $\Delta\epsilon/N_2$ with increasing N_2 is observed, however, for *primary and secondary* ammonium picrates *in benzene*. The occurrence of this fall-off and its absence in dioxane are strong indications of association through hydrogen bonding. Maryott [343] found his data for dipropyl- and dibutylammonium picrates to be consistent with a monomer-dimer equilibrium, with the respective log $K_{1,2}$ values 2.07 and 2.26 (converted to molar

TABLE 36. *Dipole moments of some substituted ammonium salts in benzene* [a]

Quaternary Ammonium Salts (25°) [b]			Partly Alkylated Ammonium Salts (30°) [c]		
Cation	Anion	μ, Debye units	Cation	Anion	μ, Debye units
i-Am$_4$N$^+$	Pi$^-$	18.3	i-Am$_3$NH$^+$	Pi$^-$	11.9 [b] 13.3
i-Am$_4$N$^+$	SCN$^-$	15.4	Bu$_3$NH$^+$	Pi$^-$	11.9 (12.2) [b] 13.1 [d] 11.4
Bu$_4$N$^+$	Pi$^-$	17.8 [d] 15.0	Et$_3$NH$^+$	Pi$^-$	11.7
Bu$_4$N$^+$	ClO$_4^-$	14.1	Et$_2$(PhCH$_2$)NH$^+$	Pi$^-$	11.8
Bu$_4$N$^+$	Br$^-$	11.6	(PhCH$_2$)$_3$NH$^+$	Pi$^-$	12.0
Bu$_4$N$^+$	CH$_3$COO$^-$	11.2	Bu$_3$NH$^+$	I$^-$	[b] 8.1 [d] 7.7
			Bu$_3$NH$^+$	Br$^-$	[b] 7.6
			Bu$_3$NH$^+$	Cl$^-$	[b] 7.2
			Bu$_2$NH$_2^+$	Pi$^-$	11.5 (12.1)
			Pr$_2$NH$_2^+$	Pi$^-$	11.5
			C$_8$H$_{17}$NH$_3^+$	Pi$^-$	(12.1)
			C$_{18}$H$_{37}$NH$_3^+$	Pi$^-$	(12.3)

[a] A few of the measurements were made in other solvents, as indicated in footnotes c and d. All alkyl radicals were straight-chain except *iso*-amyl.

[b] From work of C. A. Kraus and co-workers as summarized in ref. [342].

[c] Results of A. A. Maryott (30°) [23, 343] except as noted otherwise. Values given in parentheses were determined in dioxane.

[d] Determined by Davies and Williams (18–20°) [344] in benzene, dioxane, *m*-xylene, or mixtures of these solvents.

REFERENCES:

[23] A. A. Maryott, J. Res. NBS **41**, 7 (1948).
[342] C. A. Kraus, J. Franklin Inst. **225**, 687 (1938).
[343] A. A. Maryott, J. Res. NBS **41**, 1 (1948).
[344] M. Davies and G. Williams, Trans. Faraday Soc. **56**, 1619 (1960).

units). Aggregation of the primary alkylammonium picrates apparently is still more extensive.

We have just noted (fig. 10) that in the case of *tributylammonium* picrate in benzene the ratio $\Delta\epsilon/N_2$ is not measurably affected by altering the concentration of the salt. However, Maryott observed [23] that $\Delta\epsilon/N_2$ decreases with increasing dilution of *tribenzylammonium* picrate in benzene, indicating that this salt undergoes partial dissociation into picric acid and tribenzylamine. He devised a procedure for calculating both the *dipole moment* of the salt and the (1:1) *acid-base equilibrium constant* (at 30° and 40°). The dipole moment (see table 36) was found to be essentially the same as values obtained for stable picrates. It is noteworthy that this method of determining an acid-base equilibrium constant yielded values in almost perfect concordance with one obtained from spectral absorbance data (25°) for solutions containing a fixed concentration of picric acid and varying quantities of tribenzylamine [20].

b. Dielectric polarization of other acid-base complexes in benzene. Numerous additional measurements of dipole moments of salts and other acid-base complexes have been reported in recent years, but it seems likely that in some instances the values are too low. These are instances in which experi-

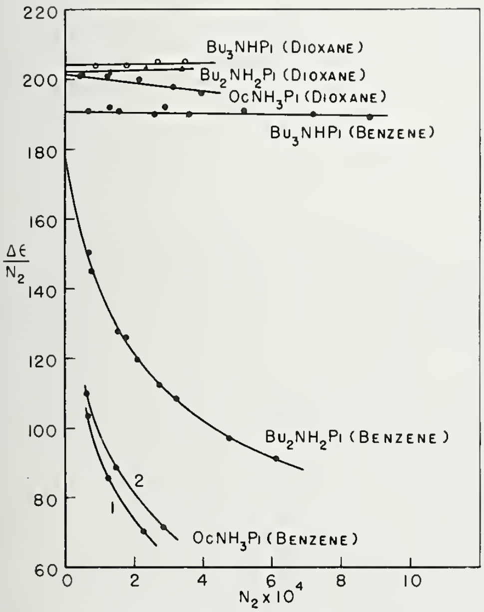


FIGURE 10. *Variation of dielectric constant of benzene or dioxane with concentration of dissolved primary, secondary, or tertiary ammonium picrate. The rate of change of the dielectric constant with changing mole fraction of solute* ($\Delta\epsilon/N_2$) *is plotted against* N_2.

Reprinted with permission from A. A. Maryott, J. Res. NBS 41, 1 (1948). (Ref. No. 343.)

mental conditions, only sketchily described, appear to have been such that the acid-base complex would be partly dissociated into the constituent acid and base, and the description (also sketchy) of the method used in calculating dipole moments does not indicate that the investigators were aware of, and made proper allowance for, the acid-base dissociation.

Table 37 contains results of Sobczyk and Syrkin [345, 346] for eight 1:1 acid-base complexes in benzene. The bases represented comprise five aliphatic amines (two tertiary, two secondary, and one primary) in addition to pyridine and two related bases. The acids represented are picric acid and five carboxylic acids (benzoic, propionic, and the three chloro derivatives of acetic acid). It will be noted that the dipole moments given for the picrates of pyridine-type bases are only slightly lower than the values for picrates of stronger bases (compare table 36).

Table 37. *Dipole moments of some 1:1 acid-base complexes in benzene* [a]

Base	μ, Debye units (20–25°), where acid was:					
	C_6H_5COOH	C_2H_5COOH	$CH_2ClCOOH$	$CHCl_2COOH$	CCl_3COOH	HPi
$C_5H_{10}NMe$	3.87	....	5.97	7.87	8.78	....
Et_3N	....	3.72	6.37	....	8.82	[b] 11.7
$C_5H_{10}NH$	2.39	....	2.87	....	3.15	....
Et_2NH	....	....	2.17	....	....	....
$EtNH_2$	....	....	(1.52)	....	....	....
Pyridine	2.88	2.86	4.67	....	7.78	10.1
Quinoline	....	2.88	4.77	....	8.32	10.3
Acridine	....	2.75	4.98	....	8.60	10.9

[a] From work of L. Sobczyk and associates [345–346].

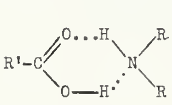
[b] Result of A. A. Maryott (30°); see table 36.

REFERENCES:

[345] L. Sobczyk and J. K. Syrkin, Roczniki Chem. **30**, 881, 893 (1956); **31**, 197 (1957). *CA* **51**, 7786, 14347 (1957).

[346] L. Sobczyk, *in* Hydrogen Bonding (Ljubljana, 1957), (D. Hadži and H. W. Thompson, Eds.), p. 323 (Pergamon Press, New York, 1959).

Sobczyk and Syrkin have concluded that the dipole moments of carboxylates of *tertiary aliphatic amines* and *pyridine-type bases* parallel in magnitude the proton-donor abilities of the acids involved. However, the strengths of the acidic components are not thought to affect measurably the dipole moments of *secondary ammonium* carboxylates, which are found to be much lower than the moments of either tertiary aliphatic ammonium or pyridinium-type carboxylates. These extremely low moments are attributed to a stable *monomeric* structure in which both of the ammonium hydrogens participate in hydrogen bonding, as indicated by formula XXXII.



(XXXII)

Tertiary aliphatic ammonium carboxylates were found to have the same dipole moment in benzene as in dioxane, and are thought to be unassociated in these two solvents. In contrast, secondary ammonium salts dissolved in dioxane were observed to show increased polarity with dilution, becoming more like tertiary ammonium salts. Sobczyk and Syrkin also concluded that piperidinium picrate is strongly associated in benzene. These findings parallel Maryott's results (see fig. 10 and related discussion).

Table 38 contains results obtained by Gur'yanova and Beskina [347] in an investigation of the association of benzoic acid in benzene, at a stoichiometric concentration in the range 0.034–0.123 *M*, with successive portions of the following bases: Two primary amines (n-$BuNH_2$, $PhNH_2$), four secondary amines (Et_2NH, i-Pr_2NH, n-Bu_2NH, $C_5H_{10}NH$), and two tertiary amines (Et_3N, n-Am_3N). They performed both "dielectrometric titrations" and "cryoscopic titrations," and made the following deductions from the combined results:

(1) At the concentrations used, benzoic acid exists as the dimer and it reacts as this species.

(2) All of the amines except aniline reacted with benzoic acid to form products with large dipole moments. This was shown by the immediate sharp rise in dielectric permeability of solutions on commencing to add an amine. The rise in permeability continued until the stoichiometric ratio C_b/C_a

TABLE 38. *Dipole moments of benzoic acid-amine complexes in benzene* [a]

Amine (μ)	μ (25°), Debye units		
	$B(HA)_2$ [b]	BHA [c]	$(BHA)_2$ [c]
n-$BuNH_2$ (1.44)	(3.92)		3.02
Et_2NH (1.26)	4.62		2.88
i-Pr_2NH (1.20)	4.80		2.75
n-Bu_2NH (1.27)	4.69		3.11
$C_5H_{10}NH$ (1.09)	4.57		3.28
Et_3N (1.02)	4.88	4.38	
n-Am_3N (1.03)	4.72	3.87	

[a] Results of E. N. Gur'yanova and I. G. Beskina [347]. The stoichiometry was determined cryoscopically.

[b] Intermediate product. B = amine, HA = benzoic acid.

[c] Final product.

REFERENCE:

[347] E. N. Gur'yanova and I. G. Beskina, J. Gen. Chem. USSR Eng. Transl. **33**, 914 (1963).

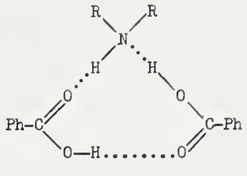
equalled 0.5. At this stage the formation of a complex of the composition $B(HA)_2$ was inferred.

(3) In the interval where C_b/C_a was in the range 0.5–1.0 complex formation followed a different pattern for primary and secondary amines than for tertiary amines. With tertiary amines the dielectric permeability rose slightly, while with the other two classes of amine there was a decrease. From these two patterns of behavior and the cryoscopic data it was deduced that primary and secondary amines formed benzoates of the composition $(BHA)_2$ whereas tertiary amines formed benzoates of the general formula BHA.

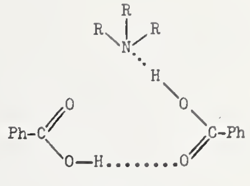
(4) After attaining the ratio $C_b/C_a = 1$ all systems again behaved similarly, there being no indication of the formation of any additional species.

Structures postulated for the different species—$B(HA)_2$, $(BHA)_2$, and BHA—are indicated below (XXXIII–XXXV). Formulas XXXIIIa and XXXIIIb apply, respectively, to secondary and tertiary ammonium benzoates.

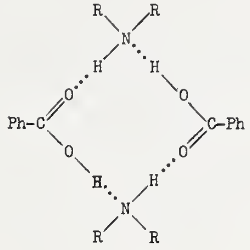
Piperidine-benzoic acid mixtures are the only ones measured both by Gur'yanova and Beskina and by Sobczyk and Syrkin. As we have seen, they agree that both hydrogens attached to a secondary ammonium nitrogen are involved in hydrogen bonding, but their conclusions differ in detail. Whereas the latter pair of authors, who postulated only 1:1 acid-base association, yielding the structure BHA, calculated 2.39 as the dipole moment of piperidinium benzoate (in benzene), two higher values—4.57 and 3.28—were obtained in the work of Gur'yanova and Beskina as the moments of the salts postulated to have the respective compositions $B(HA)_2$ and $(BHA)_2$.



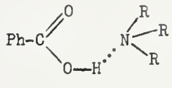
(XXXIIIa)



(XXXIIIb)



(XXXIV)



(XXXV)

In summary, those who have studied acid-base associations in benzene by measuring changes in the dielectric polarization of systems similar to the examples given consider hydrogen bond formation to be involved, and there is strong evidence that multiple hydrogen bonding occurs in secondary and primary ammonium salts (at least, those of the types which have been discussed here). Unfortunately, much of the dipole moment data so far reported for *weak* acid-base complexes is of questionable validity because the *extent* of complex formation does not seem to have been given adequate consideration. Moreover, the assumption of 1:1 acid-base association as the only form of combination may not have been warranted in some cases. The value of the method is enhanced when used in conjunction with other types of measurement.

4.3.3. Colligative Properties

The study of colligative properties is an important adjunct to investigations of possible hydrogen bonding in ion pairs. For example, in the preceding section we noted that Gur'yanova and Beskina, when studying the structures of some carboxylic acid-amine complexes in benzene, performed cryoscopic measurements in addition to dielectric polarization measurements, and that the molecular weights deduced from cryoscopic data led them to postulate a *dimeric* hydrogen-bonded structure for a secondary ammonium carboxylate rather than the *monomeric* hydrogen-bonded structure postulated by Sobczyk and Syrkin.

An earlier example of conclusions based in part on a study of colligative properties is found in the extensive investigations of physical properties of salts in benzene solutions made by Kraus and associates. The salts investigated, though mainly quaternary ammonium salts, also included a few tertiary ammonium salts. Part of their deductions from conductance and dielectric polarization measurements have been presented (sections 4.3.1c and

4.3.2a). Results which they obtained from cryoscopic determinations will be summarized in this section, together with overall conclusions [348–351].

A newer method of studying colligative properties is the "differential vapor pressure (DVP) method" used by Bruckenstein and Saito [352] for investigating various acid-base equilibria in benzene.

a. Cryoscopy. The salts studied by Kraus and coworkers included three tertiary ammonium salts, namely, tri-*i*-amylammonium picrate [348, 350], tri-*n*-butylammonium picrate [349], and tri-*n*-butylammonium iodide [349, 351]. Freezing point determinations were made over a wide range of concentrations: from 0.001 molal to the highest concentration which the solubility made feasible. When values of *n* (the apparent molecular weight of a salt divided by the formula weight) were plotted as a function of the logarithm of the molal concentration it became apparent that the solutes studied may be classified in three general types [329]. These types are illustrated in figure 11 by the following examples: *Type 1*, i-Am$_3$NHPi; *type 2*, i-Am$_4$NSCN; *type 3*, i-Am$_4$NPi.

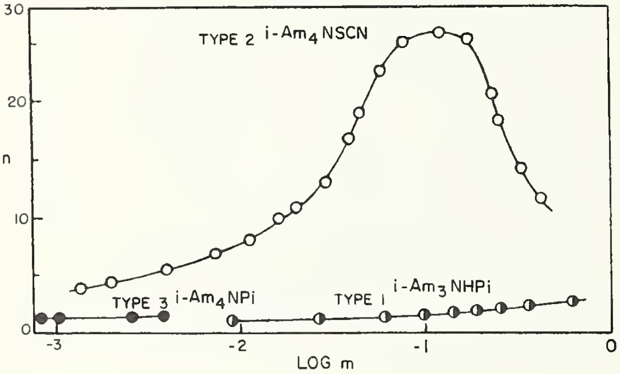


FIGURE 11. *Relation of association numbers* (n) *to the molal concentration, as determined cryoscopically for three different types of salts in benzene.*

Reproduced with minor changes from C. A. Kraus, J. Chem. Educ. **35**, 324 (1958), with the permission of the author and the publisher. (Ref. No. 329.)

Figure 11 shows very strikingly that *n*, which is a measure of the extent of self-aggregation of the solutes, is much greater for tetra-*iso*-amylammonium thiocyanate (type 2) than for the related tertiary (type 1) and quaternary (type 3) ammonium picrates Moreover, the curve for the thiocyanate displays a pronounced maximum at concentrations near 0.1 molal, but there is no indication of a maximum in the other two curves. Instead, the degree of aggregation rises very slowly with increasing concentration.

Table 39 contains additional evidence regarding the extent of aggregation of tertiary and quaternary ammonium salts in benzene. Of the salts studied, the two tertiary ammonium picrates (which show similar behavior) have the lowest tendency to form aggregates. For example, at 0.1 *m* concentration the aggregation of i-Am$_3$NHPi is still not extensive ($n=1.54$). At the same concentration aggregation of n-Bu$_3$NHI is somewhat greater ($n=2.95$). Tetra-*i*-amylammonium picrate, the only salt assigned to type 3, seems to be a little more highly aggregated, but its low solubility in benzene prevented measurements at concentrations greater than 0.0038 *m*. The much more highly associated salts assigned to type 2 (that is, the quaternary ammonium thiocyanates, iodide, and perchlorate) show individual variations in behavior: the maxima in *n* versus log *m* curves are different in magnitude and occur at different concentrations.

The examples given in figure 11 are the same as in figure 9, which displays three types of *conductance* behavior in benzene as a function of concentration. In previous discussion of figure 9 (sec. 4.3.1c) it was pointed out that portions of such conductance curves have been interpreted in terms of overlapping equilibria which involve simple ions, ion pairs, triple ions, and more complex (undefined) aggregates. It is noteworthy that the conductance curve for i-Am$_4$NSCN, which was found cryoscopically to form very large aggregates, has more inflections than the curves for i-Am$_4$NPi and i-Am$_3$NHPi, indicating the existence of a greater number of competing equilibria.

There is now a general recognition that dissociation of salts into cations and anions in water and other good ionizing media is well explained in terms of *ion-solvent* interactions. Obviously, when ion-solvent interactions are virtually non-existent, *solute-solute* interactions will assume greater importance, and they will be expected to vary in strength with such factors as the charge, composition, polarizability, size, structure, and symmetry of ions, as well as on their concentration. Such expectations have been borne out in the extensive investigations of tertiary and quaternary ammonium salts in benzene by Kraus and associates. As we have seen, these investigators discovered such salts to exhibit at least three differing patterns of associative behavior, as well as individual differences. A partial summary of their overall conclusions [348–351, 329] follows.

(1) In the most dilute salt solutions studied (below the first minimum in conductance), ion pairs are the predominant species, although there is a measurable concentration of simple ions (see 4.3.1a). Triple ions, (+−+) or (−+−), are not present in measurable quantities.

(2) Triple ions are formed in increasing proportion as the concentration increases. At first, their formation will not affect the proportion of simple ions appreciably, but a concentration will be reached where increasing conductance caused by triple ion formation will be offset by a decreasing conductance resulting from association of simple ions to form ion pairs. At this point the conductance will have its minimum value, since further increases in

TABLE 39. *Variation with concentration of the association numbers* (n) *of some salts in benzene* [a]

Salt	Moles of salt per 1000 g of benzene								
	0.001	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
n-Bu_3NHPi	1.01	1.07	....	....	....	....	....	....	....
i-Am_3NHPi	1.01	1.07	(1.12)	(1.30)	(1.54)	(1.91)	(2.18)	(2.40)	(2.52)
n-Bu_3NHI	1.12	1.4	(1.6)	(2.25)	(2.95)	(4.4)	(5.75)	(6.65)	(7.15)
$AgClO_4$	1.15	1.7	....	....	....	....	....	....	....
i-Am_4NPi[b]	1.3	....	....	....	....	....	....	....	....
n-Bu_4NSCN	2.4	4.2	(6)	(12)	(20)	(30)	(31.6)	(20.7)	(29)
i-Am_4NSCN	3.2	7.8	10.9	(19.5)	(25.6)	(23.5)	(15.5)	(12.2)	....
n-AmN(*n*-Bu_3)I	3.1	4.4	(5.8)	(9.8)	16.6	(21.6)	(21.4)	(19.7)	17.0
n-Bu_4NClO_4	3.0	5.0	....	....	....	....	....	....	....

[a] From results reported by Copenhafer and Kraus (see their tables I and II) [350] and by Young and Kraus (Table IV) [351]. Values in parentheses were obtained by interpolation.

[b] At the solubility limit (0.0038 *m*) $n = 1.4$.

REFERENCES:

[350] D. T. Copenhafer and C. A. Kraus, J. Am. Chem. Soc. **73**, 4557 (1951).
[351] H. S. Young and C. A. Kraus, J. Am. Chem. Soc. **73**, 4732 (1951).

concentration will increase the probability of triple ion formation.

(3) A succeeding stage is quadrupole formation. To account for dielectric polarization data it is postulated that in quadrupoles the constituent dipoles are sometimes in parallel and sometimes in anti-parallel alignment. Figure 11 and table 39 indicate that *i*-Am_3NHPi is only 6 percent associated to quadrupoles at the lowest concentration studied cryoscopically, while at the highest concentration, association has reached a little more than the quadrupole stage. It will be recalled that no significant self-association of tertiary ammonium salts was detectable in dielectric polarization measurements, which are made at much lower concentrations (see 4.3.2a). Association of *i*-Am_4NPi is somewhat more extensive, about 40 percent being associated to quadrupoles at the highest concentration studied (0.0038 *m*).

(4) Except at very low concentrations the experimental results have not provided definite clues as to the composition of aggregates.

(5) The type of behavior exhibited by a salt seems to depend on the following constitutional factors: In *type 1*, the salt is composed of two large ions which are hydrogen bonded; in *type 2*, a large cation is combined with a smaller anion; and in *type 3*, the cation and anion are both large, as in type 1 (but are not, of course, hydrogen bonded).

(6) The following are some characteristic differences in the physical behavior of the three types:

Type 1. The ion-pair dissociation constant (table 32) and dipole moment (table 36), as well as the extent of aggregation, are comparatively small. (All these properties are consistent with the hypothesis of hydrogen bonding.) The conductance minimum appears at a relatively high concentration, and the increase in conductance between the minimum and maximum is great.

Type 2. The ion-pair dissociation constant and the dipole moment are both relatively large. The first conductance minimum lies at much lower concentrations than for type 1, and the increase between minimum and maximum is much smaller. Conductance increases occur in a series of steps.

Type 3. The ion-pair dissociation constant and dipole moment are both somewhat larger than for type 2. (As previously noted, only one example of this type has been observed, and the highest concentration studied was 0.0038 *M*.)

It can hardly be expected that phenomena observed for the mixtures frequently dealt with can be readily understood when concentration effects on the behavior of individual solutes in aprotic solvents are so varied and imperfectly understood. The need for much further study of aprotic solutions is clear. In the present state of knowledge the most dilute range appears best suited for attempts to ascertain quantitative relationships, with proper attention to possible competing interactions of solutes with glass and other container materials.

b. The differential vapor pressure (*DVP*) *method* [352]. In this method the state of aggregation of solute particles is determined by measuring the difference in temperature of a pure solvent and a solution having the same equilibrium partial pressure of solvent. Interest in its use has been stimulated by recent developments in thermistors and other new instrumentation. It has the great merit of permitting flexibility in the choice of temperature.

Bruckenstein and Saito [352] explored the applicability of the method to the study of acid-base equilibria in benzene. The reacting base (B) and acid (HX) were contained in a thermostated chamber (apparently held at or near the laboratory temperature). The reactants included several carboxylic acids of the acetic or benzoic acid series and representative primary, secondary, and tertiary aliphatic amines. After the determination of Δt by measurements of voltage changes, values of i (eq 34) were plotted as a function of R (eq 35), as indicated in figure 12.

$$i = (\Delta t \text{ for } B + HX,\ C_B = x\text{-molar}) / (\Delta t \text{ for } C_{10}H_8 \text{ soln., } x\text{-molar}) \quad (34)$$

$$R = C_{\mathrm{HX}}/C_{\mathrm{B}} \quad (35)$$

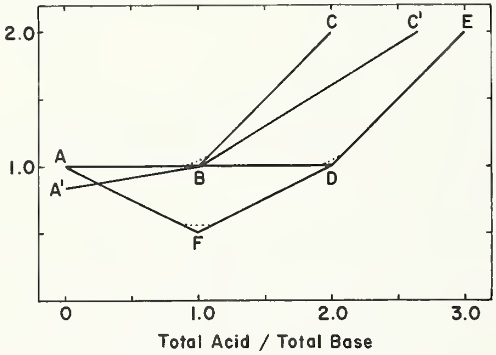


FIGURE 12. *Hypothetical acid-base titration curves in benzene; see text for explanation.*

Reproduced with minor changes from S. Bruckenstein and A. Saito, J. Am. Chem. Soc. **87**, 698 (1965), with the permission of the authors and the publisher. (Ref. No. 352.)

The analytical (stoichiometric) concentration of the base, symbolized here by C_{B}, was usually 0.01 *M*, but was also 0.05 *M* and 0.1 *M* in some experiments.

The several titration "curves" shown in figure 12 are hypothetical, and correspond to various situations in which the products formed have compositions such as BHX, BHX · HX, and $(BHX)_2$. The shape of a curve will be modified if a reactant is dimeric or partly dimerized. The hypothetical curves correspond to the five situations described below.

(1) *ABC:* B and HX are monomers and react quantitatively, the only reaction product being BHX.

(2) *A'BC:* Like (1) except that B is partly dimerized.

(3) *ADE:* B and HX, which are monomers, form BHX and then BHX · HX. There are no additional products.

(4) *ABC':* Like (3) except that a little BHX · HX is formed at the same time as BHX.

(5) *AFDE:* Monomeric B and HX associate in 1 : 1 ratio to form $(BHX)_2$. (No other product is formed.)

The curves will have rounded portions (see short dashes) whenever reactions do not proceed quantitatively.

Possible use of the DVP method for determining the self-association constants of the bases and acids was tested. The i-values obtained for 0.01-*M* amines differed from 1 by no more than 5 percent, but i for 1,3-diphenylguanidine (another base included in the investigations) indicated partial self-aggregation (compare sec. 4.1.3). That is, the value of i (0.87) corresponds to 78 percent monomer, the remainder being the dimer (if these are assumed to be the only species present). The method failed to yield accurate dimerization constants for the carboxylic acids. However, the constant obtained for benzoic acid was in approximate agreement with results by other methods (see table 24).

An example of the third type of curve (ADE) was obtained on adding trichloroacetic acid to the tertiary amine benzyl-*N*,*N*-dimethylamine; that is, base and acid reacted quantitatively to form monomeric BHX, which added further HX to give BHX · HX. In contrast, 0·01-*M* dibenzylamine, though associating in 1 : 1 ratio with trichloroacetic acid, yielded $(BHX)_2$; further acid gave a practically quantitative yield of the acid salt BHX · HX. (In both cases nonquantitative formation of $BHX(HX)_2$ was thought to occur on the continued addition of HX.) These conclusions as to the composition of the salt species formed parallel those of Gur'yanova and Beskina using benzoic acid instead of trichloroacetic acid (see table 38).

As noted above, Gur'yanova and Beskina deduced hydrogen-bonded structures for secondary and tertiary ammonium benzoates in benzene from their dielectric polarization data (compare formulas XXXIII–XXXV), and related acid-base systems studied in carbon tetrachloride are believed from infrared evidence to form hydrogen-bonded ion pairs. However, Bruckenstein and Saito, who also performed infrared measurements, consider their infrared data to indicate the absence of hydrogen bonding. Infrared evidence will be considered further in section 4.3.5.

4.3.4. Spectral Absorbance in the Visible and Ultraviolet Regions

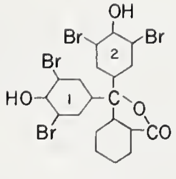
The differentiating character of benzene as a solvent has been very strikingly illustrated in systematic studies of acid-base reactions employing an indicator dye as one of the reactants. The most extensive investigation of this type so far performed has been reported in a series of papers dealing with visual and spectrophotometric observations of the behavior of bromophthalein magenta (BPM)—which is a phenolic indicator of the triphenylmethane class—following the addition of different types of organic bases. Solutions of bromophthalein magenta in benzene and other aprotic solvents are yellow in color. The yellow tone can be converted at will to practically any color of the rainbow by adding the proper base in a suitable amount. Such behavior is, of course, a marked departure from indicator behavior in aqueous solutions, where all bases (or all acids) cause uniformly similar color changes. The extraordinary range of colors exhibited in reactions of bromophthalein magenta with bases in aprotic solvents has received a logical explanation in terms of hydrogen bonding [14, 5, 21, 31, 15].

This section will be devoted largely to describing and discussing the color reactions of bromophthalein magenta. However, it should be emphasized at the outset that this compound is by no means unique in signaling the occurrence of hydrogen bonding through easily observable changes in electronic absorption spectra. For example, several indicators which are widely known through their extensive use in aqueous solutions have been found to show behavior analogous to that of BPM when in aprotic solutions. Examples are halogen derivatives of phenolsulfonephthalein (phenol red), such as bromophenol blue and bromocresol green [29]. Further examples have been found among nitrophenols such as picric acid [20], trinitro-*m*-cresol (methylpicric acid) [20], and 2,4-dinitrophenol [17]. Hydrogen bonding has also been inferred from the occurrence of spectral shifts in the near-ultraviolet region—for example, in studies of the association of α- and β-naphthol with triethylamine and other proton acceptors in *n*-heptane solution [353].

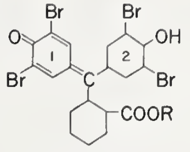
Two papers on spectrophotometric studies of complex anions containing actinide elements [413, 414] will be referred to in section 4.3.5*c*.

a. Bromophthalein magenta. The accompanying formulas show that bromophthalein magenta (XXXVII) bears a close structural relationship to 3′,5′,3″,5″-tetrabromophenolphthalein (XXXVI) and also to bromophenol blue (3′,5′,3″,5″-tetrabromophenolsulfonephthalein) (XXXVIII). Davis and Schuhmann, who studied both the ethyl and the *n*-butyl ester of tetrabromophenolphthalein (XXXVII, R=Et or *n*-Bu), adopted the respective names and symbols "bromophthalein magenta E" (BPM–E) and "bromophthalein magenta B" (BPM–B) for these compounds [14]. The two esters differ slightly in physical properties, such as the lower melting point and greater solubility in hydrocarbons shown by BPM–B, but no differences in their chemical behavior as phenols were observed.

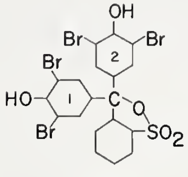
It is readily perceived that (XXXVI) may be regarded as the isomer of a *hypothetical* carboxylic acid in which the proton forming part of the –OH group attached to ring 1 has migrated to convert the lactoid COO– to a –COOH group. The yellow color of the esters (XXXVII) is explained by the quinoid structure of ring 1. Evidently the lactone ring of (XXXVI) is too stable for ready conversion of (XXXVI) to its yellow quinoid isomer or for salt formation with added bases when in benzene solution. In contrast, the *esters* react instantaneously with alkylamines and other bases of comparable strength—not, however, with bases as weak as aniline and pyridine.



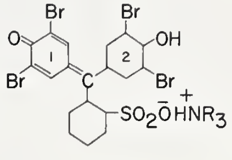
(XXXVI)



(XXXVII)



(XXXVIII)



(XXXIX)

"Sultones" (XXXVIII) are much more reactive than lactones (XXXVI). Thus, bromophenol blue, although it gives a colorless solution in dry benzene, reacts instantaneously in 1 : 1 ratio with added bases, strong or weak, to form the yellow salt indicated by (XXXIX). The spectral absorbance of (XXXIX) is very similar to that of the corresponding form of a closely related indicator, bromocresol green (3′,5′,3″,5″-tetrabromo-2′,2″-dimethylphenolsulfonephthalein). Transmittance curves for the latter indicator are shown in figure 13. The three

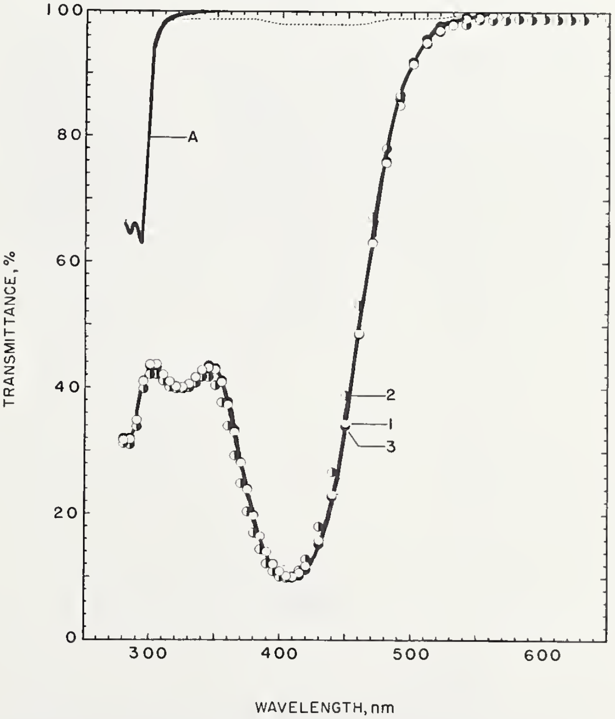
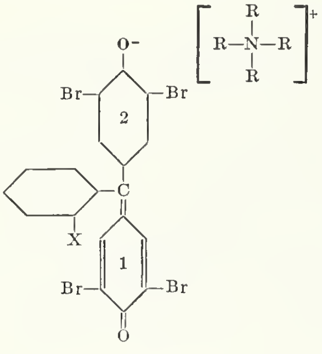


FIGURE 13. *Spectral transmittance of bromocresol green,* 5×10^{-5} M *in benzene: As prepared (faintly dashed line); in the presence of five molar equivalents of acetic acid (curve A); and in the presence of one molar equivalent of mono-, di-, or tri-*n*-amylamine (curves 1 to 3, respectively).*

Reproduced from figure 5 of M. M. Davis, P. J. Schuhmann, and M. E. Lovelace, J. Res. Natl. Bur. Std. **41**, 27 (1948). (Ref. 29.)

essentially identical curves numbered 1 to 3 were obtained by adding one equivalent of mono- di-, and tri-*n*-amylamine, respectively. The absorbance of (XXXIX) is very similar to that of (XXXVII) [29]. The "first stage" in the neutralization of bromophenol blue and other sulfonephthaleins is not observed in their aqueous solutions, as the sultone structure (XXXVIII) is unstable in water and yields the yellow ionized species analogous to (XXXIX). In solvents like benzene, toluene, chlorobenzene, and anisole it has provided a means for estimating the relative strengths of aniline or pyridine derivatives [85, 354] and of several carboxylic acids [355].

Quaternary ammonium salts of bromophthalein magenta E or B (XL) are found to give blue solutions,



(XL)

whatever the class of solvent used (see table 40, last column). The shift to a deep color is explained by the resonance hypothesis. One obviously important valence-bond structure is that in which the electronic patterns of rings 1 and 2 are quinoid and phenolate, respectively, and a second important structure is the one in which these electronic patterns are reversed. Figure 14 shows the type of spectral absorption curve obtained for quaternary ammonium salts of bromophthalein magenta dissolved in benzene (see curve labeled "Bu_4N salt") [14]. The most striking feature of the absorption curve is a strong band of symmetrical appearance, centered near 605 nanometers (millimicrons). As mentioned already, the solutions have a blue tone by transmitted light. Benzene solutions containing a quaternary ammonium salt *together with* unchanged bromophthalein magenta will, of course, have colors ranging from green-blue to yellow-green, according to the relative proportions of the acid and its quaternary ammonium salt.

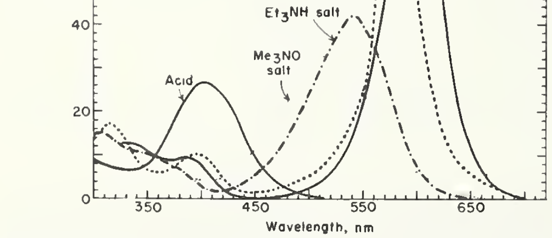


FIGURE 14. *Spectral absorption curves of bromophthalein magenta* E (*or* B) *and several of its salts in benzene solution.*
See M. M. Davis and P. J. Schuhmann, J. Res. NBS **39**, 221 (1947), figures 21 and 22. (Ref. No. 14.)

Solutions containing *tertiary ammonium salts* of bromophthalein magenta are strikingly dissimilar in color to solutions of quaternary ammonium salts of this acid. The dissimilarity can be appreciated by comparing the absorption curves given in figure 14 for the two types of salt. It will be noted that the curve labeled "Et_3NH salt" (which is typical of absorption curves obtained for tertiary ammonium salts) has $\lambda_{max.}$ near 540 nanometers (nm) instead of near 605 nm. It resembles the curve for the n-Bu_4N salt in being symmetrical, but it is broader and the intensity of absorption is only about half as great. It is well to take note here that the usual procedure for obtaining absorption curves for tertiary and other incompletely substituted ammonium salts is to add an amine to a benzene solution of the indicator acid, at first in minute quantities and then in gradually increasing amounts until a limit has been reached beyond which shifts in absorbance are no longer measurable. (It is assumed in this discussion that the base itself is colorless in the visible region and that its cation also is colorless.) The need for an excess of amine is apparent when we recall that salts of the type BHA when in aprotic solvents are in equilibrium with the constituent acid and base. In the reaction of bromophthalein magenta with triethylamine in benzene, the association constant is $\sim 2.7 \times 10^4$ (molar units, 25°) [15].

With tertiary amines, the limiting color is magenta. As would be expected, the intermediate colors observed are various orange and scarlet tones. Table 40 shows (see next to last column) that tertiary ammonium salts of bromophthalein magenta display the magenta color when dissolved in hydrocarbons, halogenated hydrocarbons, ethers, and carboxylic acid esters (tributyl phosphate behaves differently [14]). On the other hand, in ketones, alcohols, bases like aniline or pyridine, and in nitroparaffins or nitroaromatic solvents, the characteristic color is the same as for quaternary ammonium salts.

In interpreting these observations, Davis and coworkers adopted an explanation along the same lines as those offered by Wynne-Jones [325] and by Kraus [327] (see section 4.3.1 and 4.3.2). That is, they concluded that in tertiary ammonium salts of bromophthalein magenta E and B the cation is hydrogen-bonded to the anion, as indicated by (XLI). A more general representation of this structure is $BH^+ \ldots A^-$ (or $BH^+ \ldots \bar{O}R$) [14]. The magenta tone,

Table 40. *Effect of solvent and added base on the color of Bromophthalein Magenta* (BPM)[a]

Solvent[b]	Type of base added[c]				
	0	I	II	III	IV
Hydrocarbons:					
Benzene (2.3)	Yellow	Red-purple	Purple-blue	Magenta	Blue.[d]
Carbon tetrachloride (2.2, 20°)	Yellow	Red-purple	Purple-blue	Magenta	Blue.[d]
Cyclohexane (2.0, 20°)	Yellow	Red-purple	Purple-blue	Magenta	Blue.[d]
Toluene (2.4)	Yellow	Red-purple	Purple-blue	Magenta	Blue.[d]
Halogenated Hydrocarbons:					
Chlorobenzene (5.6)	Yellow	Red-purple	Red-purple	Magenta	Blue.[d]
Chloroform (4.8, 20°)	Yellow	Red-purple	Red-purple	Magenta	Blue.[d]
1,2-Dichloroethane (10.2)	Yellow	Magenta	Magenta	Magenta	Blue.[d]
Ethers:					
Anisole (4.3)	Yellow	Magenta	Magenta	Magenta	Blue.[d]
1,4-Dioxane (2.2)	Yellow	Magenta	Magenta	Magenta	Blue.[d]
Ethyl ether (4.3, 20°)	Yellow	Magenta	Magenta	Magenta	Blue.[d]
Esters:					
Benzyl benzoate (4.9, 20°)	Yellow	Red-purple	Red-purple	Magenta	....
Butyl stearate (3.1, 30°)	Yellow	Magenta	Magenta	Magenta	....
Ethyl acetate (6.0)	Green-yellow	Red-purple	Red-purple	Magenta	Blue.[d]
Methyl benzoate (6.6, 20°)	Green-blue	Red-purple	Red-purple	Magenta	....
Tributyl phosphate (8.0, 30°)	Blue-green	Blue[d]	Blue[d]	Blue[d]	....
Ketones:					
Acetone (20.7)	Yellow to blue[e]	Blue[d]	Blue[d]	Blue[d]	Blue.[d]
Cyclohexanone (18.3, 20°)	Yellow to green[e]	Blue[d]	Blue[d]	Blue[d]	....
Methyl *iso*butyl ketone (13.1, 20°)	Yellow to blue[e]	Blue[d]	Blue[d]	Blue[d]	....
Alcohols:					
Ethanol, 95% (27.9?)	Blue[d]	Blue[d]	Blue[d]	Blue[d]	Blue.[d]
n-Propyl alcohol (20.1)	Green-blue	Blue[d]	Blue[d]	Blue[d]	....
n-Butyl alcohol (17.5)	Green	Blue[d]	Blue[d]	Blue[d]	....
2-Heptanol (9.2, 22°)	Green-yellow	Blue[d]	Blue[d]	Red-purple	....
Nitrogenous Bases:					
Aniline (6.9, 20°)	Green-blue	Purple-blue	Purple-blue	Purple-blue	Blue.[d]
Pyridine (12.3)	Green-blue	Green-blue	Blue[d]	Blue[d]	....
Micellaneous:					
Acetonitrile (37.5, 20°)	Green-blue	Blue[d]	Blue[d]	Blue[d]	....
Nitrobenzene (34.8)	Yellow	Green[f]	Green-blue[f]	Green[f]	Blue.[d]
Nitromethane (35.9, 30°)	Yellow	Purple-blue	Blue[d]	Blue[d]	....

[a] Visual observations using BPM–B; although BPM–B is more soluble in hydrocarbons than BPM–E no differences in chemical behavior have been observed. This is a condensation of table 7 of M. M. Davis and P. J. Schuhmann, J. Res. NBS **39**, 221 (1947) [14].

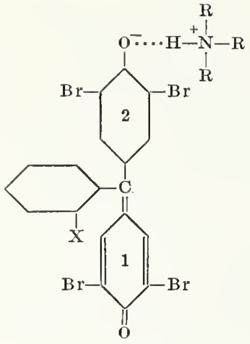
[b] Numbers in parentheses are values of ϵ, at 25° unless otherwise indicated.

[c] Key to identity of bases: 0, none; I, n-$C_8H_{17}NH_2$; II, n-Bu_2NH; III, Et_3N; IV, n-Bu_4N salt of BPM–B.

[d] Blue without purple tinge.

[e] Yellow in concentrated solution, bluer on dilution.

[f] The yellower color tones observed in $PhNO_2$ are to be expected because the solvent itself is yellow.

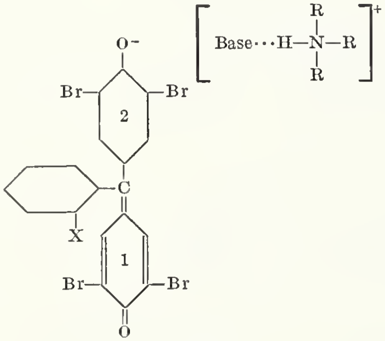


(XLI)

intermediate in the color scale between yellow and blue, is consistent with the hypothesis that the proton exerts a residual effect on the anion, as indicated in (XLI). It should be emphasized that the cation is regarded as being held by a *specific bond* to a phenolate-type oxygen. (It should also be noted that such bonds are not as stable as ordinary chemical bonds and are regarded as being continually broken and re-formed, like other kinds of hydrogen bonds.) In summary, the formation of hydrogen-bonded ion pairs is regarded as being an "incipient ionization . . . an intermediate step in the complete transfer of a proton . . ." [14, 20, 5, 25].

The difference in the structure of quaternary ammonium salts and that of incompletely substituted ammonium salts is conveniently pointed up by referring to the first group as consisting of "ion pairs" [326–329] and the latter group as consisting of "*hydrogen-bonded* cation pairs" [356, 31].

Rupture of the hydrogen bond in tertiary ammonium salts ($R_3NH^+...X^-$) can occur either so as to yield R_3N and HX or so as to form R_3NH^+ and X^-. The second type of change appears not to occur—at least with tertiary ammonium salts of bromophthalein E or B—unless a second base is present to form a new type of hydrogen bond (XLII)



(XLII)

with the cation. This reaction may be expressed in general terms by eq 36 [24, 327, 5, 21]:

$$R_3NH^+...X^- + \text{base} \rightleftharpoons R_3NH^+... \text{base} + X^- \qquad (36)$$

If the added base is as strong as aniline or pyridine, such a reaction appears to occur in the case of the triethylammonium salt of bromophthalein magenta E or B, despite the low dielectric constants of these solvents. On adding water or an alcohol reaction (eq 36) is probably additionally promoted by the following reaction:

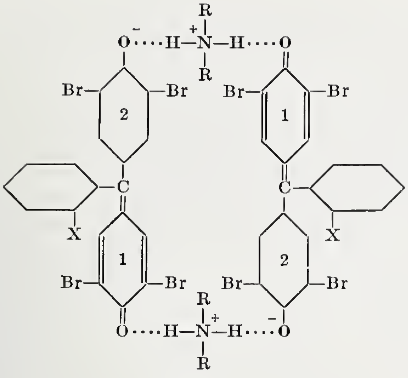
$$X^- + ROH \rightleftharpoons RO^-H^+...X^- \qquad (37)$$

However, for our present discussion the essential reaction is the one represented by eq 36, which accounts for the color shift from magenta to blue. (Some weight should probably be ascribed to the *dielectric constant* of nitrobenzene or nitroparaffins.) Ethers (for example, dioxane) and esters of carboxylic acids are not basic enough to bring about reaction (36), judging by the magenta color of solutions.

Secondary ammonium salts of bromophthalein magenta in benzene show a color behavior which, though astonishing when first seen, has found a satisfactory explanation in terms of hydrogen bonding. In referring again to figure 14 it will be noted that the absorption curve labeled "Et_2NH_2 salt" (which resembles very closely the curves obtained for other secondary ammonium salts) is similar to the curve obtained for the Bu_4N salt. That is, in both cases the principal absorption band in the visible region is steep, rather narrow, and fairly symmetrical. However, $\lambda_{max.}$ for the secondary ammonium salt is displaced about 30 nm toward the ultraviolet (that is, to a region near 575 nm). Moreover, the "wings" of the main absorption band are more pronounced. (The seemingly lower intensity of absorption of the quaternary ammonium salt is attributed, at least in part, to difficulties in ascertaining precisely its molar absorbance because it reacts with glass by ion exchange [14].)

The difference in the color of benzene solutions of quaternary ammonium and secondary ammonium salts of bromophthalein magenta has been indicated by describing the former as "blue without purple tinge," and the latter as "cornflower blue" or "purple-blue" [14]. The range of colors obtained on adding a secondary amine to bromophthalein magenta (in benzene) in gradually increasing amounts until the limiting color has been attained will be different, obviously, from the sets of colors obtained by mixing the indicator with a tertiary ammonium or quaternary ammonium salt.

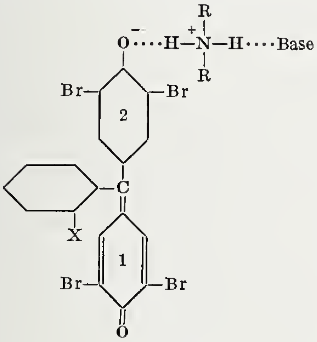
The finding that secondary ammonium salts give cornflower blue solutions in benzene (and in other hydrocarbon solvents), instead of magenta solutions, is explained by postulating that two molecules of salt associate by hydrogen bonding in the manner indicated in (XLIII). That is, association occurs because the "spare" ammonium hydrogen of each molecule of salt can become bonded to the quinoid oxygen (ring 1) of the other molecule [14]. (It seems probable that the two anions lie in essentially parallel planes, united by two cations.) The dimeric structure should be stabilized by resonance.



(XLIII)

It might be thought that the cornflower blue color is caused by traces of impurities (for example, water), rather than by the formation of a dimeric salt. However, Davis and Schuhmann found [14] that the cornflower blue is obtained *only in the absence of impurities.* A mere trace of an electron-donor molecule (for example, ethanol) causes a color shift toward magenta. Subsequent *large* additions of alcohol cause a shift from magenta back to blue, the final blue tone being, however, the "blue without purple tinge" which is characteristic of quaternary ammonium salts in *all* solvents.

The shift from cornflower blue toward magenta is satisfactorily explained by postulating that the "spare" secondary ammonium hydrogen becomes bonded to the traces of added base (XLIV), this new



(XLIV)

hydrogen bond being formed at the expense of the former bond to quinoid oxygen of a second molecule of indicator. That is, the salt is now a *monomeric* species, consisting—like (XLI)—of hydrogen-bonded ion pairs. It is also easily understood why secondary ammonium salts of bromophthalein magenta give *magenta* solutions in dioxane, anisole, and other ethers (see table 40), in contrast to their cornflower blue tone in hydrocarbon solvents.

The ultimate shift back to blue in a largely alcoholic medium is explained in the same way as for tertiary ammonium salts—compare (XLII).

To recapitulate our conclusions, the very striking color phenomena just discussed, like the phenomena observed in studies of conductance, dielectric polarization, and colligative properties, indicate that acid-base behavior in aprotic solvents is significantly affected by two types of hydrogen bonding, namely,

(1) Hydrogen bonding of cations to anions, which can occur in tertiary, secondary, and primary ammonium salts; and

(2) Bonding of "spare" cationic protons to electron-donor atoms, which is to be looked for in reactions involving secondary or primary amines. Obviously, effects on acid-base behavior which arise from hydrogen bonding of the second type will be enhanced when a secondary amine is replaced by a *primary amine.* Studies of the behavior of bromophthalein magenta E with primary amines in benzene have shown that the expected complications exist [14]. Clearly, the simplest overall pattern of acid-base behavior will occur in reactions involving a tertiary amine, making it desirable to select this type of base as a reference compound for systematic comparisons of acidic strengths in aprotic media.

In the introductory discussion of bromophthalein magenta (E or B) it was mentioned that this acid reacts measurably in hydrocarbon solvents with bases comparable in strength to aliphatic amines. The most extensive investigations of basic behavior in benzene made so far have involved tertiary aliphatic amines or 1,3-diarylguanidines [14, 5, 15, 21, 31]. Both groups of bases yield magenta solutions. The following bases have also been found (in qualitative tests) to yield magenta solutions: Hexamethylenetetramine [5], most common alkaloids [14], diphenylformamidine [17], and diphenylacetamidine [17]. In detailed studies minor differences in the absorption bands of magenta solutions may be observed—for example, the main absorption band obtained on adding 1,3-diphenylguanidine is located a few nanometers nearer the ultraviolet than the corresponding band produced by adding triethylamine [15].

It has been concluded tentatively that the following guanidine derivatives resemble secondary aliphatic amines in their association with bromophthalein magenta: Monoalkyl-, monoaryl-, 1,1-dialkyl-, and 1,3-dialkylguanidines [17].

The instability of the dimeric structure assigned to secondary ammonium salts in hydrocarbon solvents upon addition of traces of an ether, alcohol, or other type of base suggests that the color behavior of a secondary amine with bromophthalein magenta will be modified when ether or hydroxyl groups are present within the molecule. In keeping with expectation, adding a small amount of morpholine to bromophthalein magenta causes the original yellow color to change to cornflower blue, but on continued addition of morpholine the cornflower blue color shifts toward magenta. Similarly, a trace of methylmonoethanolamine produces a blue color slightly tinged with red, while large amounts cause a shift toward magenta [14].

Adding a *tertiary amine oxide* to bromophthalein magenta in a hydrocarbon solvent produces a still different color tone (rose), as shown in figure 14 (see curve labeled "Me_3NO salt") [14, 31]. Tribenzylamine oxide and trimethylamine oxide have been found to produce almost identical absorption curves [31]. The salts formed in these cases are considered to have the general formula $R_3NOH^+...A^-$. The characteristic absorption band in the visible region is fairly symmetrical and resembles that for tertiary ammonium salts except in being somewhat flatter and displaced about 20 nm toward the ultraviolet. It is inferred from this displacement that the phenolic proton of bromophthalein magenta remains closer to its original position after bonding to a tertiary amine oxide than after interaction with a tertiary amine.

The anion of bromophthalein magenta is exceptionally polarizable, and this accounts for its strongly differentiating behavior with various types of cations. With acids having less polarizable anions the differentiating phenomena and their underlying causes are less easily recognized. The examples given suggest many other potential uses of this indicator for studies of basic behavior.

b. Halogen derivatives of phenolsulfonephthalein. The close similarity of the structures of bromophthalein magenta (XXXVII) and bromophenol blue which has been half-neutralized by a base (XXXIX) has been pointed out. In the "second-stage reaction," which involves neutralization of phenolic OH, *bromophenol blue* shows a varied behavior closely similar to that just described for bromophthalein magenta E (or B), and so do related sulfonephthaleins, for example, *bromocresol green*, *iodophenol blue* (the iodine analog of bromophenol blue), and *tetrabromophenol blue* (3′,5′,3″,5″-tetrabromphenoltetrabromosulfonephthalein) [29].

For lack of more suitable indicators the sulfonephthaleins, though designed for applications in aqueous solutions, were used in early studies of acid-base behavior in benzene and other aprotic solvents. An important example is work by LaMer and Downes, who described very complex color phenomena in the following words [357]: "If Brom Phenol Blue is added to a benzene solution of pure [carboxylic acid such as dichloroacetic acid, salicylic acid, or benzoic acid], the solution remains colorless. As base [piperidine or dimethylamine] is added, a yellow color appears which cannot be discharged by addition of acid. It becomes more intense the greater the amount of base added, until a reversible color change from yellow to red takes place, analogously to the color change in water from yellow to purple. If the acid is very dilute, the color will change progressively from yellow to a yellow-purple mixture, to a yellow-red mixture and finally to red without any yellow present on the addition of base. On the other hand, if Brom Phenol Blue is added to a benzene solution of a pure base, a purple color is observed. If the base is moderately concentrated (greater than 0.01 *M*) the addition of acid changes the purple to a red color and finally when an excess of acid is added, changes the red to a yellow. The change from purple to red is an irreversible change, for no matter how great an excess of base is added to the red solution, the purple color will not be regenerated. If the base is extremely dilute, the addition of an excess of acid will change the purple color directly to yellow. . . ." This complex behavior can be understood by applying the observations and conclusions pertaining to secondary ammonium salts of bromophthalein magenta in benzene. [The color changes just re-referred to should not be confused with a *physical* phenomenon, known as "dichromatism," which bromophenol blue and certain other sulfonephthalein indicators exhibit under some conditions. For example, in its alkaline range in water (*p*H 4.6 or greater) bromophenol blue transmits blue light when in thin films, whereas thicker layers of the same solution transmit light of a red tone. Behavior of this sort is observed when a light-absorbing material has two or more absorption bands in the visible which differ greatly in intensity. In such a case the color transmitted also depends on the quality of the source—for instance, a solution transmitting a blue color in a room illuminated by daylight will appear red under illumination by an artificial source which does not emit blue light [358].]

As noted earlier, the first stage of neutralization of bromophenol blue and related sulfonephthaleins provides a useful reaction for estimating relative strengths of aniline- or pyridine-type bases in aprotic solvents—a role that bromophthalein magenta cannot fill. In general, however, the sulfonephthaleins are less suitable reagents for acid-base studies in aprotic solvents, as the acids and their salts are not very soluble and the first- and second-stage reactions tend to overlap [29].

c. Nitrophenols. As indicated in our earlier discussion, the compounds that have been most extensively studied with respect to their conductance (sec. 4.3.1) and dielectric polarization (sec. 4.3.2) in benzene and other aprotic solvents have been quaternary or incompletely alkylated ammonium *picrates*. We have seen that two important conclusions from such studies are: (1) Ion-pair dissociation of imcompletely alkylated ammonium picrates is much less extensive than that of quaternary ammonium picrates (see table 32); and (2) the dipole moments of incompletely substituted ammonium picrates (~ 11–12 Debye units) are lower by several units than the moments of quaternary ammonium picrates (see table 36). Such results led to the deduction that the incompletely substituted ammonium salts exist largely as hydrogen-bonded ion pairs when in benzene and like solvents.

The comparative electronic absorption spectra of quaternary ammonium picrates and partly substituted ammonium picrates in benzene give additional strength to this conclusion. As representative evidence, absorption curves are given in figure 15 for picric acid and three types of picrates, all in benzene solution (5×10^{-5} *M*). It will be seen that the curves for these picrates, although all

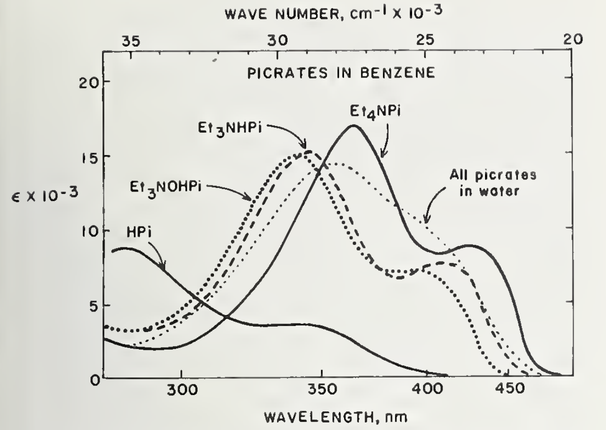


FIGURE 15. *Comparative spectral absorption curves of picric acid and some of its salts (5×10^{-5} M) in benzene and in water.*

See M. M. Davis Abstrs. Papers 145th Meeting Am. Chem. Soc., New York, N.Y., September 1963, p. 18T. (Ref. No. 359)

having the same basic shape (the envelope of two overlapping bands), are increasingly shifted toward the infrared in the order:

$$Et_3NOHPi < Et_3NHPi < Et_4NPi$$

[359]. This is the same as the order of spectral shifts observed for benzene solutions of bromophthalein magenta and several of its salts (fig. 14), and the interpretation is similar.

The curves presented in figure 15 are representative for at least a few members of the three classes of salts indicated. For example, within each of the following groups the salts (in all cases, 5×10^{-5} M in benzene) were found to have the same absorbance within experimental uncertainty at wavelengths $> \sim 300$ nm: (1) Et_4NPi, n-Pr_4NPi, and n-Bu_4NPi [360]; (2) Et_3NHPi, n-Bu_3NHPi, and i-Am_3NHPi [361]. Furthermore, the absorbance curve determined for 5×10^{-5} M Et_3NOHPi [361] is not measurably different from that determined for a mixture of HPi (same molarity) with two equivalents of $(PhCH_2)_3NO$ [31].

Some other examples of shifted curves for picrates in benzene, and also for trinitro-m-cresol and two of its salts, were reported earlier [31].

The spectral absorbance of the picrates listed above and also that of numerous other picrates was determined in water when solubilities permitted [360, 361]. Doing this provided a good test of purity, as all pure picrates yielded the same absorbance curve in water (see fig. 15)—except, of course, for varying contributions by different cations. This identity of absorbance in aqueous solutions obviously occurs because of the essentially complete ionization of all picrates in water, including picric acid itself ($pK_a = 0.33$ [362]). Figure 15 provides a very good illustration of the leveling character of water as a solvent in contrast to the differentiating character of benzene.

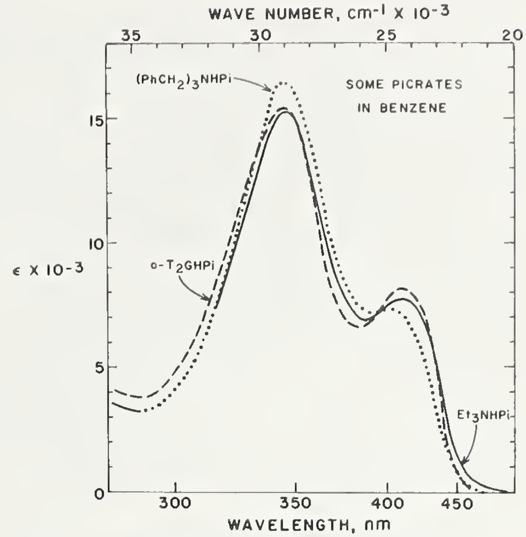


FIGURE 16. *Comparative spectral absorption curves of di-o-tolylguanidinium picrate* (o-T_2GHPi), *tribenzylammonium picrate, and triethylammonium picrate in benzene* [*20, 361*].

Differentiating absorption curves of salts in benzene are not limited to the examples given. Additional examples are presented in figure 16. The three curves were determined carefully using purified materials (usually $5 \times 10^{-5}M$). The curve shown for tribenzylammonium picrate is the calculated as well as experimentally determined limiting curve obtained in studying the association of picric acid with tribenzylamine [20]; the absorbance of 1,3-di-o-tolylguanidinium picrate was found to be almost identical with that of 1,3-diphenylguanidinium picrate [361]; and, as mentioned earlier, the absorbance curve for Et_3NHPi is practically identical with the curves obtained for n-Bu_3NHPi and i-Am_3NHPi. It is apparent, however, that the electronic absorption of tertiary ammonium picrates is not always the same. Comparing the curves for tribenzylammonium and triethylammonium picrates one sees that the "primary" (higher-frequency) band, though appearing in the same (or very nearly the same) region in each case, may vary in intensity. It is also evident that the lower absorbance of triethylammonium picrate in the region of the primary band is compensated by greater absorbance in the region of the "secondary" band. The secondary band seems strongest in the case of ditolylguanidinium picrate; its primary band seems to be shifted a little toward higher frequencies. (An analogous hypsochromic shift was observed in comparing the absorption curves of the diphenylguanidinium and triethylammonium salts of bromophthalein magenta E [15].)

Picrates ($5 \times 10^{-5}M$) prepared from three dialkylamines (piperidine, diethylamine, and di-n-propylamine) yielded almost exactly the same absorption curve in benzene [361]. Although this curve is perceptibly different from the one obtained for Et_3NHPi, etc., the difference is much less striking than for secondary and tertiary ammonium salts of bromophthalein magenta at the same concentration, consisting merely of a slightly reduced intensity of absorption in the region ~ 335 to ~ 405 nm. It will be recalled that Maryott postulated an appreciable tendency for secondary ammonium picrates to dimerize in benzene, thus accounting for a pronounced falling off of the dielectric polarization with increasing concentrations (see fig. 10 and related discussion).

Von Halban and Szigeti noted additional examples of differentiating spectral behavior in a survey of some dioxane, chloroform, and ethylene chloride solutions of picrates and naphthopicrates [363]. The two "partial" bands of Pi^- were sharply separated, as in benzene. The difference between quaternary ammonium salts and incompletely substituted ammonium salts was particularly noteworthy.

Analogous differentiating effects have been observed for 2,4-dinitrophenolates. For example, in determining the equilibrium constants for 1:1 association of 2,4-dinitrophenol with mono-, di-, and tri-*n*-butylamine in chlorobenzene, Bayles and Chetwyn obtained three different limiting absorption curves [364]. Figure 17 presents absorption curves for 2,4-dinitrophenol and its Et_3NH and *n*-Bu_4N salts in benzene, and also for the phenol and its sodium salt in water [17]. As with picrates, two overlapping bands are clearly detectable in the curves for benzene solutions. The intermediate location of the curve for the Et_3NH salt supports the inclusion of this compound in the category of hydrogen-bonded ion pairs.

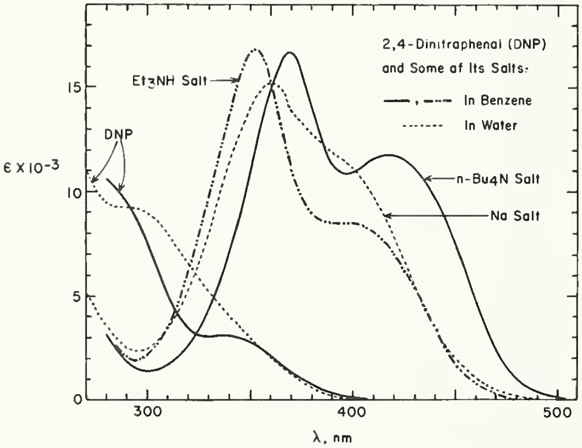
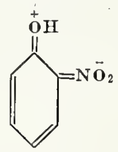
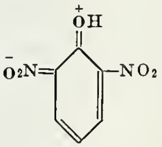


FIGURE 17. *Comparative spectral absorption curves of 2,4-dinitrophenol and some of its salts in benzene and water* [17].

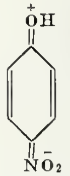
A recent review [365] has divided progress in electronic absorption spectroscopy into two main periods. During the first period, which extended into the mid-1940's, absorbance data were interpreted according to classical vibration theory, as exemplified by Lewis and Calvin's "theory of electronic oscillations" [366, 367]. According to this theory a planar organic molecule having a conjugated system which extends in two directions will have two optical axes, and when the molecule absorbs light there will be electronic oscillations along both axes, giving rise to absorption bands of different frequencies. The one at lowest frequencies, called the *x-band*, is associated with the most extended conjugated system. The second band is referred to as the *y-band.* The resonance hypothesis has provided a good explanation why *ortho*-nitrophenol (XLV) and *para*-nitrophenol (XLVII) both have a rather strong electronic absorption band, especially when in the anionic state [368], and it is reasonable to identify these bands with the *x*- and *y-bands*, respectively, of Lewis and Calvin. The principal absorption band of 2,6-dinitrophenol (XLVI), like that of *o*-nitrophenol, should be an *x-band.* Only one resonance structure (XLVIII) is given here for 2, 4-dinitrophenol, but obviously this acid and its salts should have an *x-band* as well as a *y-band*; the same holds for picric acid (XLIX) [359].



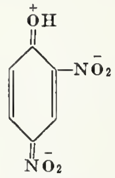
(XLV)



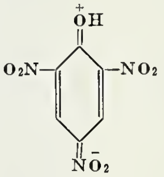
(XLVI)



(XLVII)



(XLVIII)



(XLIX)

During the second main period in the development of electronic absorption spectroscopy, which has seen an extensive application of quantum mechanics in the interpretation of spectra, the view has been adopted that the strongest absorption bands in the spectra of benzene derivatives are displaced bands of benzene itself [365, 369–371]. The approximate locations and intensities of the benzene bands are as follows: (1) A very strong band near 180 nm ($\epsilon \sim 10^5$); (2) a less intense band near 200 nm ($\epsilon \sim 10^3$ to 10^4); (3) a still weaker band near 255 nm ($\epsilon \sim 300$). Various names or code designations have been advocated for the three bands; for this discussion it is convenient to adopt the adjectives "*second primary*," "*primary*," and "*secondary*," which were applied to the benzene bands in the order listed above [369]. We shall be concerned only with the primary and secondary bands, as the displaced "second primary" band does not appear in the spectral range under discussion.

Relationships between the primary and secondary bands of benzene and the displaced primary and secondary bands appearing in substituted benzenes were especially well demonstrated in

Doub and Vandenbelt's measurements of the spectra of an extensive series of mono- and polysubstituted derivatives, dissolved in water [369–371]. An observation which is especially pertinent to this discussion is their finding that the absorption curve of β-resorcylic (2,4-dihydroxybenzoic) acid approximates a summation of the curves for salicylic (*o*-hydroxybenzoic) and *p*-hydroxybenzoic acids: *p*-Hydroxybenzoic acid has a strong, symmetrical band at λ 255 (ε 14,000); salicylic acid has a weaker band at λ 303 (ε 3,600); and corresponding bands appear for β-resorcylic acid at λ 256 (ε 13,600) and λ 295 (ε 5,500). The structural similarity of β-resorcylic acid and 2,4-dinitrophenol is quickly recognized; however, the two like substituents in the former compound are electron-donor groups and the third substituent is an electron-withdrawing group, while the reverse is true for 2,4-dinitrophenol. It is evident that Doub and Vandenbelt's *primary* and *secondary* bands correspond, respectively, to Lewis and Calvin's *y*- and *x-bands*.

Although the primary and secondary bands of picrates and 2,4-dinitrophenolates overlap strongly when water is the solvent (see figs. 15 and 17), it can be recognized that their shapes and relative intensities are about the same as for benzene solutions. (The resolution of strongly overlapping band systems is aided by referring to figures which Vandenbelt and Henrich constructed by making summations of two symmetrical absorption bands; the widths and relative intensities of the bands were varied, as well as the separation of band maxima [372, 371].) The pronounced overlapping observed for aqueous solutions seems to result from a "red-shift" of the primary band, and this shift can be attributed to solvation of the nitro group, since hydrogen-donor solvents, especially water, are known to cause marked bathochromic shifts in the electronic absorption of *para*-substituted nitrobenzenes [371]. Another example of a strong bathochromic effect of solvation of a *para*-quinoid isomer can be seen in comparing the positions and intensities of absorption bands of *o*- and *p*-nitrophenols as given in a tabulation by Wheland [368]. The values obtained, (a) in 0.1-*N* aqueous perchloric acid and (b) as the anions in water, are as follows: (a) *o*-Nitrophenol, λ max 350 nm, ε max 2,500; *p*-nitrophenol, λ max 320 nm, ε max 9,000. (b) *o*-Nitrophenolate, λ max 420 nm, ε max 5,000; *p*-nitrophenolate, λ max 400 nm, ε max 15,000. It is evident that the band locations are not greatly different for the *ortho*- and *para*-isomers, and again presumably because hydration of the latter has a strong bathochromic effect.

The intensity of absorption seems always to be substantially greater for primary than for secondary bands.

Comparisons have been made of the absorption curves of tetra-*n*-butylammonium and triethylammonium mono- and polynitrophenolates when dissolved in benzene [359, 17]. In this solvent the primary and secondary bands are always much more widely separated than in water. This is illustrated very strikingly in figure 18, which compares the absorption curves of the Et_3NH salts of *p*-nitrophenol, 2,6-dinitrophenol, and picric acid in benzene. (NOTE: The curve for Et_3NHPi was determined with a 5×10^{-5} *M* solution; the other two absorption curves are limiting curves, obtained on adding Et_3N in excess to 10^{-4} *M* 2,6-dinitrophenol or *p*-nitrophenol.)

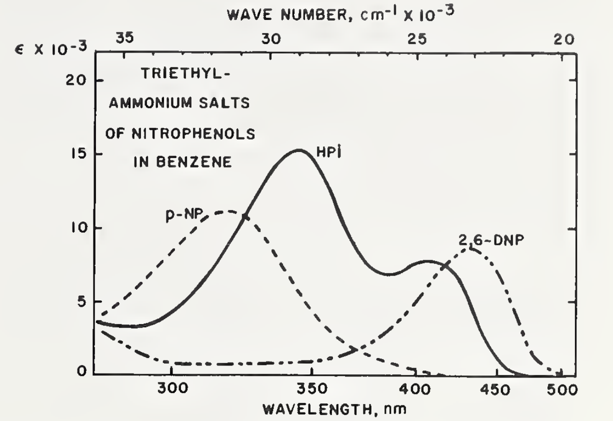


FIGURE 18. *Comparative spectral absorption curves of triethylammonium salts of* p-*nitrophenol, 2,6-dinitrophenol, and picric acid in benzene* [359].

The absorption spectra of mono- and polynitroanilines, determined both in benzene [17] and in methanol [373], show the expected parallelism with the spectra of corresponding nitrophenols.

In molecules possessing primary and secondary bands the primary band has sometimes been found to gain in intensity at the expense of the secondary band, or vice versa. For instance, Kamlet and associates recently discovered, while studying effects of *N*-alkyl and *N,N*-dialkyl substitutions on the ultraviolet absorption of 2,4-dinitroaniline in methanol, that bulky substitutents on the amino nitrogen may lead to inhibition of $(^+R_2N{=}C_1{-}C_2{=}NO_2^-)$ resonance and enhancement of $(^+R_2N{=}C_1{-}C_4{=}NO_2^-)$ resonance [373]. It is conceivable that steric influences are at least partly responsible for the band intensity shifts indicated in figure 16.

This brief review has shown the exceptional sensitivity of electronic absorption spectroscopy as a tool for studying the properties of acidic indicators like bromophenol blue, bromophthalein magenta, 2,4-dinitrophenol, and picric acid in aprotic solvents. Obviously, considerably more labor is required than in studying acid-base equilibria in a leveling solvent, but far more information is attained.

d. α-Naphthol, β-naphthol, and phenol [353]. Nagakura and Gouterman have evaluated acid-base association constants from shifts in the near-ultraviolet absorption bands of phenol and α- and β-naphthols caused by adding triethylamine, ethyl ether, or nitromethane. It is well known that except for Et_3N these are all weak proton donor or acceptor compounds. The spectral shifts were ascribed to hydrogen bond formation for reasons such as the following: (1) The absorption of each phenolic acid (HA) shifts to longer wavelengths when a proton acceptor (B) is added, and curves for solutions containing varying proportions of base and acid intersect at one or more sharply defined isosbestic points. (2) Satisfactory equilibrium constants were calculated on the assumption of 1:1 acid-base association.

The calculated association constants (K_{BHA}) are listed in table 41. Judging relative reactivities by the magnitudes of K_{BHA} values, it is clear that α-naphthol is the strongest of the three acids and phenol, the weakest. It is also clear that, as would be expected, triethylamine and nitromethane are, respectively, the strongest and weakest of the proton acceptors.

TABLE 41. *Comparative equilibrium constants* (K_{BHA}) *for some acid-base associations in* n-*heptane* (25°) *as evaluated from near-ultraviolet absorbance data* [a]

B (proton acceptor)	K_{BHA}, where *HA* is:		
	α-Naphthol	β-Naphthol	Phenol
Et_3N	121	103	83.8
Et_2O	15.7	14.5	10.8
$MeNO_2$	3.3	2.6	

[a] See S. Nagakura and M. Gouterman, J. Chem. Phys. **26**, 881 (1957), Table IV. K_{BHA} is the equilibrium constant corresponding to $B + HA \rightleftarrows BHA$. Approximate molar concentrations were: C_{HA}, (2.2 to 4.3) $\times 10^{-4}$; C_B, 0.01 to 0.5.

REFERENCE:

[353] S. Nagakura and M. Gouterman, J. Chem. Phys. **26**, 881 (1957).

In infrared spectroscopy the relative strengths of hydrogen bonds have often been judged from the comparative shifts of O–H stretching frequencies on hydrogen bond formation. It is noteworthy that corresponding shifts of ultraviolet absorption bands of α- and β-naphthol are different for the L_a (primary) and L_b (secondary) bands: when the *primary* bands are being compared the shift is greater for α-naphthol than for β-naphthol, but when *secondary* bands are being compared, the reverse is true [353].

4.3.5. Spectral Absorbance in the Infrared

The extensive use made of infrared spectroscopy during the past quarter century for studying hydrogen bond formation has been illustrated numerous times in preceding discussion. Only a small fraction of the IR studies have been concerned with hydrogen bonding between cations and anions. Since 1950 there have been a few investigations of this type of bonding in *dry* aprotic solvents, and since 1960, additional investigations have been made using *wet* aprotic solvents. The second group of studies are a result of the widespread interest in processes for extracting acids from aqueous solutions into amine-containing aprotic solvents. A third group of investigations has dealt with hydrogen bonding in *crystalline* salts. The association of cation-anion pairs by hydrogen bonds seems to be closely similar in crystals and in aprotic solvents, and results from all three types of investigation will be summarized.

It is well known that the formation of a hydrogen bond X–H...Y is very commonly recognized by the following changes in the X–H stretching band: a shift to lower wave numbers; an increase in intensity; a considerable broadening; and, in many cases, a splitting to two or more component bands. Hydrogen bonding in amine salts, $N^+–H...X^-$ is often inferred from changes involving the N–H stretching band [374–376], but other infrared absorption bands also contribute supplemental or substitute information.

a. Measurements of crystals. It is appropriate to include mention of some deductions made by studying compilations of x-ray diffraction data. Early in 1951, in a symposium on "Hydrogen Bonds," Donohue reported ". . . the rather remarkable fact that only in very exceptional cases does a hydrogen atom bonded to nitrogen or oxygen occupy a position such that hydrogen bond formation is impossible. Thus in the case of the hydrochlorides . . . all three hydrogen atoms of the $-NH_3^+$ groups form $\bar{N}$–H...Cl bonds . . ." [377]. In a subsequent study of more extensive x-ray diffraction data, Fuller reached complete agreement with Donohue's main conclusions, stating that "almost without exception, molecules in a crystal arrange themselves so that the maximum number of hydrogen bonds is formed . . ." [378].

The infrared measurements of crystals were usually made with mulls, a liquid hydrocarbon and/or a halogenated hydrocarbon being employed as the suspending medium. In some cases a film of solid was prepared by sublimation or by evaporation of solvent. Early studies of salts were made by Lord and Merrifield [374], who reported that the IR spectra of tertiary amine hydrohalides indicate the presence of strong $N^+–H...X^-$ bonds. For example, they observed that the spectrum of triethylamine hydrochloride shows no band in the usual $N^+–H$ stretching region; instead, there is a very strong band (a well-defined doublet with two weaker satellites) centered at 2540 cm^{-1}. The same band appears with slight modifications in the spectrum of a chloroform solution. In the view of these authors the characteristics of the displaced bands "are incompatible with a simple electrostatic model of the hydrogen bond . . . (instead) a quantum-mechanical model is undoubtedly required."

Waldron observed independently [379], in a detailed study of $MeNH_3^+Cl^-$, that the N–H stretching frequencies are lower in the cation than in the neutral molecule, and he concluded that "part of the reduction in frequency is undoubtedly due to hydrogen bonding to the anion."

The solid hydrohalides of 19 different amines were studied in detail by Sandorfy and associates, and in many cases measurements were also made with solutions in water [375, 376]. The bases represented were primary, secondary, and tertiary amines, both aliphatic and aromatic, and also pyridine; HCl, HBr, and HI were the acids represented. Omitting all details, the main observations and conclusions may be summarized as follows:

(1) Hydrogen bond formation was detected in all of the hydrohalides. Its existence was shown by a displaced NH^+ stretching band and by the other spectral changes considered characteristic of hydrogen bond formation (that is, splitting, increased intensity and breadth).

(2) In the solid state, the hydrogen bonds are of the type $N^+–H...X^-$, whereas in aqueous solutions, they are of the $N^+–H...O$ type.

(3) In *aliphatic* amine hydrohalides the hydrogen bond is very largely electrostatic in character. Delocalization of charge is more extensive in *aromatic* amine hydrohalides.

(4) Tertiary amines form stronger $N^+–H...X^-$ bonds than do primary and secondary amines. This is consistent with the greater concentration of positive charge in tertiary ammonium ions.

(5) A tertiary ammonium ion forms a stronger hydrogen bond with Cl^- than with Br^- or I^-.

Marzocchi, Fryer, and Bambagiotti [380] studied the N–H stretching band in the salts formed by 1:1 association of *hexamethylenetetramine* with HCl, HBr, HI, and $HClO_4$, and attributed the structure of the ν(N–H) bands of the hydrohalides to $N^+–H...X^-$ bonding. They concluded that there is little, if any, hydrogen bonding in the perchlorate. They believe that a quantum-mechanical treatment of the hydrogen bond is required to account for hydrogen bonding in salts like those studied, but consider that no theory so far proposed accounts adequately for the spectral changes observed. As in the IR measurements by Sandorfy and associates the comparative spectral shifts indicated that the strengths of cation-to-anion hydrogen bonds decrease in the order $Cl^- > Br^- > I^-$.

In analogous investigations of Lipovskii and Nikitina a shifted ν(N–H) band of crystalline trialkylammonium fluorides was attributed to the structure $R_3N^+–H...F^-$ ($R = Et$ or $C_{10}H_{21}$). As expected, the hydrogen bond to F^- was found to be even stronger than the bond to Cl^- [381].

Hydrogen bonding in crystalline *ammonium* halides has received careful study. An example is an investigation of NH_4F and ND_4F (25 and −195 °C) in which the expected evidence of strong $N^+–H...F^-$ bonds was found. The authors emphasized that the stretching N–H band of NH_4F is *not broad*, showing that band broadening is not an invariable consequence of strong hydrogen bonding [382]. (*Neutron diffraction data* for ND_4Br (−195 to 200 °C) should also be noted: they indicated that the formation of $N^+–H...X^-$ is an important stabilizing influence in ammonium halides [383].)

Table 42 is a compendium of conclusions from some additional investigations. In drawing general conclusions from these and the other studies just reviewed it is necessary to bear in mind that the data and interpretations of different investigators are sometimes in partial disagreement. (For example, Mathieu and Poulet [387] believe that the free stretching N–H frequency of NH_4^+ should be assigned a value higher than values used by Waddington [386] and others.) However, the combined results indicate complete agreement that strong $N^+–H...X^-$ bonds exist in solid ammonium and

TABLE 42. *Occurrence of hydrogen bonds $N^+–H...X^-$ in crystalline ammonium and substituted ammonium salts as deduced by IR spectroscopy*[a]

$N^+–H...X^-$ Present		$N^+–H...X^-$ Weak or Absent	
Anion	References	Anion	References
Br^-	[388]	ClO_4^-	[386, 388]
Cl^-	[388]	BF_4^-	[384–386, 388]
I^-	[388]	BCl_4^-	[388]
HF_2^-	[386, 388]	BPh_4^-	[386, 388]
N_3^-	[386]	PF_6^-	[386, 388]
NCO^-	[386]	$BeF_4^=$	[385]
NCS^-	[386]	$SiF_6^=$	[385]
NO_2^-	[386]	$TiF_6^=$	[385]
NO_3^-	[386, 388]	$GeF_6^=$	[385]
[b] $SO_4^=$	[389]	$PbCl_6^=$	[385, 388]
[c] SO_3F^-	[386]	$SnCl_6^=$	[385]
[c] $CH_3SO_3^-$	[386, 388]	$PtCl_6^=$	[385]
		$PtBr_6^=$	[385]
		AlF_6^{-3}	[385]
		CrF_6^{-3}	[385]

[a] At room temperature. The cation was NH_4^+, $MeNH_3^+$, $Me_2NH_2^+$, Me_3NH^+, Me_3ND^+, Et_3NH^+, Et_3ND^+, PyH^+, or PyD^+. Additional references to hydrogen bonding in halides are given in the accompanying text.

[b] Similar results were obtained with $(C_{10}H_{21})_3NH^+$ salts. The samples were viscous liquids. A weaker hydrogen bond is thought to form to an oxygen of HSO_4^-. Hydrogen bonding to $SO_4^=$ causes a decrease in the symmetry of this ion [389].

[c] This salt may resemble NH_4I, where the cation is thought to form one hydrogen bond to I^- and to be free to rotate about this bond [386].

REFERENCES:

[385] B. Cox and A. G. Sharpe, J. Chem. Soc., p. 1798 (1954).
[386] T. C. Waddington, J. Chem. Soc., p. 4340 (1958).
[388] R. H. Nuttall, D. W. A. Sharp, and T. C. Waddington, J. Chem. Soc., p. 4965 (1960).
[389] A. A. Lipovskii and M. G. Kuzina, Russ. J. Inorg. Chem. (English Transl.) **10**, 740 (1965).
[384] G. L. Coté and H. W. Thompson, Proc. Roy. Soc. (London) **A210**, 217 (1951).

incompletely substituted ammonium *halides.* The *polyatomic anions* also listed in *column 1* are of types considered from other kinds of physical evidence to be highly polarizable, so that their inclusion in this group is not in conflict with expectation.

Neither is it surprising for IR spectroscopic measurements to indicate that hydrogen bonds fail to form between NH_4^+ or related cations and the *complex anions* listed in *column 3* — or, at most, to be very weak. Obviously, in such anions the negative charge on a single oxygen or halogen will be much smaller than in the anions of column 1, and they will behave as weaker bases.

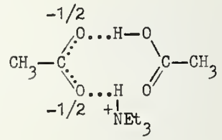
However, in some cases hydrogen bonding to complex anions is believed to occur. For example, Lipovskii and Kuzina [389] consider that Et_3NH^+ and $(C_{10}H_{21})_3NH^+$ form hydrogen bridges to the dioxotrisulfatouranate(VI) ion, $[UO_2(SO_4)_3]^{-4}$. In this anion bidentate coordination of each $SO_4^=$ to uranium is postulated. The evidence for hydrogen bonding is a decrease in the symmetry of $SO_4^=$ as well as a displaced ν(N—H) frequency. From similar evidence they concluded that $SO_4^=$ forms strong bonds to tertiary ammonium ions. Moreover, as indicated in table 42, Waddington and associates inferred that two related anions, SO_3F^- and $CH_3SO_3^-$, can also become hydrogen bonded to cations. In contrast with their findings for $SO_4^=$, Lipovskii and Kuzina observed no distortion of ClO_4^-.

Infrared data of Hadži and associates indicate strong hydrogen bonding in adducts of pyridine oxide and 2-picoline oxide with HCl and HBr and also in the adduct of trimethylamine oxide with *p*-nitrophenol [390, 391]. (Compare figs. 14 and 15 and related discussion.)

b. Results using dry aprotic solvents. The principal infrared evidence for the existence of hydrogen-bonded ion pairs in dry aprotic solvents has come from investigations by Barrow and associates [392–395]. In a series of experiments resembling photometric titrations, Barrow and Yerger studied spectral changes accompanying the gradual addition of triethylamine [392], diethylamine [393], or *n*-butylamine [394] to carbon tetrachloride or chloroform containing varying fixed concentrations of acetic acid. The infrared absorbance data were used to ascertain the compositions and probable structures of acid-base adducts formed at various relative and total concentrations of acid and base, and also to determine the relative stabilities of different products as measured by equilibrium constants. In conjunction with the experiments they also determined equilibrium constants for the association of Et_3N with $CDCl_3$ [118] and for the dimerization of acetic acid [265] in the same two solvents. Subsequently, Barrow investigated the reaction of pyridine with some aliphatic carboxylic acids in chloroform [395] and Bell and Barrow studied the association of dimethylformamide, pyridine, and triethylamine with phenol-*d*, *p*-nitrophenol, and *p*-nitrophenol-*d* in this solvent [396]. Some of the experiments and their principal conclusions will be summarized briefly.

Reactions between acetic acid and triethylamine in carbon tetrachloride. In separate experiments triethylamine was added gradually to acetic acid of five different initial concentrations in the range 0.001 *M* to 1.0 *M*. Absorbance measurements were made at several wavelengths, each wavelength being near the peak of an absorption band. The principal bands measured were ones attributed to carboxylate, carbonyl in dimeric acetic acid and also in the monomeric acid, and OH in the dimer. As expected, adding Et_3N caused some bands to diminish in intensity and others to become stronger. Some important conclusions from this investigation were:

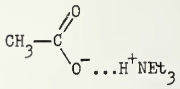
(1) Half-neutralizing 0.1-*M* AcOH in CCl_4 with Et_3N produces an acid salt, $Et_3N(HOAc)_2$, which has considerable stability. The assigned structure (L) is shown below.



(L)

In (L) the anion is shown as having *carboxylate* character. This term does not imply complete ionization of the salt, but merely that the anionic charge is about equally distributed on the two oxygens, since one oxygen is hydrogen bonded to the cation and the other is hydrogen bonded to an extra molecule of acetic acid.

(2) Continued addition of triethylamine causes gradual conversion of the acid salt to the 1:1 adduct, Et_3NHOAc (LI).



(LI)

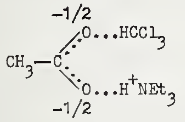
It is important to note that in (LI) the attachment of the cation to the anion does not involve merely general electrostatic forces. Instead, the cation is considered to form a *specific attachment* to *one* of the anionic oxygens, "undoubtedly by a hydrogen bond." The negative charge resides essentially on the bonded oxygen instead of being shared by both oxygens. The analogy between (LI) and structures previously presented (XLI, XLIV) for certain hydrogen bonded salts of bromophthalein magenta is easily recognized.

(3) The acid salt (L) is not formed in measurable amounts when Et_3N is added to acetic acid solutions as dilute as 0.001 *M*. Instead, adding Et_3N appears to lead directly to the production of the 1:1 salt (LI).

Reactions between acetic acid and triethylamine in chloroform. In experiments closely paralleling those performed in carbon tetrachloride the results for chloroform solutions were as follows:

(1) As before, the first product obtained on adding triethylamine to 0.3-*M* acetic acid was an acid salt (L).

(2) Continuing the addition of Et_3N led gradually to the formation of a 1:1 salt. However, its IR spectrum differs in some respects from that of (LI), and it was concluded that the salt can be solvated by $CHCl_3$, as indicated in (LII). This interpretation is supported by the observation that on adding a very large excess of Et_3N the spectrum shifts toward that of (LI); such a shift is predictable from the ability of Et_3N to associate with $HCCl_3$ (see section 3.4.5a) in competition with the C=O group. An additional conceivable structure is one resembling (LII) except in having $HCCl_3$ hydrogen-bonded to *both* oxygens. The over-all reaction leading to its formation is indicated by eq 38:



(LII)

$$CH_3COOH + 2Et_3N + 2HCCl_3 \rightleftharpoons CH_3C(O\ldots HCCl_3)_2^- + (Et_3N)_2H^+. \qquad (38)$$

However, (LII) is considered a more likely product.

Log K values for reactions involving acetic acid and triethylamine. Table 43 contains comparative equilibrium constants (expressed as the logarithms) for reactions involving acetic acid and aliphatic

TABLE 43. *Values of log* K *(25–30°, molar units) for some acid-base reactions, from infrared absorbance data* [a, b, c]

Stoichiometric Concns.		Reacting Species		Product	Solvent	Log K
HOAc	Base	(1)	(2)			
Base = Et_3N [392]						
0.001	0.001–0.025	HA	B	BHA	CCl_4	2.90
0.10, 0.30	0.05–0.50	$B(HA)_2$	B	2BHA	CCl_4	0.20
0.001	0.0005–0.005	HA	B	BHA	$CHCl_3$	3.48
0.3	0.15–0.50	$B(HA)_2$	B	2BHA	$CHCl_3$	1.34
Base = Et_2NH [393]						
0.0008	0.0002–0.004	HA	B	BHA	CCl_4	3.45
0.0008–0.01	0.0016–0.020		2BHA	$(BHA)_2$	CCl_4	2.38
0.10, 0.30	0.075–0.40	$B(HA)_2$	B	$(BHA)_2$	CCl_4	1.20
0.0008	0.0004–0.004	HA	B	BHA	$CHCl_3$	3.48
0.10, 0.30	0.10–0.60	$B(HA)_2$	B	2BHA	$CHCl_3$	2.00
Base = *n*-$BuNH_2$ [394]						
0.0008	0.0008–0.008	HA	B	BHA	CCl_4	2.78
0.0008	0.0008–0.0064	HA	$B.HCCl_3$	$BHA.HCCl_3$	$CHCl_3$	3.45

[a] From average values of K given in tables of Barrow and Yerger [392–394].

[b] HA signifies acetic acid; B signifies Et_3N, Et_2NH, or *n*-$BuNH_2$.

[c] See accompanying discussion.

REFERENCES:

[392] G. M. Barrow and E. A. Yerger, J. Am. Chem. Soc. **76**, 5211 (1954).
[393] E. A. Yerger and G. M. Barrow, J. Am. Chem. Soc. **77**, 4474 (1955).
[394] E. A. Yerger and G. M. Barrow, J. Am. Chem. Soc. **77**, 6206 (1955).

amines in carbon tetrachloride and chloroform. The first section of this table contains data for reactions where Et_3N was a participant. In the calculations of equilibrium constants allowance was made for the estimated extent of two competing reactions, namely, the self-association of acetic acid [265] and the association of Et_3N with $CDCl_3$ (which was assumed to behave like $CHCl_3$) [118]. The values of log $K_{1,2}$ adopted for acetic acid in carbon tetrachloride and chloroform, respectively, were 3.30 and 2.40; log K for 1:1 association of Et_3N with $CHCl_3$ was assumed to be -0.44 [392]. Assuming all of the equilibrium constants to be substantially correct, one may deduce the following:

(1) In CCl_4 (at room temperature) AcOH has a greater tendency to dimerize than to associate in 1:1 ratio with Et_3N.

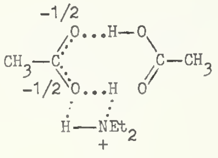
(2) In $CHCl_3$, the reverse is true. A twofold explanation which can be offered for the solvent effect is that (a) acetic acid is less completely dimerized in $CHCl_3$ than in CCl_4 (see section 4.2.2d) and (b) solvation of the 1:1 salt by $CHCl_3$ as in (LII) has a stabilizing effect. (Although the 1:1 association of $CHCl_3$ with Et_3N is a competing reaction, its extent is negligibly small.)

(3) The conversion of $Et_3N(HOAc)_2$ to Et_3NHOAc by adding an excess of Et_3N occurs much more extensively in $CHCl_3$ than in CCl_4. As in (2), this can be attributed largely to solvation of the 1:1 salt by $CHCl_3$; see (LII) and eq 39.

$$\begin{aligned} &CH_3C(O\ldots HOCOCH_3)O^-\ldots H^+NEt_3 \\ &\qquad + Et_3N + 2CHCl_3 \\ &\qquad \rightleftharpoons 2CH_3C(O\ldots HCCl_3)O^-\ldots H^+NEt_3. \end{aligned} \tag{39}$$

Reactions in carbon tetrachloride and chloroform involving acetic acid and diethylamine. Products formed and log K values. Yerger and Barrow's experiments with diethylamine were similar to the ones using triethylamine. Some parallelism of results was expected, of course, but the ability of the diethylammonium ion to form *two* bonds to proton acceptors was a complicating factor. In brief, the conclusions and explanations were as follows:

(1) Just as with Et_3N, the half-neutralization of relatively concentrated (0.1 M) acetic acid in either solvent yields an acid salt (LIII). (However, the acid salt was not formed in detectable amounts in 0.0008 M acetic acid solution.) Structure (LIII) is the same as (L) except in having *two* hydrogen bonds from the cation to the anion; the two bonds are to the same oxygen. The formation of (LIII) is thought to occur by the addition of Et_2NH to *dimeric* acetic acid (eq 40).

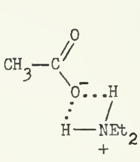


(LIII)

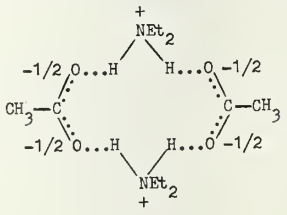
$$(CH_3COOH)_2 + Et_2NH \rightleftharpoons (CH_3COOH)_2HNEt_2. \tag{40}$$

Log K for this reaction (CCl_4) was estimated to be approximately 4.18.

(2) In CCl_4 the complete neutralization of acetic acid is believed to yield two products—a monomeric salt (LIV), which is formed in dilute solutions, and a dimeric salt (LV), which predominates in concentrated solutions. Log K for the dimerization (eq 41) was estimated to be 2.38.



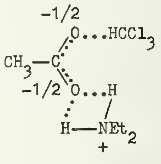
(LIV)



(LV)

$$2CH_3COOH_2NEt_2 \rightleftharpoons (CH_3COOH_2NEt_2)_2. \tag{41}$$

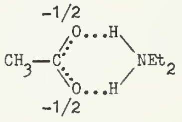
The dimeric salt was not detected in chloroform solutions, but only a monomeric salt thought to be solvated by chloroform (LVI), an analog of (LII).



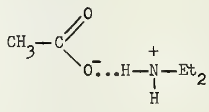
(LVI)

Structure (LIV) is probably not completely planar. It is more likely that the hydrogen bonds from $Et_2NH_2^+$ to O^- are directed toward the nonbonded orbitals, thus permitting maximum interaction. Similar considerations apply to the other diethylammonium salts.

Two additional structures—see (LVII) and (LVIII)—were considered as possible alternatives to (LIV) [393], but were rejected for reasons that will not be detailed here.



(LVII)



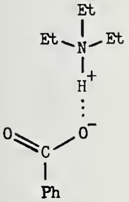
(LVIII)

(3) The equilibrium constants for reactions involving Et_2NH are either about the same as for the corresponding reactions involving Et_3N or somewhat larger. For example, log K for the 1:1 association of B with HA in chloroform has the same value

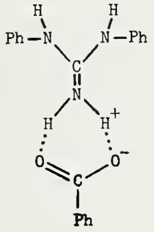
(3.48) when B is Et_2NH as when B is Et_3N. A reasonable explanation for the similar association constants is that in both $Et_2NH_2OCOCH_3$ and $Et_3NHOCOCH_3$ the C=O group is hydrogen bonded to $CHCl_3$, as shown in (LII) and (LVI); such solvation would help to stabilize the carboxylate structure. A corresponding stabilization results from the hydrogen bonding of excess HA to BHA, giving $B(HA)_2$—see (L) and (LIII).

The dimerization of diethylammonium acetate, yielding (LV), is obviously not possible for a salt with only one proton attached to the ammonium nitrogen. The three examples of hydrogen bonding just mentioned all bring about increased association of B with HA.

An explanation along similar lines was proposed by Davis and Paabo [15] to account for the following observations: In benzene solution, benzoic acid is almost as strong as bromophthalein magenta E when the criterion of strength is the value of log K (25°, molar units) for 1:1 association with Ph_2G (1,3-diphenylguanidine), the values of log K for benzoic acid and bromophthalein magenta being 5.32 and 5.41, respectively. However, when Et_3N is used as the reference base instead of Ph_2G, the corresponding values of log K are 3.58 and 4.44, signifying that benzoic acid is an appreciably weaker acid than bromophthalein magenta. The structure postulated for triethylammonium benzoate is (LIX)—a close analog of Barrow and Yerger's proposed structure for triethylammonium acetate (LI). Davis and Paabo suggested that diphenylguanidium benzoate can assume a cyclic, more stable structure (LX) by *dual* hydrogen bonding of the cation to the anion.



(LIX)

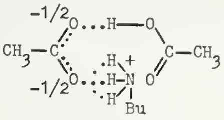


(LX)

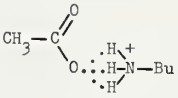
(One of the resonating structures)

The cyclic structure postulated for diphenylguanidinium benzoate is unusual (perhaps almost unique), being constructed by hydrogen bonding of a resonant cation to a resonant anion. Phenolates of triethylamine and diphenylguanidine (for example, their salts with bromophthalein magenta) would be less dissimilar than the two carboxylates shown above [15].

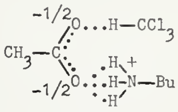
Reactions in carbon tetrachloride and chloroform involving acetic acid and n-butylamine. Products postulated and log K *values.* n-Butylamine, like diethylamine and triethylamine, is convertible into an acid salt (LXI) in concentrated CCl_4 and $CHCl_3$ solutions. The 1:1 salts, which are close analogs of diethylammonium salts, are the monomeric acetate (LXII) and its dimer (LXIII), formed in CCl_4, and the solvated monomeric acetate (LXIV) which is formed in $CHCl_3$. According to table 43 the 1:1 monomer, although less stable in CCl_4 than the corresponding diethylammonium and triethylammonium acetates, is equally stable in $CHCl_3$, thus providing additional support for the postulate that the stability of alkylammonium carboxylates is enhanced by hydrogen bonding to proton-donor solvents.



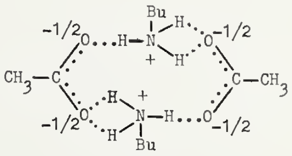
(LXI)



(LXII)



(LXIV)



(LXIII)

In summing up their overall conclusions from these sets of studies Yerger and Barrow stated that in all systems containing acetic acid and a primary, secondary, or tertiary aliphatic amine a hydrogen bond forms between the alkylammonium ion and one oxygen atom of the acetate ion. Multiple hydrogen bonding to a single oxygen atom occurs when more that one cationic proton is available for bonding, and appears to lead to the formation of bridged dimers in relatively concentrated solutions of primary and secondary ammonium acetates [394]. We have already seen (sec. 4.3.2b) that dielectric polarization data for related acid-base systems in benzene have received similar interpretations.

The Barrow and Yerger studies have also illustrated how the apparent strengths of bases, as measured by ability to form 1:1 adducts with acids, may be altered by a change of solvent [393]. According to table 43, by the criterion of log K values for 1:1 adduct formation the three amines vary in strength in the following order, when dissolved in CCl_4:

$$Et_2NH > Et_3N > n\text{-}BuNH_2.$$

By the same criterion the strengths of Et_3N and n-$BuNH_2$ become equal to that of Et_2NH in $CHCl_3$.

It seems reasonable to attribute this "leveling effect" in large measure to the ability of $CHCl_3$ to form hydrogen bonds to carboxylate atoms of alkylammonium acetates, thereby enhancing the stability of these salts.

Other studies of tertiary amine-carboxylic acid interactions in aprotic solvents. Barrow [397] and Cook [398] have studied hydrogen bonding interactions of amino acids, with special interest in factors that promote zwitterion formation. As expected, the results indicate the existence of hydrogen bonding interactions analogous to those occurring in the Et_3N-AcOH system. However, the comparative extent of intra- and intermolecular bonding is determined in part by the molecular geometry.

As a part of his investigation Cook examined the Et_3N-AcOH system (0.1 *M*) in five aprotic solvents: Benzene, carbon tetrachloride, chloroform, 1,2-dichloroethane, and dichloromethane. He also studied the reaction in a dipolar aprotic solvent (acetonitrile) and in the absence of a diluent. In agreement with Barrow and Yerger [392] he deduced that a stable 2:1 acid-base complex forms in all benzene solutions containing an excess of the acid and that the continued addition of Et_3N leads to the replacement of the 2:1 complex by a 1:1 complex. He reached the same conclusions using the other five solvents, as well as in the absence of a solvent.

However, Cook is in disagreement with Barrow and Yerger as to the nature of the 1:1 complex. As we have noted, Barrow and Yerger postulated structure (LI) for the 1:1 complex; Barrow [395] calls this a "proton-transferred ion-pair species." In Cook's view the ion pair species (LI) is in *tautomeric equilibrium* (eq. 42) with an isomeric hydrogen bonded complex (LXV) in an inert solvent like CCl_4:

$$\underset{\text{(LXV)}}{Et_3N\ldots HOC(=O)CH_3} \rightleftharpoons \underset{\text{(LI)}}{Et_3NH^{+}\ldots{}^{-}OC(=O)CH_3} \tag{42}$$

Like Barrow and Yerger, he considers that the proton-transferred species becomes more stable in a solvent that can hydrogen bond to carbonyl [compare (LII)]. He has arranged the six solvents used in his work in the order of increasing ability to promote proton transfer:

$$C_6H_6 \approx CCl_4 < C_2H_4Cl_2 < CH_2Cl_2 < CH_3CN < CHCl_3.$$

This order is based on the comparative ratios of the intensities of the carboxylate and carbonyl peaks in the different solvents.

We referred earlier (sec. 4.3.3b) to Bruckenstein and Saito's studies [352] of amine-carboxylic acid interactions in benzene by the "DVP" method and by infrared absorption spectroscopy. Examples of acid-base systems for which they obtained IR absorbance data are listed below.

Bases: Dodecylamine, dibenzylamine, piperidine, *N,N*-dimethylbenzylamine.

Acids: Benzoic, trichloroacetic, trifluoroacetic. The stoichiometric molar concentrations, C_B and C_{HX}, were $0.01n$ and $0.01n'$, respectively, n and n' usually having the value 1 but sometimes additional values in the range 0.5–5.0.

The overall results were interpreted as denoting the formation of several species of salt, including B^+HX^-, $(BH^+X^-)_2$, $BH^+HX_2^-$, and $BH^+X(HX)_2^-$, thus being in partial agreement with the findings reported above. The authors also postulate hydrogen bonding in complex anions: for example, a structure similar to the anionic portion of (L) is considered possible for HX_2^-. However, in pronounced disagreement with the authors just referred to, Bruckenstein and Saito concluded that their IR data provide *no evidence of cation-to-anion hydrogen bonding.*

Reactions between carboxylic acids and pyridine in chloroform. As a sequel to Barrow and Yerger's investigations of amine-acetic acid interactions in CCl_4 and $CHCl_3$, Barrow performed two types of spectroscopic titrations to ascertain the associative behavior of pyridine (Py) with seven aliphatic acids (RCOOH) in $CHCl_3$ [395]. The strengths of the acids covered a span of more than four *pK* units. In the order of increasing strength, as indicated by *pK* values, the acids were:

$$CH_3COOH,\ CH_2ClCH_2COOH,\ CH_2ICOOH,\ CH_2ClCOOH,\ CHCl_2COOH,\ CCl_3COOH,\ CF_3COOH.$$

In the first type of titration, Py was added gradually to RCOOH (maintained at 0.1 *M* concentration throughout). Barrow deduced that where $R{=}CF_3$ or CCl_3 stoichiometric acid-base association occurred at Py concentrations up to 0.05 *M*, yielding the 1:2 salt $Py(HA)_2$; to this product he assigned a hydrogen-bonded structure analogous to (L). With weaker acids, formation of $Py(HA)_2$ was less complete, 1:1 association being increasingly favored until with $R{=}CH_3$ or CH_2ClCH_2 only a 1 : 1 adduct seemed to form. As evidence of the formation of $Py(HA)_2$ Barrow pointed out that the 6.97 μ absorption band of Py had been replaced by two bands (a weak band near 6.12 μ and a second band near 6.72 μ), both of which he assigned to PyH^+; furthermore, the "characteristic carboxylate band" had appeared. According to Barrow's tabulated results the CO_2^- band varies in location, occurring at 6.00 μ in the formation of $Py(HOCOCF_3)_2$ and gradually shifting to longer wavelengths with decreasing acid strength until it appears at 6.41 μ for $Py(HOCOCH_2I)_2$.

Barrow was especially interested in the nature of the 1:1 adducts. According to a commonly held view, the association of a weak proton acceptor such as Py ($pK_a \sim 5.2$ at 20°) with a *weak* Brønsted acid like CH_3COOH (pK_a 4.76 at 25°) is properly formulated as in eq 43. The product, symbolized by B...H–A, is referred to as a "hydrogen-bonded complex." The

$$B + H\text{–}A \rightleftharpoons B...H\text{–}A \quad (43)$$

H–A bond is considered to have retained its covalent character, the hydrogen bond to B being the result of electrostatic attraction. In contrast, a similar interaction with a *strong* acid such as CCl_3COOH ($pK \sim 0.65$) is considered to involve incipient proton transfer and is therefore formulated according to eq 44. In the product, which is distinguished from that of

$$B + H\text{–}A \rightleftharpoons B\text{–}H^+...A^- \quad (44)$$

equation 43 by the appellation "hydrogen-bonded ion pair," the bond $B\text{–}H^+$ is thought to have gained a covalent character and the hydrogen bond to have become essentially electrostatic in nature. Barrow wished to ascertain whether the acid-base associations represented by these two equations are *limiting examples of a single type* of reaction or, instead, represent *two different* reactions. The first situation corresponds to a series of *single-minimum* potential energy curves for the proton, with the minimum shifting gradually from a position near A to a position nearer B as HA increases in strength. The second situation corresponds to a *double-minimum* potential energy curve. (See sec. 4.6; fig. 24.)

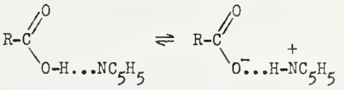
Potential energy curves for different types of proton-transfer reactions in aprotic solvents will be discussed more completely in sec. 4.6. In the meantime it will suffice to mention that, if a double-minimum curve applies, one will expect there to be two potential troughs (wells) of *unequal depth* in reactions involving either very weak (fig. 24(a)) or very strong (fig. 24(b)) acids. In the former case the proton will remain near A, and in the latter case, near B. On the other hand, with acids of intermediate strengths one may expect to find reactions where the two potential troughs are *about equal* in depth (fig. 24(c)); here, the proton may be able to shift rapidly from one minimum (near A) to the second minimum (near B) by leaping over or tunneling through the potential barrier. The problem of whether the single-minimum or double-minimum potential energy curve applies, apart from its theoretical interest, obviously has a practical importance in attempts to construct scales of relative acid and base strengths by determining equilibrium constants or shifted spectral frequencies.

To ascertain the nature of the 1:1 adducts, Barrow performed a second series of "titrations" in which RCOOH was added gradually to Py in $CHCl_3$ (maintained at 0.2 *M* concentration). He concluded that his seven acids can be divided into three classes, as follows:

Class 1, consisting of the two weakest acids ($R = CH_3$ or CH_2ClCH_2). These acids associate with Py according to eq 43—that is, they form the "nonproton-transferred species" Py...HOCOR. As supporting evidence for this conclusion he noted that an absorption band of Py found at 6.33 μ in CCl_4 shifts gradually to 6.24 μ when the solvent is changed successively to $CHCl_3$, *n*-BuOH, and CH_3COOH. In his view the gradual shift signifies that nonproton-transferred species are formed in the three solvents (that is, Py...$HCCl_3$, Py...HOBu, and Py...$HOCOCH_3$), the differing shifts in the 6.33-μ band of Py indicating a difference in the degree of electrostatic attraction between Py and the proton donor.

Class 2, consisting of the two strongest acids ($R = CF_3$ or CCl_3). The product consists of "proton-transferred" ion pairs (eq 44). The principal evidence is the appearance of the PyH^+ bands near 6.12 μ and 6.72 μ, with approximately the same intensity as in $Py(HA)_2$. These two strong acids were found to combine stoichiometrically with pyridine.

Class 3, composed of the three acids of intermediate strengths (that is, $R = CH_2I$, CH_2Cl, or $CHCl_2$). According to Barrow the double-minimum concept was experimentally verified in these cases, the products indicated by eqs 43 and 44 being present simultaneously in tautomeric equilibrium:


(45)

(LXVI) (LXVII)

The following observations were presented as evidence:

(1) The simultaneous appearance of the band near 6.24 μ which he regards as characteristic of the nonproton-transferred complex Py...HOCOR and the two bands (near 6.12 μ and 6.72 μ) attributed to PyH^+ in proton-transferred ion pairs (for example, in $CCl_3COO^-...H\text{–}\overset{+}{N}C_5H_5$ and $CF_3COO^-...H\text{–}\overset{+}{N}C_5H_5$).

(2) Intensification of the two PyH^+ bands and reduced intensity of the Py...HOCOR band with increasing strength of the acid.

(3) Alterations in relative band intensities when a mixture of Py and $CHCl_2COOH$ (both 0.4 *M*) in chloroform was heated from 25° to 55° by short warming in an oven: the intensity of the 6.24-μ band increased by about 45 percent while that of 6.72-μ band decreased by about 16 percent. (However, the 6.12-μ band appeared to *increase* in intensity.)

(4) Inability to detect any Py band that appeared to assume *continuously* the character of PyH^+ with increasing strength of RCOOH.

In short, Barrow considers that his combined results are most consistent with the hypothesis that a hydrogen-bonded complex and a hydrogen-bonded ion pair are *not* limiting examples of a single type of product. It should be noted, however, that he did not find completely satisfying explanations for two observations: (1) The wavelength shift in the carbonyl-carboxylate band near 5.80 to 5.85 μ is much smaller on ion-pair formation than would be expected; (2) the band splitting expected in the case of a tautomeric equilibrium is absent.

In the case of the pyridine-acetic acid system equilibrium constants were determined for two reactions (eqs 46 and 47) by performing "spectroscopic titrations" of 0.05 *M* acetic acid and combining the results with dimerization constants [265] for acetic acid in chloroform and carbon tetrachloride.

$$2\mathrm{Py} + (\mathrm{CH_3COOH})_2 \rightleftharpoons 2\mathrm{CH_3COOH}\cdot\mathrm{Py} \qquad (46)$$

$$\mathrm{Py} + \mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COOH}\cdot\mathrm{Py}. \qquad (47)$$

The equilibrium constants (molar units) are as follows: (1) For the reaction of acetic acid as the dimer (eq 46), log $K = 1.60$; (2) for its reaction as the monomer (eq 47), log K values are 2.34 (CCl_4 as solvent) and 1.85 ($CHCl_3$ as solvent). The last two constants may be compared with the log K values obtained for the $Et_3N-AcOH$ system: 2.90 (in CCl_4) and 3.48 (in $CHCl_3$) (see table 43). The reversed solvent effects for the two systems provide, in Barrow's opinion, an additional reason for believing that the $Py-CH_3COOH$ and Et_3N-CH_3COOH reactions yield different types of product. As readers will recall, the greater value of log K for the Et_3N-CH_3COOH system in $CHCl_3$ was attributed to stabilization of the carboxylate structure by hydrogen bonding of the solvent to carboxylate-carbonyl: see (LII). Evidently, when Py replaces Et_3N as the base the carboxylate-carbonyl does not become a sufficiently good proton acceptor for hydrogen bonding to $CHCl_3$, and the role of this solvent changes to that of a competitor of CH_3COOH in the formation of hydrogen bonds to pyridine. These examples illustrate well the inadequacy of the dielectric constant of a solvent as a single clue to its modifying effect on acid-base behavior.

Barrow's studies of 1:1 Py-RCOOH systems have recently been extended by Johnson and Rumon [399] to $Py-C_6H_5COOH$ and 17 additional adducts in which the base was either pyridine, 3,5-lutidine, 2,6-lutidine, or 2,4,6-collidine, and the acid was benzoic or a substituted benzoic acid; $Py-CF_3COOH$ and $Py-CCl_3COOH$ were also included. The adducts were examined as *solids*, and eight representative adducts were also examined in *acetonitrile* solution. Johnson and Rumon were interested in the relation between the type of hydrogen bonding (that is, $B\ldots H-A$ or $B-H^+\ldots A^-$) and ΔpK_a(aq.) (that is, pK_a of base $-$ pK_a of acid), and they were also concerned with the question of single-minimum versus double-minimum potential energy curves. In accord with common practice, the appearance of two widely separated ν-NH or ν-OH bands was taken as evidence of a double-minimum potential for the proton-stretching motion and of a low barrier between the two minima, while a single ν-NH or ν-OH band below 1700 cm^{-1} was regarded as indicating a single-minimum potential function. From a detailed examination of the absorption curves, with particular attention to bands in the ν-NH, ν-OH, ν-C=O, and ν-C–O regions, they concluded that the adducts can be classified in four groups: Classes A and B, which are of type $B\ldots H-A$, and classes C and D, which are of type $B-H^+\ldots A^-$. Class A merges gradually into Class B, and even Class D shows gradations in behavior. The following brief summary indicates their line of reasoning: The spectra of *Class A* are closely similar to those of the parent dimeric acids, for example, the CO_2H band does not indicate perturbation; however, two new, well-defined ν-OH bands indicate strong H bonding between the base and the acid. In *Class B*, the bands in the ν-C–O region are still those characteristic of RCO_2H, but there is considerable broadening of the ν-C=O band and the two new ν-OH bands. Among characteristics of *Class C* spectra are the disappearance of certain bands attributable to ν-NH and ν-OH, and to ν-C–O as in the CO_2H group; a broadening and more complex character of the ν-C=O band; and a broad and intense absorption in the proton deformation region below 1200 cm^{-1}. *Class D* adducts have distinct ν-NH and ν-CO_2^- bands, although they still show varying amounts of spectral broadening.

The complete list of adducts is given in table 44, together with values of ΔpK_a(aq.) and the type of hydrogen-bonded structure deduced (including inferences with respect to double- and single-minimum potential energy functions). The following conclusions should be emphasized:

(1) An abrupt change in the spectral characteristics of adducts occurs near ΔpK_a 3.75, signaling a transition from $B-H\ldots A$ to $B-H^+\ldots A^-$.

(2) In cases where a double-minimum function is indicated by two NH or OH bands it is believed that the band doubling is due to proton tunneling through a low energy barrier.

(3) No one of the single-minimum or double-minimum systems showed a change in spectral characteristics observed for the solid state after being dissolved in MeCN. Evidently, a tautomeric equilibrium between $B\ldots H-A$ and $B-H^+\ldots A^-$, which is not expected in the solid state, does not occur in MeCN.

(4) Cooling samples to liquid nitrogen temperature caused little change in the spectra, thus ruling out the possibility of attributing band doubling to a tautomeric equilibrium.

It is pertinent to mention at this point some *dielectric polarization* studies of $Py\cdot CH_3COOH$, $Py\cdot CH_2ClCOOH$, and $Py\cdot CCl_3COOH$ in *benzene*, published in 1962 by Davies and Sobczyk [400]. The polarization data yielded for the three complexes the respective dipole moments (Debye units, 20–21°) 2.97, 4,57, and 7.68. (An earlier study, which was cited in table 37, yielded slightly different

TABLE 44. *The nature of hydrogen bonding in solid 1:1 pyridine-benzoic acid and some related complexes, and its relationship to* ΔpK_a [a]

Base	RCOOH	ΔpK_a	Type of Adduct [b]	Class
Pyridine	2,4-Dimethylbenzoic	1.05	B...H–A (d)	A
	p-Toluic	0.86	B...H–A (d)	A
	Benzoic	1.03	*B...H–A (d)	A
	p-Chlorobenzoic	1.25	B...H–A (d)	A
	3,4-Dichlorobenzoic	1.62	*B...H–A (d)	B
	2,4-Dichlorobenzoic	2.55	B...H–A (d)	B
	4-Nitrobenzoic	1.81	B...H–A (d)	B
	3,5-Dinitrobenzoic	2.41	*$B{-}H^+...A^-$ (s)	C
	2,4-Dinitrobenzoic	3.81	*$B{-}H^+...A^-$ (s)	C
	Trichloroacetic	4.58	*$B{-}H^+...A^-$ (d)	
	Trifluoroacetic	5.00	*$B{-}H^+...A^-$ (d)	
3,5-Lutidine	3,5-Dinitrobenzoic	3.52	$B{-}H^+...A^-$ (s)	
	2,4-Dinitrobenzoic	4.92	$B{-}H^+...A^-$ (s)	
2,6-Lutidine	Benzoic	2.50	*B...H–A (d)	
	3,5-Dinitrobenzoic	3.88	$B{-}H^+...A^-$ (d)	
	2,4-Dinitrobenzoic	5.28	$B{-}H^+...A^-$ (d)	
2,4,6-Collidine	3,4-Dichlorobenzoic	3.99	$B{-}H^+...A^-$ (d)	D
	2,4-Dichlorobenzoic	4.92	*$B{-}H^+...A^-$ (s)	C or D
	3,5-Dinitrobenzoic	4.78	$B{-}H^+...A^-$ (d)	D
	2,4-Dinitrobenzoic	6.18	$B{-}H^+...A^-$ (d)	D

[a] This table is a partial summary of conclusions of Johnson and Rumon from a detailed study of IR absorption bands; samples were examined as mulls and also, in some cases, in acetonitrile solution [399]. $\Delta pK_a = (pK_a, \text{base} - pK_a, \text{acid})_{aq}$.

[b] The symbol (d) signifies that the hydrogen bond is believed to be a double-minimum type, and (s), that it is believed to be a single-minimum type. An asterisk signifies that the adduct was examined in MeCN solution.

REFERENCE:

[399] S. L. Johnson and K. A. Rumon, J. Phys. Chem. **69**, 74 (1965).

values.) These dipole moments are considered to indicate a definite hydrogen-bonding interaction in all three cases, with the trichloroacetate having the $B{-}H^+...A^-$ type of structure. The authors also concluded that in the frequency range up to 1700 MHz the solute particles behave like rigid-dipole molecules, with no evidence of a "proton jumping process." (However, they do not consider proton jumping to be necessarily excluded in other acid-base complexes. Neither is it considered excluded for the three above-mentioned complexes in a different frequency range.)

Reaction of phenol-d, p-nitrophenol, and p-nitrophenol-d with amines in halohydrocarbons. To obtain further evidence of possible tautomerism in acid-base adducts, Barrow, in coauthorship with C. L. Bell [396], studied the association of 0.05 *M* phenol-*d* with *N,N*-dimethylformamide, pyridine, and triethylamine (apparently in large excess) in *carbon tetrachloride* and *chloroform*, by infrared spectroscopy. As in Barrow's infrared studies of Py-RCOOH systems [395], there seemed to be band splitting.

In addition, they determined the *electronic absorption curves* of *p*-nitrophenol (6×10^{-5} *M*), mixed with triethylamine (0.1 *M*), in the following four solvents: Cyclohexane, chloroform, ethylene chloride, ethanol. The *cyclohexane* solution gave an absorption curve with a *single* strong band near *308* nm; this was attributed to $Et_3N...HOC_6H_4\text{-}p\text{-}NO_2$. An *ethanol* solution of *p*-nitrophenol made basic with triethylamine (or KOH) also yielded an absorption curve with a single strong band, but the band was centered at *400* nm. However, when either *chloroform* or *ethylene chloride* was the solvent, an absorption band appeared in *each of these regions.* This seeming "band splitting" in the ultraviolet was interpreted as confirmation of Barrow's hypothesis (based initially on infrared results) that a good many 1:1 salts, when dissolved in an aprotic solvent, are present as an equilibrium mixture of the *non-proton-transferred* species (B...H–A) and the *proton-transferred* species ($B-H^+...A^-$). Triethylammonium *p*-nitrophenolate and pyridinium dichloroacetate are regarded as authentic examples of such salts.

A few analogous studies by others (for example, measurements of the electronic absorption curves of ethylene chloride solutions containing a fixed amount of *p*-nitrophenol and varying amounts of triethylamine [401]) have given comparable results and have received similar interpretations, and there seems to be a fairly wide acceptance of Barrow's theory.

Comments on the double-minimum hypothesis as applied to 1:1 acid-base complexes in aprotic organic solvents. It seems to this writer that there is a serious obstacle to accepting Barrow's hypothesis: Band splitting in the ultraviolet seems to have been observed only when the solvent was *chloroform or ethylene chloride.* No one seems to have observed band splitting when the solvent was a hydrocarbon. For example, Bell and Barrow's ultraviolet absorption curve for triethylammonium *p*-nitrophenolate in *cyclohexane* contains only one absorption band [396], and band splitting has also been found lacking in the ultraviolet curves for this salt in *toluene* [404] and in *benzene* [17] (see fig. 25). How can this discrepancy be explained?

A clue can be found in table 32, which includes examples of solvent effects on ion-pair dissociation constants of some tertiary ammonium picrates. Table 32 indicates there to be an enormous difference in the ion-pair dissociation of two closely similar salts (*i*-Am_3NHPi and Bu_3NHPi) when one of the two is dissolved in benzene, and the other is dissolved in ethylene chloride; that is, log K (where K is the ion-pair dissociation constant) is -20.60 for *i*-Am_3NHPi dissolved in benzene, and -7.68 for Bu_3NHPi dissolved in ethylene chloride. A few other pertinent examples are to be found in table 33. These results of Kraus, Fuoss, and their associates, like the still earlier conductance investigations of Walden [322], have received inadequate recognition because attention has been focused for so long on water and water-like solvents. Actually, it is more than 50 years since Walden's experiments provided clear-cut evidence that *in the strictest sense* practically none of the so-called "non-ionizing" organic solvents is properly labelled as such. He found that ionic dissociation of salts *can* occur in aprotic solvents like chloroform, dichloromethane, 1,2-dichloroethane (ethylene chloride), and even in solvents of dielectric constant as low as 2 to 3 (for instance, benzene, carbon bisulfide, carbon tetrachloride, and toluene). The single absorption band (near 400 nm) observed for triethylammonium *p*-nitrophenolate in ethanol is considered to indicate that in this solvent the salt is present as solvated ions, instead of as B...H–A. The overall reaction of triethylamine with *p*-nitrophenol can be represented as:

$$Et_3N + HOC_6H_4NO_2 + (m+n)EtOH \rightleftharpoons (Et_3NH^+)mEtOH + (^-OC_6H_4NO_2)nEtOH. \quad (48)$$

In chloroform or ethylene chloride, which have only limited ability to play a corresponding role, part of a salt can be expected to be present as the 1:1 acid-base adduct and part as ionic species. The proportion of ions should change with dilution.

If our supposition is correct, the two solvents can be included in the large group of solvents that promote partial, but not complete, ionic dissociation of acid-base adducts. Among these solvents are acetic acid [405, 406], acetonitrile [407], and nitrobenzene [24]. In acetic acid, for example, Kolthoff and his associates have formulated 1:1 acid-base interactions as:

$$B + HA \underset{\text{Ionization}}{\rightleftharpoons} BH^+A^- \underset{\text{Dissociation}}{\rightleftharpoons} BH^+ + A^-. \quad (49)$$

In their terminology [406], the shifting of the proton from A toward B is referred to as "ionization," and the separation of cations from anions through solvation is called "dissociation." To arrive at a satisfactory description of acid-base behavior in this solvent in numerical terms, equilibrium constants corresponding to both these processes have had to be determined. Analogous treatments have been applied to acetonitrile and nitrobenzene solutions (for example, see table 34). We venture to predict that in future investigations ionic dissociation of many acid-base adducts will be found to occur to a measurable, though perhaps only minute, extent in halogen-containing aliphatic hydrocarbons such as those mentioned above. Depending on the nature and concentration of the dissolved species, simple ions, complex ions, or mixtures of these may be formed (sec. 4.3.3a). This is a matter of considerable importance in view of the extensive use of such solvents in infrared spectroscopy.

Another conceivable explanation of the seeming "band splitting" is the presence of unsuspected impurities. The chemical instability of the aliphatic halohydrocarbons was often overlooked in early exploratory spectroscopic work, but a number of recent papers have included comments on their reactivity with organic bases; some examples were given in section 3.4.6, and since that section was written other examples have been encountered. Furthermore, solvents like chloroform and ethylene chloride react very readily with atmospheric water and oxygen when not protected from daylight (apparently yielding hydrogen chloride as one of the products) [131], and it is not easy to maintain them in a highly pure condition after the customary stabilizer has been removed.

Another possibility for the introduction of an impurity into acid-base systems like those being discussed is the spontaneous partial conversion of the tertiary amine to its oxide. It was discovered during investigations of a related acid-base system in benzene, in which the base was tribenzylamine, that tribenzylamine oxide was formed on very brief exposure of the solutions (at 25°) to air; even though the yields were extremely small, the amine oxide—which, like other tertiary amine oxides, is a very good proton acceptor—affected spectrophotometric results (in the visible region) [31]. Similarly, formation of tertiary amine oxides in scarcely more than trace amounts is now believed to account for slow drifts in the conductance of dilute solutions of tribenzyl-, triethyl-, tri-*n*-propyl, and tri-*n*-butylammonium picrates in such solvents as toluene, ethylene chloride, and *o*-dichlorobenzene [402, 403]. When such drifts were first observed, amine oxide-formation was not known to provide a plausible explanation, and they were tentatively attributed to a *slow* tautomeric change of the kind indicated by eq 45. Recent infrared investigations [390, 391] have shown that various adducts of tertiary amine oxides have characteristic absorption bands in this region. One would expect such bands to be located rather close to corresponding bands for tertiary amine-acid adducts, just as in the visible and ultraviolet regions (see figs. 14 and 15).

On heating a pyridine-dichloroacetic acid mixture in chloroform to about 55° Barrow observed certain changes in relative band intensities which he believed to be consistent with his hypothesis of a tautomeric equilibrium [395]. However, probable temperature effects on equilibria of the types indicated in eq 49 can account equally well for the spectral shifts reported.

c. Results with wet aprotic solvents [408–414]. Throughout the experiments just described, careful efforts were made to exclude moisture. We shall now review very briefly a small group of experiments, dating from about 1962, whose objective was to determine the nature of amine-acid adducts present in aprotic (or dipolar aprotic) organic solvents after vigorous shaking of an amine-containing organic solvent with an aqueous acid-containing solution. Such knowledge contributes to success in devising procedures for recovering, removing, and separating acids. In some experiments attempts were made to remove any water carried into the organic layer by centrifuging or using desiccants, but rigorous drying conditions were not employed.

The reaction postulated for 1 : 1 association of an amine (R_3N) with a monoprotic acid (e.g., HNO_3, HCl) during the extraction process is indicated by eq 50. Equation 51 is a more general expression covering polyprotic acids (e.g., H_2SO_4, H_3PO_4) as well. The symbols "org" and "aq" indicate whether a species is in the organic or the aqueous layer.

$$R_3N_{\mathrm{org}} + H^+_{\mathrm{aq}} + X^-_{\mathrm{aq}} \rightleftharpoons R_3NHX_{\mathrm{org}} \qquad (50)$$

$$nR_3N_{\mathrm{org}} + nH^+_{\mathrm{aq}} + X^{-n}_{\mathrm{aq}} \rightleftharpoons [(R_3NH^+)_nX^{-n}]_{org} \qquad (51)$$

Amines of relatively high molecular weight (e.g., tri-*n*-octyl- or tridodecylamine) are used to enhance solubility of the product in the organic layer.

In the experiments to be cited, the procedures used for determining the composition and structure of the extracted product(s) included not only conventional titrations for acid, base, and the water content of the organic layer but also the recording of IR spectra. The principal criteria relied on for detecting cation-to-anion hydrogen bonding were shifts in ν(N–H) or ν(N–D) frequencies and evidence of deformation of the anion. Investigators were guided to some extent by IR band assignments made previously in studies of solid salts.

Table 45 gives examples of extraction experiments by several investigators [408–411] in which the formation of hydrogen-bonded cation-anion pairs in the organic layer was indicated by shifted ν(N–H) frequencies. Benzene and chloroform are the principal solvents represented.

Table 46 lists examples of $R_3N^+–D...X^-$ bonding in which the solvent was carbon tetrachloride and the base was *n*-Oct_3N [412]. The anions are listed in the order of decreasing ability to function as deuterium bond acceptors. (The original paper contains examples of $R_3N^+–H...X^-$ bonding as well; for example, see fig. 5.)

The combined results given in tables 42, 45, and 46 permit the following generalizations:

(1) Conclusions about cation-anion hydrogen bonding drawn from studies of solid specimens generally agree closely with conclusions from studies using aprotic solvents. (Here and elsewhere the phrase "hydrogen bonding" is to be construed as including deuterium bond formation.)

(2) Anions of most common mineral acids (e.g., Cl^-, NO_3^-) are good hydrogen bond acceptors. This statement applies also to acid anions such as HSO_4^- and DSO_4^-.

(3) As expected, the ability of anions to function as hydrogen bond acceptors is greatest when the negative charge is largely concentrated on a single atom, as in simple ions like Cl^- or polarizable anions like NO_3^- and Pi^-. When the negative charge is diffuse, as in ClO_4^-, anions are much poorer hydrogen bond acceptors.

(4) However, even complex anions (for example, Ph_4B^-, ReO_4^-, $UO_2Cl_4^{=}$, $ZnCl_4^{=}$) may exhibit *some* ability to become hydrogen bonded to cations. It is not surprising that weak acceptors like ClO_4^- are classified sometimes as hydrogen bond acceptors and sometimes as nonacceptors.

There is no indication that small amounts of water, likely to have been present in some of these experiments, altered results significantly.

Table 47 presents examples of cation-to-anion hydrogen bonding from Ryan's studies in the *visible and near-infrared* regions [413–414]. In some experiments, the solid salt was dissolved in the aprotic or dipolar aprotic solvent; in others, the salt was formed in the organic layer by an extraction or by metathesis. The *anions* listed are mainly complexes of actinides: $U(VI)O_2Cl_4^{=}$, $Np(VI)O_2Cl_4^{=}$, $Pu(VI)O_2Cl_4^{=}$, $U(IV)Cl_6^{=}$, and $U(IV)Br_6^{=}$. Apparently $CoCl_4^{=}$, also, can function as a hydrogen bond

Table 45. *Some examples of* $R_3N^+{-}H...X^-$ *formation in "wet" aprotic solvents, deduced from shifted* ν(N–H) *frequencies* [a]

R_3N	HX	Solvents	References
$(n\text{-}C_8H_{17})_3N$	HNO_3	Benzene,[b] chloroform, "modified" dodecane,[c] nitrobenzene	[408]
$MeN(C_8H_{17})_2N$	HNO_3 [d] HCl [d] HBr [d] HI [d] $HClO_4$ [e]	Chloroform	[409]
$(n\text{-}C_8H_{17})_3N$	HNO_3, HCl, $HClO_4$, H_2SO_4, H_3PO_4	Benzene	[410]
$(n\text{-}C_{12}H_{25})_3N$	$H_2UO_2(NO_3)_4$ [f]	Benzene	[411]
	HNO_3	Kerosene	

[a] The adjective "wet" signifies that the salt R_3NHX was formed during extraction of HX from an aqueous solution into an R_3N-containing organic solvent. Temperatures seem to have been in the range 20–25°. See articles cited for concentrations used.

[b] Analogous results were obtained using DNO_3.

[c] "Modified" signifies that 6 vol.-percent of *n*-octanol was present.

[d] Strong hydrogen bonds.

[e] A weak hydrogen bond.

[f] Hypothetical formula. The acid-base reaction postulated is: $2R_3NHNO_3\,(org) + UO_2(NO_3)_2(aq) \rightleftharpoons (R_3NH)_2UO_2(NO_3)_4(org)$.

References:

[408] J. M. P. Verstegen, Trans. Faraday Soc. **58**, 1878 (1962).
[409] J. I. Bullock, S. S. Choi, D. A. Goodrick, D. G. Tuck, and E. J. Woodhouse, J. Phys. Chem. **68**, 2687 (1964).
[410] T. Sato, J. Appl. Chem. **15**, 10 (1965).
[411] T. Sato, J. Appl. Chem. **15**, 92 (1965).

acceptor. The *cations* listed are principally primary, secondary, and tertiary ammonium ions; the hydrated hydronium ion and triphenylphosphonium (a weak hydrogen-bond former) are also included. In all cases the cation is thought to be bonded to *one* of the anionic halogens. Cation-to-anion hydrogen bonding is strong enough in these examples to be detected when using dipolar aprotic solvents (acetone, acetonitrile, nitromethane) as well as with an aprotic solvent (xylene).

It is noteworthy that bonding of anions to H_3O^+aq was detected in *anion-exchange resins*, as well as in solutions. In view of this finding Ryan believes that hydrogen bonding should be considered a factor in the adsorption of anionic metal complexes as well as in their extraction into alkylamine-containing organic solvents.

As already mentioned, the results just discussed were obtained by spectrophotometry in the *visible and near-infrared*. The absorption curves of the hydrogen-bonded species listed in table 47 showed common similarities as well as distinctive differences from the curves for corresponding *quaternary* ammonium salts. The type of explanation offered for such differences may be illustrated by the case of

Table 46. *Some examples of* $(n\text{-}C_8H_{17})_3N^+{-}D...X^-$ *formation in "wet"* CCl_4, *deduced from shifted* ν(N–D) *frequencies* [a, b]

No.	Anion	No.	Anion	No.	Anion
1	$^*Cl^-$	6	Pi^-, $ThCl_6^{=}$	11	$^*SCN^-$
2	$^*Br^-$	7	$^*CN^-$, $^*I^-$, Ph_4B^-	12	$UO_2Cl_4^{=}$
3	$^*DCl_2^-$	8	ReO_4^-	13	$ZnCl_4^{=}$
4	$^*NO_3^-$	9	DSO_4^-	14	ClO_4^-
5	$CH_3SO_3^-$	10	$Cr_2O_7^{=}$		

[a] The adjective "wet" signifies that the salts were formed during extraction of DX from water into a CCl_4 solution of $(n\text{-}C_8H_{17})_3N$.

[b] The anions are listed in the order of decreasing ability to hydrogen bond to $(C_8H_{17})_3ND^+$, as indicated by the IR shifts. This list is a combination of two sets of results presented in figures by W. E. Keder and L. L. Burger [412]; asterisks indicate anions included in their figure 4, the rest of the list being taken from figure 6.

Reference:

[412] W. E. Keder and L. L. Burger, J. Phys. Chem. **69**, 3075 (1965).

TABLE 47. *Some examples of hydrogen bonding of cations to* $MO_2Cl_4^{=}$ *and* $U(IV)X_6^{=}$ *in an aprotic or dipolar aprotic solvent, deduced by spectrophotometry in the visible and near-infrared (25°)* [a]

Cation	Anion	Solvents	References
n-Oct_3NH^+	$UO_2Cl_4^{=}$	Xylene	[413]
Et_3NH^+	$UO_2Cl_4^{=}$	Acetone, acetonitrile, nitromethane	[413]
$Et_2NH_2^+$	$UO_2Cl_4^{=}$	Nitromethane	[413]
n-$OctNH_3^+$	$UO_2Cl_4^{=}$	Acetone	[413]
H_3O^+aq	$UO_2Cl_4^{=}$	Nitromethane [b]	[413]
$(C_{12}H_{25})_3NH^+$	$NpO_2Cl_4^{=}$	Xylene	[413]
$(C_{12}H_{25})_3NH^+$	$PuO_2Cl_4^{=}$	Xylene	[413]
Et_3NH^+	$PuO_2Cl_4^{=}$	Nitromethane	[413]
R_3NH^+	$UCl_6^{=}$	Acetone, acetonitrile, nitromethane [c]	[414]
$Et_2NH_2^+$	$UCl_6^{=}$	Nitromethane	[414]
n-$OctNH_3^+$	$UCl_6^{=}$	Acetone	[414]
H_3O^+aq	$UCl_6^{=}$	Acetonitrile [b]	[414]
Ph_3PH^+ [d]	$UCl_6^{=}$	Acetone, acetonitrile, nitromethane [c]	[414]
$Et_2NH_2^+$	$CoCl_4^{=}$ [e]	Acetonitrile	[414]
H_3O^+aq	$CoCl_4^{=}$ [e]	Acetonitrile [b]	[414]
Et_3NH^+	$UBr_6^{=}$ [f]	Nitromethane	[414]
$Et_2NH_2^+$	$UBr_6^{=}$ [f]	Nitromethane	[414]

[a] M signifies U(VI), Np(VI), or Pu(VI); $X^- = Cl^-$ or Br^-.

[b] The same, or a closely related, hydrogen-bonded species was detected in anion-exchange resins (examined as mulls).

[c] No specific examples are given, but all three solvents seem to have been used.

[d] A very weak hydrogen bond appears to form.

[e] $CoCl_4^{=}$ appears to be a fairly strong hydrogen bond acceptor.

[f] $UBr_6^{=}$ seems to be a weaker hydrogen bond acceptor than $UCl_6^{=}$.

REFERENCES:

[413] J. L. Ryan, Inorg. Chem. **2**, 348 (1963).
[414] J. L. Ryan, Inorg. Chem. **3**, 211 (1964).

$UCl_6^{=}$: The octahedral symmetry of the "simple" anion, $UCl_6^{=}$, existing in quaternary ammonium salts is destroyed on hydrogen bonding to R_3NH^+, etc., the distortion being sufficient to permit the occurrence of electronic transitions that are forbidden in the simple anion [414].

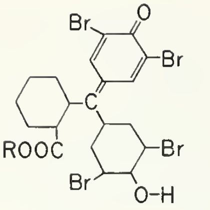
Ryan's studies of substituted ammonium salts containing $UO_2Cl_4^{=}$ as the anion indicated that cation-anion pairs which seem to be hydrogen bonded in aprotic solvents are not necessarily hydrogen bonded in the solid phase [413]. For example, he observed that the spectrum of $(Et_3NH)_2UO_2Cl_4$ as the solid is almost identical with the spectrum of the quaternary ammonium salt $(Pr_4N)_2UO_2Cl_4$. Moreover, in studying the secondary ammonium salt $(Et_2NH_2)_2UO_2Cl_4$, which has two solid phases, he observed that the solid phase which is stable at 25° has an absorption spectrum very similar to that of "simple" $UO_2Cl_4^{=}$, whereas the second solid phase, which is formed rapidly on heating to ~ 100°, has a spectrum somewhat similar to that of the salt in a nitromethane solution (in which it is thought to be hydrogen-bonded—see table 47). Probably geometrical factors sometimes prevent cation-to-anion hydrogen bonding in solid species. (It also seems possible that in some instances multiple hydrogen bonding occurs, leading to a relatively symmetrical anionic structure.)

From results cited in tables 42 and 46 it seems possible that Ph_4B^- is another anion that may hydrogen bond to R_3NH^+ when in an aprotic solvent, although not in crystalline salts.

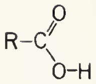
Ryan believes that hydrogen bonding of cations to chloro complex anions probably occurs widely. As expected, $UBr_6^{=}$ appears to be a weaker hydrogen bond acceptor than $UCl_6^{=}$ [414]. Indications of hydrogen bonding to $UO_2(SO_4)_3^{-4}$ and $UO_2(NO_3)_4^{-2}$ were mentioned earlier in this section [389, 411]; in these cases oxygen is the proton-acceptor atom, of course.

d. Further discussion. There seems to be a general harmony in the infrared results with respect to cation-to-anion hydrogen bonding, at least for the systems reported above, irrespective of whether the materials were examined as solids, as "dry" solutions in aprotic solvents, or as "wet" solutions. This is worth emphasizing in view of the still frequent assumption that acid-base behavior is *always* strongly affected by water, even when the latter is present only in trace amounts. As a matter of fact, we concluded earlier (sec. 4.2) that traces of water probably do have a considerable effect on the self-association of carboxylic acids. However, the hydrogen bonds in carboxylic acid dimers and those in hydrogen-bonded ion pairs are different in strength; the latter are often appreciably stronger (see association constants and thermodynamic data in sec. 5) and not easily ruptured through the agency of a comparatively weak hydrogen-bond former such as water.

It also seems desirable to take special note of the striking parallelism in the behavior of the indicator acid bromophthalein magenta (E or B) toward amines, shown in visual tests and spectrophotometry in the visible and near-ultraviolet (sec. 4.3.4*a*), and reactions of acetic acid with amines, as studied by infrared spectroscopy (sec. 4.3.5*b*). Both sets of investigations yielded strong evidence of cation-to-anion hydrogen bonding, as expressed, for example, in structures (XLI) and (LI). The close parallelism in behavior can be understood on noting the similarity of the structures written below for the indicator (XXXVII) and the carboxylic acid (LXVIII). Some years ago Madelung [415], and also Schwarzenbach and associates [416], drew attention to analogies between molecular resonance systems such as the ions of various triphenylmethane dyes and simpler ions like benzoate, carbonate, amidinium, and guanidinium. For example, the anion of benzaurin, $C_6H_5{-}C({=}C_6H_4{=}O)C_6H_4O^-$, is very similar to the benzoate ion except in having a phenyl group in-



(XXXVII)



(LXVIII)

serted between the central carbon atom and each of the oxygens. Obviously, bromophthalein magenta and related dyes, including the sulfonephthaleins, may be regarded as derivatives of benzaurin. (Similar analogies are those between $CO_3^=$ and the anion of aurin, and between cations of well-known triphenylmethane dyes like crystal violet and malachite green and the simpler cations, guanidinium and amidinium.)

The two sets of investigations also showed the readiness of a secondary ammonium ion to form an *additional* hydrogen bond by using its "spare" proton. Frequently this bonding leads to a dimeric structure; for example, compare (XLIII) with (LV). The cation-anion bond appears to be the stronger of the two kinds of hydrogen bond; see (XLIV) and (LVI) and related discussion.

It is evident that the dramatic color changes which bromophthalein magenta undergoes in hydrogen bonding reactions can be used to illustrate general principles. It is a valuable teaching aid in either lecture demonstrations or simple laboratory experiments, but for its fullest exploitation in such a manner, a higher degree of purity is desirable than is generally required in using indicators for end-point determinations.

4.3.6. Nuclear Magnetic Resonance Spectroscopy [412, 417–422]

Applications of this newer technique to studies of hydrogen bonding in ion pairs have given results in substantial agreement with those obtained by other methods.

a. Measurements of crystals. In an early application of NMR spectroscopy both the proton and the fluorine magnetic resonance spectra of powdered ammonium fluoride were measured (140–360 °K) [417]. The data indicate the presence of very *strong* $N^+–H...F^-$ bonds, in agreement with conclusions from infrared [382] and neutron diffraction [383] data.

In the case of NH_4BF_4, also, there is agreement in the results of infrared [384–386, 388] and NMR [418] investigations. It was inferred from the proton and fluorine magnetic resonance spectra (20 and 90 °K) that only "*exceptionally weak*" hydrogen bonding is possible. In the crystal the BF_4^- ion is packed with NH_4^+ in the same manner as with Rb^+, and it is impossible for any one NH_4^+ ion to form four simultaneous linear bonds to fluorine.

b. Studies of solutions.

(1) In a study of the hydrochloride, hydrobromide, and hydroiodide of pyridine in CH_2Cl_2, CH_3CN, and CH_3NO_2 it was concluded that the three salts exist as hydrogen-bonded ion pairs in these solvents [419], in agreement with Cook's conclusions from an infrared investigation of the same salts as solids [423].

(2) Following earlier exploratory studies by Keder and Wilson [420], Keder and Burger [412] completed comparative infrared and proton magnetic resonance (PMR) investigations of hydrogen bonding in "wet" CCl_4 solutions of numerous tri-*n*-octylammonium salts. Some of their IR results (for *deuterium* bonding) have already been summarized (see table 46 and related discussion). Table 48 is a summary of conclusions about *hydrogen* bonding, obtained by the PMR method.

Table 48. *Some examples of* $(n\text{-}C_8H_{17})_3N^+–H...X^-$ *formation in "wet"* CCl_4, *deduced from chemical shifts of* N–H *protons* [a–c]

No.	Anion	No.	Anion	No.	Anion
1	$*Cl^-$	6	Pi^-	12	$*CN^-$
2	$CH_3SO_3^-$	7	$*HCl_2^-$	13	$Cr_2O_7^=$
3	$ThCl_6^=$	8	$*NO_3^-$	14	$UO_2Cl_4^=$
4	Ph_4B^-	9	ReO_4^-	15	$*SCN^-$
5	$*Br^-$	10	HSO_4^-	16	ClO_4^-
		11	$*I^-$	17	$ZnCl_4^=$

[a] The adjective "wet" signifies that the salts were formed during extraction from water into a CCl_4 solution of $(n\text{-}C_8H_{17})_3N$. The probe temperature was ~ 33°.

[b] The anions are listed in the order of decreasing ability to hydrogen bond to $(C_8H_{17})_3NH^+$, as indicated by the chemical shifts. This list is a combination of two sets of results presented in figures by W. E. Keder and L. L. Burger [412]; asterisks indicate anions included in their figure 4, the rest of the list being taken from figure 6.

[c] To compare these NMR results with conclusions from parallel experiments in which shifted ν(N–D) frequencies were determined, see table 46.

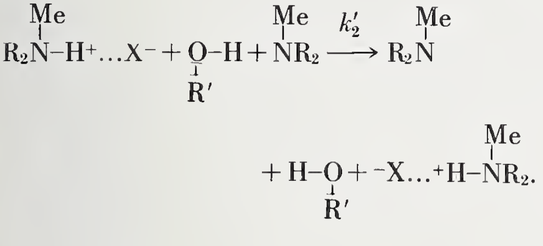
Reference:

[412] W. E. Keder and L. L. Burger, J. Phys. Chem. **69**, 3075 (1965).

Experimental procedures were analogous in the two sets of investigations. It was found that two fairly good linear correlations of N–D stretching frequencies and chemical shifts of N–H protons exist: one for relatively simple anions and another for more complex anions (compare tables 46 and 48, in which the simpler anions are marked with an asterisk). By both methods, Cl^- is the best proton or deuteron acceptor among the anions studied, while ClO_4^- and $ZnCl_4^=$ are the two poorest acceptors.

(3) Experimental results from a PMR investigation of the rates of proton transfer (35°) between nine methyl-substituted ammonium *salts* and their conjugate amines in *t-butyl alcohol* ($\epsilon = 11.4$ at 30°) have been interpreted as evidence of cation-anion hydrogen bonding in this solvent [421, 422].

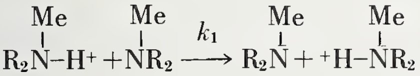
The cations represented were $MeNH_3^+$, $Me_2NH_2^+$, and Me_3NH^+; and the anions (X^-) were $p\text{-}CH_3C_6H_4SO_2O^-$, Br^-, CF_3COO^-, and Cl^-. The solvent is considered to be a participant in the proton transfer reaction, which may be represented by eq. 52 (where R signifies H or Me, and R′ signifies *t*-Bu):



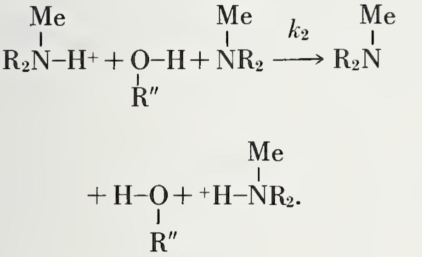
$$R_2\overset{Me}{N}\text{–}H^+\ldots X^- + \underset{R'}{O}\text{–}H + \overset{Me}{N}R_2 \xrightarrow{k_2'} R_2\overset{Me}{N} + H\text{–}\underset{R'}{O} + {}^-X\ldots{}^+H\text{–}\overset{Me}{N}R_2. \qquad (52)$$

It is not known whether more than one molecule of *t*-BuOH is involved in the transfer of a proton from salt to amine.

In analogous earlier experiments with *water* or *methanol* as the solvent, the proton transfer reaction had been found to involve *dissociated ions*, proceeding either by a direct proton transfer, as indicated by eq 53, or by an indirect transfer involving a molecule of solvent, as indicated by eq 54 (where $R'' = H$ or Me):

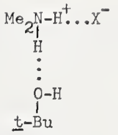


$$R_2\overset{Me}{N}\text{–}H^+ + \overset{Me}{N}R_2 \xrightarrow{k_1} R_2\overset{Me}{N} + {}^+H\text{–}\overset{Me}{N}R_2 \qquad (53)$$



$$R_2\overset{Me}{N}\text{–}H^+ + \underset{R''}{O}\text{–}H + \overset{Me}{N}R_2 \xrightarrow{k_2} R_2\overset{Me}{N} + H\text{–}\underset{R''}{O} + {}^+H\text{–}\overset{Me}{N}R_2. \qquad (54)$$

The reactions proceed much more slowly in *t*-butyl alcohol than in the other two hydroxylic solvents. Moreover, the proton-transfer rates in *t*-BuOH were found to follow second-order kinetics (first order each in the substituted ammonium salt and the corresponding amine), whereas a mechanism involving dissociated cations would require the rate to depend on the square root of the salt concentration. Still further, the rate constants in *t*-BuOH are substantially smaller for the trimethylammonium salts than for the mono- and dimethylammonium salts, and they also vary according to the anion. For such reasons, as well as because of certain features of the NMR spectra, it was concluded that in *t*-BuOH these substituted ammonium salts all exist as *hydrogen-bonded ion pairs*, in which one NH proton is bonded to the anion and any remaining NH protons are bonded to the solvent, as suggested by (LXIX):



(LXIX)

For the trimethylammonium salts, k_2' increases in the following order:

$$Cl^- < CF_3COO^- < Br^- < p\text{-}CH_3C_6H_4SO_2O^-.$$

The NH chemical shift follows a slightly different order for the di- and trimethylammonium salts, increasing in the order:

$$CF_3COO^- < Cl < p\text{-}CH_3C_6H_4SO_2O^-.$$

4.3.7. Concluding Discussion of Hydrogen-Bonded Ion Pairs

It has been thought necessary to place considerable emphasis on cation-anion hydrogen bonding, since the evidence—being scattered and, for the most part, fragmentary—has been widely overlooked. Nevertheless, it is clear that abundant and diverse evidence of cation-anion hydrogen bonding has been accumulated in studies of incompletely substituted ammonium salts, both as solutions in aprotic or dipolar aprotic solvents and as crystalline solids. In some cases the hydrogen bonds are strong enough to persist in moisture-containing aprotic solvents or in a hydroxylic solvent like *tert.* butyl alcohol.

Restating briefly some of the experimental results, we note, for example, that *incompletely substituted* ammonium salts have been found to differ from their *completely substituted* analogs in the following respects: (1) The ion-pair dissociation (eq 32) is much less extensive in solvents like benzene, chlorobenzene, ethylene chloride, or nitrobenzene, although closely comparable in extent in water, alcohols, or a basic solvent such as pyridine (for instance, see table 33). (2) The dipole moments are several Debye units smaller (compare table 36). (3) The tendency toward self-aggregation with increasing concentration in an aprotic solvent, as measured cryoscopically, is substantially less (table 39, fig. 11, and related discussion). (4) Colored salts formed with indicators like BPM–E and HPi are not so "deep" in color (that is, the main absorption bands are shifted to higher frequencies)—see figures 14, 15, and 17. Although the spectrochemical results furnish the most concrete evidence of cation-anion hydrogen bonding in the incompletely substituted salts, the other physicochemical data, especially conductance data, provide strong "circumstantial evidence." Additional direct evidence is supplied by results obtained for incompletely substituted ammonium salts using infrared and proton magnetic resonance spectroscopy. In short, it is overwhelmingly evident that many incompletely substituted ammonium salts and their completely substituted analogs exhibit strongly differentiating chemical and physical behavior in aprotic media, which is satisfactorily explained by the postulate that in the incompletely substituted salts a strong hydrogen bond unites the ammonium nitrogen and the anion. When the anion is polyatomic (for example, the anion of a carboxylic acid or of bromophthalein magenta, nitric acid, sulfuric acid, or a sulfonic acid), the nitrogen is hydrogen bonded to a *specific atom*, most commonly oxygen.

That cation-anion hydrogen bonds are much stronger than bonds of the better-known category $B\ldots H{-}A$ is indicated by values of $-\Delta G$ and $-\Delta H$ for reactions yielding $B{-}H^{+}\ldots A^{-}$. For example, the overall change in enthalpy (*minus* ΔH) in the 1:1 association of diphenylguanidine with benzoic acid or one of the toluic acids in benzene appears to be about 16 kcal/mole (25°, molar units), and for association of diphenylguanidine with three stronger acids (*o*-, *m*-, and *p*-chlorobenzoic acids) the enthalpy change appears to be in the vicinity of 18 to 19 kcal/mole [33]. These results may be contrasted with the values, ranging from about 4 to 7 or 8 kcal/mole, which formerly were regarded as representative for hydrogen bonding reactions [102]. (Thermodynamic constants obtained for other acid-base reactions yielding hydrogen-bonded ion pairs will be included in sec. 5.)

The closely parallel behavior of primary, secondary, and tertiary amines in leveling solvents has led chemists to regard them as varying only in relative strengths, and until quite recently comparative investigations of their acid-base behavior in aprotic media had not been performed. It is now apparent from experimental results cited above that physicochemical behavior in aprotic media sometimes sharply differentiates tertiary ammonium salts from secondary and primary ammonium salts. To provide a brief recapitulation of the evidence, the following examples may be mentioned: (1) Maryott found (see fig. 10 and related discussion) that increasing the mole fraction (N_2) of tributylammonium picrate *in benzene* produces essentially no change in the ratio $\Delta\epsilon/N_2$, signifying that Bu_3NHPi does not form aggregates to a measurable degree in the concentration range investigated. Closely similar results were obtained for solutions of n-$OctNH_3Pi$, n-Bu_2NH_2Pi, and n-Bu_3NHPi *when the solvent was dioxane.* In contrast, $\Delta\epsilon/N_2$ dropped off sharply with increasing values of N_2 in the case of n-Bu_2NH_2Pi *in benzene*, the data being consistent with the postulate of a monomer-dimer equilibrium; the dropping-off was still sharper for solutions of n-$OctNH_3Pi$ in benzene. (2) From the combined results of "dielectrometric titrations" and "cryoscopic titrations" of benzoic acid with amines in benzene, Gur'yanova and Beskina reached analogous conclusions (see table 38 and related discussion). (3) Applying the differential vapor pressure method in titrations of amines with carboxylic acids in benzene, Bruckenstein and Saito reached exactly comparable conclusions (sec. 4.3.3b). (4) In visual and spectrophotometric experiments, using benzene and other aprotic solvents, and with bromophthalein magenta and related phenolsulfonephthalein derivatives as reference acids, Davis and Schuhmann deduced that the tertiary ammonium salts are monomeric, whereas the secondary ammonium salts are dimerized through dual hydrogen bonding of cations to anions; the primary ammonium salts show clear but less well-defined indications of self-association through hydrogen bonding (sec. 4.3.4). (5) Applying infrared spectroscopy in studying the association of acetic acid with triethylamine, diethylamine, and *n*-butylamine in carbon tetrachloride, Barrow and Yerger concluded that salts having two or three protons attached to the ammonium nitrogen are extensively dimerized (sec. 4.3.5).

Experiments with salts having a common cation (R_3NH^+)—notably, Keder and Burger's studies, by IR and NMR spectroscopy, of numerous n-Oct_3NH^+ or n-Oct_3ND^+ salts in "wet" CCl_4 [412]—have shown that anions vary in their ability to become hydrogen bonded to cations (see tables 46 and 48). In 1939 Kilpatrick predicted [424] that this ability would be found to increase with increasing basic strength of the anion, and his prediction has proven to be correct. Hantzsch and co-workers arranged various well-known acids in the order of decreasing strength, as established in several series of semi-quantitative experiments employing static (indicator) or kinetic methods; in part of their work the solvent was chloroform or acetic acid, while other experiments were performed using concentrated aqueous solutions [19, 425, 426]. Three such lists follow:

$$HClO_4 > HI > HBr > RSO_3H > HCl > HNO_3 > CCl_3COOH$$

$$HClO_4 > CCl_3SO_3H > CH_3C_6H_4SO_3H > H_2SO_4 > HNO_3 > CCl_3COOH$$

$$CCl_3COOH > CBr_3COOH > CH_2ClCOOH > CH_2BrCOOH > HCOOH > CH_3COOH.$$

The first two lists indicate differences in the strengths of acids that, at usual concentrations in water, are leveled to the same strength. On comparing the above lists with the extended lists in tables 46 and 48 and the fragmentary lists given elsewhere in the discussion, it becomes evident that, with few exceptions, the relative ability of anions to hydrogen bond to cations parallels ability to combine with protons to form neutral Brønsted acids. For example, the anion of HCl, which is one of the weakest in the group of strong acids, is widely regarded as possessing the ability to become hydrogen bonded to cations, whereas ClO_4^-, the anion of the strongest known Brønsted acid, exhibits little or no ability to become hydrogen bonded to cations.

An understanding of the broad principles governing hydrogen bonding and its influence on acid-base behavior is valuable in many ways. For example, it might be thought that ability of anions to become hydrogen bonded to cations would promote ease of extractability into amine-containing aprotic solvents, but this is evidently not the case. From the series of experiments cited above [412], Keder and Burger concluded that "the most weakly hydrogen-bonded salts are those whose anions extract most strongly. This indicates that anion-cation bonding in the organic phase is of little importance in determination of the relative anion extractability. Rather, it appears that those anions which are the best proton acceptors extract most poorly because of their greater solvation in the aqueous phase. . . ."

Factors determining the proton-acceptance ability of anions are generally well-known—they include charge, size, and polarizability, and possible steric factors must also be borne in mind [4, 427]. Obviously, anions will be better able to become hydrogen bonded to cations when their negative charge is highly localized. The perchlorate ion is noted for its small polarizability [427]. In contrast, the picrate ion is regarded as highly polarizable, with its negative charge probably localized largely on the phenolic oxygen atom; however, its high polarizability is partly offset by the bulkiness of the nitro groups present in the 2- and 6-positions, which impede the close approach of any bulky cation acid [4]. Our survey has shown that carboxylate ions and the anions of bromophthalein magenta and related indicators have a marked propensity for hydrogen bonding to cations. This should be expected, since anions of these chemical types are known to be good proton acceptors.

In section 4.3.5a we cited the conclusion of Sandorfy and associates that tertiary ammonium ions form stronger hydrogen bonds to halide ions than do primary and secondary ammonium ions; this difference is understandable, since Et_3NH^+ can form only one cation-anion hydrogen bond and the cationic charge is highly localized. Davis and Schuhmann [428] explained certain features of absorption curves for mixtures of bromophthalein magenta E with primary amines in benzene along similar lines: that is, as signifying that multiple hydrogen bonding by a single cation leads to individually weaker cation-anion hydrogen bonds. It should again be emphasized that it is likely to prove advantageous to use tertiary amines as reference bases, in preference to primary and secondary amines, when determining comparative acid strengths in aprotic solvents or titrating acids in such media.

4.4. Hydrogen Bonding of Cations to Neutral Proton Acceptors

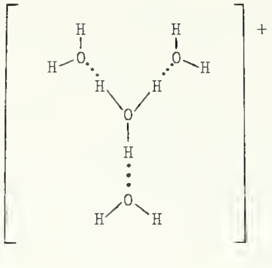
4.4.1. Introduction

Two types of hydrogen bonding remain to be discussed: (a) Hydrogen bonding of *cations* (for example, H_3O^+, Ph_2CH^+, PyH^+, R_3NH^+, R_3N^+OH) *to neutral proton acceptors*, which will be discussed in this section; and (b) hydrogen bonding of *anions* (ArO^-, Cl^-, $RCOO^-$, etc.) *to neutral proton donors*, which will be discussed in section 4.5. Evidence will be presented that many cations of the types mentioned (symbolized by BH^+) can form hydrogen bonds to their conjugate bases (B), giving $B{-}H^+...B$, or to other neutral proton acceptors (B′) of widely varying acceptor ability, yielding $B{-}H^+...B'$. Similarly, anions (symbolized by A^-) can become hydrogen bonded either to their conjugate acids (HA), forming $A^-...H{-}A$, or to other proton donors (HA′), both strong and weak, giving $A^-...H{-}A'$. Such associations are not invariably 1:1, but this is the ratio most commonly encountered

It is often convenient to refer to such complex cations or anions as "*conjugate ions*," a term introduced by Kolthoff [429]. Kolthoff also coined the more specific designations "*homoconjugate*" and "*heteroconjugate*"; these are convenient when one wishes to indicate whether a conjugate ion is homogeneous in composition (that is, $B{-}H^+...B$ or $A^-...H{-}A$) or of heterogeneous composition ($B{-}H^+...B'$ or $A^-...H{-}A'$). Heteroconjugate ions in which B′ or HA′ is a *weak* proton donor and/or acceptor molecule and constitutes *all or part of the solvent* are more familiarly known as "solvated ions." We shall adopt Kolthoff's terminology for the hydrogen-bonded cations and anions about to be discussed, reserving Kraus and Fuoss's expression "triple ions" [326, 328] for *non-hydrogen-bonded* ion aggregates, $M^+X^-M^+$ and $X^-M^+X^-$, formed through electrostatic attractions (see secs. 4.3.1c and 4.3.3a).

4.4.2. Solvated Cations

a. Solvated hydronium ions. It is generally accepted that the proton forms a very stable complex with one molecule of H_2O—namely, the hydronium ion, H_3O^+. Furthermore, on the basis of experimental evidence such as that summarized by Clever [34], the hydronium ion is now believed to exist in most aqueous solutions (all but extremely concentrated solutions) mainly as the trihydrated species indicated below (LXX); this is probably in equilibrium with the mono- and dihydrated species. Recent extraction experiments by Diamond, Tuck, and others [430–435] have contributed additional evidence that H_3O^+ bonds to its conjugate base, H_2O, in the manner indicated by (LXX), and also to other proton acceptors; this is referred to as "primary" ("first-shell") solvation. Further ("secondary") solvation of the primary unit is now believed to occur [430]. An example of secondary solvation will be given presently.



(LXX)

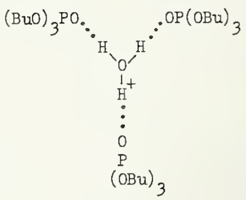
Experiments have demonstrated the feasibility of extracting numerous *mineral acids* (for example, $HClO_4$, H_2SO_4, HNO_3, hydrogen halides) and *complex metal acids* ($HFeCl_4$, $HAuCl_4$, $HInBr_4$, and others) into basic organic solvents. From this list Diamond and coworkers selected $HClO_4$ (often with tracer $HReO_4$) for most experiments where the main objective was to determine the composition of solvated hydronium ions present in the organic layer after extraction procedures. They recognized that the anions of these acids—which, as we have just seen, do not bond readily to protons or proton donors—were not likely to transport enough water into the organic layer to confuse the experimental results. Other acids used were HBr, $HAuCl_4$, and $HAuBr_4$. At first, several basic organic solvents were used as extractants—for example, ethers, ketones, and esters (notably Bu_3PO_4) [430, 431]—but in later work the organic extractant consisted of an aprotic solvent (carbon tetrachloride, isooctane, or xylene) containing tributyl phosphate [432–434] or trioctylphosphine oxide [434, 435]. The compositions of extracted cations were determined by such means as measuring volume changes, acid-base and Karl Fischer titrations, and ascertaining the water content of the organic layer by IR spectroscopy.

As expected, the compositions deduced for extracted species were found to depend on such variables as the strengths and relative proportions of competing proton donors and acceptors, and also on the steric availability of the acceptor atom. For example, in the extraction of $HClO_4$ into dilute (< 0.1 *M*) Bu_3PO_4 in CCl_4, the nature of extracted species was found to depend on the stoichiometric ratio Bu_3PO_4/H^+: When this exceeds 3, the only two species thought to be extracted into the organic layer are $Bu_3PO_4 \cdot H_2O$ and ion pairs in which the cation composition is $3Bu_3PO_4 \cdot H_3O^+ \cdot yH_2O$, y having a value between 0 and 1. However, when Bu_3PO_4/H^+ exceeds 1 but is less than 3, several solvated species may be present in the organic layer. When the aqueous acid is very concentrated (~ 10 *M*), no water is extracted into the organic layer, and the extracted species is then believed to be (LXXI) [432]:

$$Bu_3PO_4H^+ClO_4^-$$

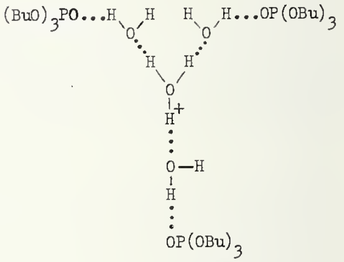
(LXXI)

Structures considered reasonable for two types of solvated hydronium ions are given below (LXXII, LXXIII):



(LXXII)

(Primary solvation of hydronium ion)



(LXXIII)

(Note both primary and secondary solvation)

In (LXXII), each hydronium proton is bonded directly to a phosphate oxygen, while in (LXXIII), three H_2O molecules act as intermediate bridges. Structure (LXXI) is an ion pair with perhaps a weak cation-anion hydrogen bond.

Analogous structures were inferred for the products resulting from extractions of perrhenic acid (containing radioactive ReO_4^-) [432] and HBr [433] into a Bu_3PO_4-containing aprotic solvent, as well as from extractions of $HClO_4$ [435], $HReO_4$ [435], $HAuCl_4$ [434], and $HAuBr_4$ [434] (the latter three acids being used in tracer amounts) into an aprotic solvent containing Oct_3PO.

The following are some of the principal over-all conclusions of the authors cited, with respect to extractions of acids from aqueous solutions into organic media of the types mentioned [433–435]: (1) When the acid is strong and only moderately concentrated, the proton is extracted as H_3O^+ and becomes trisolvated in the organic layer. (2) The extent of hydration of H_3O^+ in the organic phase depends on the strength and concentration of the base (B). (3) The cation composition $H_3O^+ \cdot 3B \cdot yH_2O$ ($0 \leq y \leq 3$) should be found for any strong acid. (4) Oct_3PO, being a stronger base than Bu_3PO_4, can be expected to compete better with H_2O for the hydronium ion, and is more likely to form the primary solvent layer, as in (LXXII). (5) If the anion is large and very weakly basic, it enters, and remains in, the organic layer as an ion, being "essentially ejected from the aqueous . . . phase because of its disturbance of the hydrogen-bonded water structure". The more hydrophobic, feebly basic, and bulky the anion, the more easily is it ejected into the organic layer [434]. (6) In aprotic organic solvents the anions pair with solvated cations. (Ion pairing does not occur, of course, in organic extractants of high dielectric constant.) (7) Extraction of $HClO_4$ from concentrated aqueous solutions into a carbon tetrachloride solution of Oct_3PO yields $Oct_3POH^+ ... ClO_4^-$ [compare (LXXI)] and perhaps also a hydrate such as (LXXIV):

$$Oct_3POH^+ ... OH_2 ... ClO_4^-$$

(LXXIV)

(8) If the extracted anion (e.g., NO_3^-, CCl_3COO^-, CH_3COO^-) is moderately basic, it will compete for the proton with water and the extractant, and if successful, will form the *molecular acid* (HA), which can form only one hydrogen bond to the base B. The anion will then appear in the organic layer as monosolvated HA—for example, $Bu_3PO_4 \cdot HOCOCCl_3$, $Bu_3 PO_4 \cdot HONO_2$, $Oct_3PO \cdot HONO_2$.

Such extractions provide excellent examples of practical situations in which the outcome depends on which among various competing hydrogen bonding reactions are allowed to become dominant.

Brief mention should be made of Diamond's discussion of the extractability of uni-univalent salts in which *both the cation* (for example, a quaternary ammonium or phosphonium ion) *and the anion* (such as a homolog of CH_3COO^-) are large and hydrophobic (or at most poorly hydrated) [436]. In such instances ion pairing occurs in water, and the ion pairs tend to be ejected completely from water. Their extractability into aprotic solvents is correspondingly facilitated, to an extent increasing with their bulkiness and hydrophobicity. Such ion pairing is not considered to result from electrostatic attraction or to involve solvation, but is attributed principally to attempts of water to preserve its hydrogen-bonded structure, and it has been christened "*water structure-enforced ion pairing.*"

Mention should also be made of Douglas and McDaniel's brief review [437] of probable hydration of H_3O^+ in solid acid hydrates, including $H_2SnCl_6 \cdot 8H_2O$, the tri- and tetrahydrates of $HAuCl_4$, and hydrates of HBr and HCl.

b. Miscellaneous solvated cations. Solvation of incompletely substituted ammonium ions and related cations, regarded for a long time as the probable cause of various chemical and physical phenomena, is very plausibly accounted for in terms of hydrogen bonding. A number of examples of cation solvation have already been mentioned. For instance, we mentioned earlier (sec. 4.3.1a) Walden and Birr's discovery that the mobilities of Me_4N^+, $Et_2NH_2^+$, and n-$BuNH_3^+$, although very similar in acetonitrile, are very different in water, decreasing in the order named [324]. These authors concluded that decreasing mobilities in water probably correspond to increasing degrees of solvation, the closely similar mobilities in acetonitrile indicating lack of solvation. Later studies by others have added support to these conclusions as it has become increasingly evident that MeCN is a much poorer proton acceptor than water [438, 71].

Using similar reasoning, Trotman-Dickenson offered a plausible explanation of anomalies in the relative basicities of ammonia and primary, secondary, and tertiary amines in certain solvents [439, 440]. For example, the relative strengths of NH_3, $MeNH_2$, Me_2NH, and Me_3N in water, when expressed as the pK_a values of the corresponding conjugate acids, are, respectively, 9.24, 10.62, 10.77, and 9.80. If the relative strengths in water varied strictly in accordance with the predicted inductive effect of alkyl substitutions, Me_3N would, of course, have the highest pK_a value; instead, this base appears to be weaker in water than the other two methylamines. Trotman-Dickenson believes that such anomalies are caused mainly by differences in the extent of stabilization of the various cations by hydration, which obviously will depend on the number of protons available for bonding to H_2O. This explanation, which has won general acceptance, has been substantiated by later findings that mono-, di-, and tri-n-butylamine increase progressively in basicity—in accord with prediction—when the basic strength is determined (by an indicator method) in aprotic solvents like chlorobenzene, bromobenzene, or fluorobenzene [354, 365, 441].

Turning to other types of physicochemical measurements, it is appropriate to recall four investigations, reviewed above in more detail, in which patterns of acid-base behavior observed when using an aprotic or dipolar aprotic solvent (or no solvent) were found to be modified by adding or substituting a hydrogen bond-forming solvent: (1) Experiments of Witschonke and Kraus (see table 35), in which the conductance of certain incompletely substituted ammonium salts in nitrobenzene increased on the addition of a basic solvent (water, pyridine, piperidine, or triethylamine), the increase being proportionate to the basicity and concentration of the added solvent; (2) Maryott's dielectric polarization experiments (see fig. 10), in which $OctNH_3Pi$, Bu_2NH_2Pi, and Bu_3NHPi exhibited differentiating behavior in benzene ($\epsilon = 2.27$) but essentially uniform behavior in dioxane ($\epsilon = 2.21$); (3) visual and spectrophotometric investigations of bromophthalein magenta and its salts in varied organic solvents, by Davis and co-workers (sec. 4.3.4a); (4) Chenon and Sandorfy's infrared investigations [375], which led them to conclude that amine hydrohalides form $N^+–H ... X^-$ bonds in the solid state, but $N^+–H ... O$ bonds when in aqueous solutions (see sec. 4.3.5a). In each of these investigations, the effects of addition of, or replacement by, a basic solvent were attributed to hydrogen bonding of cations to the basic solvent in question.

The examples just cited have all involved n-electron donors. Evidence of cation solvation by π-

electron donors, obtained in systematic extraction experiments by Bucher and Diamond [442], should also be reviewed briefly. In the experiments referred to ~ 0.2 *M* $HClO_4$ (containing radioactive $HReO_4$ as tracer) was extracted from water into various organic diluents containing trilaurylamine (~ 0.1 *M*), the principal objective being to determine the role played by the diluent. Experimental techniques included preparation of radioisotopic Re and subsequent γ-counting, forward and back extractions, acid-base and Karl Fischer titrations, freezing point measurements, and vapor pressure measurements. Table 49 lists most of the diluents used and their dielectric constants, and also indicates their comparative effectiveness in promoting the extraction of $HClO_4$. The measure of effectiveness is the value of K_1 (given here as its logarithm) for the extraction corresponding to eq 50 (sec. 4.3.5c), where $R = C_{12}H_{25}$ and $X^- = ClO_4^-$.

TABLE 49. *Comparison of dielectric constants and effectiveness of diluents used in extracting* $HClO_4$ *from water* [a, b]

Diluent	ϵ [c]	Log K_1(22°)
Triethylbenzene	2.26	4.38
Trimethylbenzene	2.28	4.52
Benzene	2.28	6.57
Tetrachloroethylene	2.30	4.52
Anisole	4.33	8.08
Chlorobenzene	5.62	7.62
o-Dichlorobenzene	9.93	8.18

[a] This is a slightly revised version of Table VI of J. J. Bucher and R. M. Diamond, J. Phys. Chem. **69**, 1565 (1965).

[b] Relative effectiveness is indicated by the magnitude of K_1, the equilibrium constant for the following reaction (compare eq 50):

$$(C_{12}H_{25})_3N_{org} + H^+_{aq} + ClO^-_{4\,aq} \rightleftharpoons (C_{12}H_{25})_3NH^+ \cdot ClO^-_{4\,org}.$$

"Aq" and "org" signify the aqueous and organic phases, respectively.

[c] As given in the reference cited.

REFERENCE:

[442] J. J. Bucher and R. M. Diamond, J. Phys. Chem. **69**, 1565 (1965).

The following are some of the conclusions reached by Bucher and Diamond (by reasoning that will not be restated here):

(1) Benzene solvates $(C_{12}H_{25})_3NH^+$ by interaction of its π-electrons with the cationic proton, rendering it more stable in the organic phase.

(2) *sym.*-Trimethylbenzene (mesitylene) and *sym.*-triethylbenzene interact similarly, but the extent of interaction, as expected, is reduced by steric blocking by the substituent alkyl groups.

(3) Tetrachloroethylene, which has a single pair of π-electrons that are somewhat shielded by the adjacent chlorine atoms, has an overall effectiveness very similar to that of triethylbenzene.

(4) Anisole is a more effective diluent on account of being an n-electron donor as well as a π-electron donor.

(5) The relatively high effectiveness of chlorobenzene and *o*-dichlorobenzene stems from their higher dielectric constants, which lead to "electrostatic solvation" of the ions—not to any specific chemical interaction with them.

A few other examples of cation "solvation" will be encountered in the discussion of heteroconjugate cations (sec. 4.4.5; see table 53).

4.4.3. Homoconjugate Cations

a. Studies using aprotic or dipolar aprotic solvents. Homoconjugate cation formation has been studied in *acetonitrile* [444–446], *benzene* [5, 21], *o-dichlorobenzene* [448, 449], and *nitrobenzene* [24, 443, 447]. The evidence was obtained by three types of measurement: (1) Absorption spectrophotometry in the visible region [5, 21]; (2) conductance [24, 444, 448, 449]; and (3) potentiometry [445–447]. Miscellaneous examples are listed in table 50. Results of a comprehensive study of homoconjugate cation formation are summarized in table 51.

Homoconjugate cation formation was postulated by Davis and Hetzer to account for color phenomena observed in spectrophotometric studies of the association of bromophthalein magenta E (usually $2.5 \times 10^{-5} M$) with 1,3-diphenylguanidine [5] and with 1,3-di-*o*-tolylguanidine [21] in *benzene*. On gradually increasing the concentration of the base they observed a rapid shift in color from the yellow of the indicator to the magenta of its 1:1 salt, followed by a slower shift toward blue. The absorbance data were consistent with the assumption of two slightly overlapping reactions:

(1) Association of the base (B) and acid (HA) in 1:1 ratio, yielding hydrogen-bonded ion pairs (eq 44); and

(2) reaction of BHA with a second molecule of base (eq 55):

$$B + H{-}A \rightleftharpoons B{-}H^+ \ldots A^- \qquad (44)$$

$$B{-}H^+ \ldots A^- + B \rightleftharpoons (B{-}H^+ \ldots B)A^-. \qquad (55)$$

1,2,3-Triphenylguanidine showed similar behavior [5] except that the "*primary*" (eq 44) and "*secondary*" (eq 55) reactions seemed to overlap more. It was thought that still other competing associations occur at high concentrations, but these were not studied.

When 1,3-diphenylguanidine,

PhNH–C(=NH)NHPh,

was the reacting base the equilibrium constant (K_{BHA}) corresponding to eq 44 was found to be 2.2×10^5 (liter mole^{-1}, 25°). Replacing one *ortho* hydrogen in each phenyl group by *methyl* would be expected to increase the basicity of the molecule, whereas placing a *phenyl* group on the 2-nitrogen should reduce the basicity. In agreement with expectations, K_{BHA} increased to 1.1×10^6 when diphenylguanidine was replaced by di-*o*-tolylguanidine, but dropped to 525 when it was replaced by 1,2,3-triphenylguanidine.

TABLE 50. *Examples of homoconjugate cations* ($B–H^+ ... B$)

Base	Solvent	Anion	Method of study[a]	Estimated formation constants	References
$(PhNH)_2C=NH$	C_6H_6	$(BPM–E)^-$[b]	VIS	[c] 15.5	[5]
	CH_3CN	CH_2CN^-	C	[d] 20	[444]
	CH_3CN	ClO_4^-	EMF	None	[446]
$(PhNH)_2C=NPh$	C_6H_6	$(BPM–E)^-$[b]	VIS	[c] ~ 22	[5]
$(o\text{-}MeC_6H_4NH)_2C=NH$	C_6H_6	$(BPM–E)^-$[b]	VIS	[c] 6.4	[21]
Py	$PhNO_2$	Pi^-	C	[d, e] 56	[24, 443]
	$o\text{-}C_6H_4Cl_2$	Pi^-	C	[c] $<<1$	[448]
	$o\text{-}C_6H_4Cl_2$	Pi^-	C	[d] 19,000	[448]
	CH_3CN	ClO_4^-	EMF	[d] 4	[445, 446]
$MeNH_2$; $EtNH_2$	$PhNO_2$[f]	ClO_4^-	EMF[g]	[d, h] 10^3-10^4	[447]
$i\text{-}PrNH_2$	$PhNO_2$[f]	ClO_4^-	EMF[g]	[d, h] 10^3-10^4	[447]
Me_2NH; Et_2NH	$PhNO_2$[f]	ClO_4^-	EMF[g]	[d, h] 10^3-10^4	[447]
Me_3N, Et_3N	$PhNO_2$[f]	ClO_4^-	EMF[g]	[d, h] 10^3-10^4	[447]
Bu_3N	$o\text{-}C_6H_4Cl_2$	Br^-	C	....	[448]
	$o\text{-}C_6H_4Cl_2$	Pi^-	C	[c] 25	[448]
	$o\text{-}C_6H_4Cl_2$	Pi^-	C	[d] 560	[448]
Bu_3NO	$o\text{-}C_6H_4Cl_2$	Pi^-	C	[d] 1.9×10^7	[449]

[a] Meaning of symbols: C, conductance; EMF, potentiometry; VIS, absorbance in the visible region.

[b] $(BPM–E)^-$ signifies the anion of bromophthalein magenta E.

[c] *This* formation constant is for the reaction $B–H^+ ... A^- + B \rightleftharpoons (B–H^+ ... B)A^-$; molar units, 25°.

[d] *This* formation constant corresponds to $BH^+ + B \rightleftharpoons BH^+ ... B$ (apparently molar units; 25° unless indicated otherwise).

[e] Calculated by Kolthoff [443], using results of Witschonke and Kraus [24].

[f] Traces of CH_3COOH and $(CH_3CO)_2O$ were present.

[g] The base, usually 0.001 *M*, was titrated with ~ 0.034 *M* HCl.

[h] Experiments were done at ~ 20°. Aliphatic amines seemed to react slowly with $PhNO_2$.

REFERENCES:

[5] M. M. Davis and H. B. Hetzer, J. Res. NBS **46,** 496 (1951).
[21] M. M. Davis and H. B. Hetzer, J. Res. NBS **48,** 381 (1952).
[24] C. R. Witschonke and C. A. Kraus, J. Am. Chem. Soc. **69,** 2472 (1947).
[443] I. M. Kolthoff, D. Stŏcesocá, and T. S. Lee, J. Am. Chem. Soc. **75,** 1834 (1953).
[444] W. S. Muney and J. F. Coetzee, J. Phys. Chem. **66,** 89 (1962).
[445] J. F. Coetzee, G. R. Padmanabhan, and G. P. Cunningham, Talanta **11,** 93 (1964).
[446] J. F. Coetzee and G. R. Padmanabhan, J. Am. Chem. Soc. **87,** 5005 (1964).
[447] D. Feakins, W. A. Last, and R. A. Shaw, J. Chem. Soc., p. 2387 (1964).
[448] E. K. Ralph, III, and W. R. Gilkerson, J. Am. Chem. Soc. **86,** 4783 (1964).
[449] W. R. Gilkerson and E. K. Ralph, III, J. Am. Chem. Soc. **87,** 175 (1965).

A large value for K_{BHA} is indicative of a strong interaction of B and HA. Hence, the "secondary" equilibrium constants might be expected to vary in the opposite sense (in the absence of strong steric effects). This appears to be a correct prediction, since the respective secondary equilibrium constants found for 1,3-di-*o*-tolylguanidine, 1,3-diphenylguanidine, and 1,2,3-triphenylguanidine are 6.4, 15.5, and ~ 22.

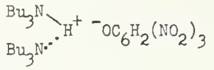
Probably the first concrete evidence of homoconjugate cation formation was obtained by Witschonke and Kraus [24]. In an investigation already referred to (for example, see table 35 and related discussion) they found that the conductance of pyridinium picrate in *nitrobenzene* can be augmented by adding surplus pyridine, although a similar increase in conductance does not occur on adding pyridine to a quaternary ammonium picrate (for example, Me_4NPi). Subsequently, Kolthoff and coworkers [443] used data of Witschonke and Kraus to calculate the equilibrium constant corresponding to eq 56:

$$BH^+ + B \rightleftharpoons BH^+ ... B. \qquad (56)$$

The value which they obtained is 56. In a still later calculation, Ralph and Gilkerson [448] obtained a slightly different value (58).

Gilkerson and Ralph have performed investigations paralleling those of Witschonke and Kraus, but with *o-dichlorobenzene* as the solvent and Py, *n*-Bu_3N, and *n*-Bu_3NO as the bases. In all cases, adding an excess of base to the picrate brought about increased conductivity. They consider this to be best explained by Witschonke and Kraus's hypothesis of hydrogen bonding of BH^+ to B [448, 449].

Gilkerson and Ralph have suggested (LXXV) as a reasonable structure for $(Bu_3N)_2HPi$:



(LXXV)

The plane of the benzene ring in Pi^- is considered to be perpendicular to the N–H...H plane, and at least one butyl group on each molecule of amine is believed to lack rotational freedom. Such a model, they think, permits almost as close approach of cation and anion as in $Bu_3NH^+ \ldots {}^-OC_6H_2(NO_2)_3$.

The remaining examples listed in table 50 were deduced in potentiometric investigations, mainly by Feakins and coworkers [447]. In their work the solvent was *nitrobenzene.* When aliphatic amines were titrated with perchloric acid, inflections appeared in the titration curves near the half-point. The only reasonable explanation was BHB^+ formation. Homoconjugate cation formation was inferred for $MeNH_2$, $EtNH_2$, *i*-$PrNH_2$, Me_2NH, Et_2NH, Me_3N and Et_3N, but was not detected for diphenylguanidine, piperidine, *N*-methylmorpholine, di-*N*-ethylaniline, or *p*-toluidine. Because of its mode of preparation the perchloric acid solution contained traces of acetic acid and its anhydride. It should also be mentioned that the aliphatic amines appeared to react slowly with the solvent. Feakins and associates concluded that the amines listed form fairly stable homoconjugate cations in nitrobenzene, the estimated formation constant (eq 56) in each case being about 10^3 to 10^4. In their opinion, a conjugate cation as unstable as PyH^+Py would not be detected in such experiments.

In comparing the formation constants listed in column 5 of table 50, it should be borne in mind that some of these constants correspond to eq 55, and others to eq 56. Moreover, all of the experiments were exploratory in nature, and in some cases several competing equilibria had to be taken into account and simplifying assumptions had to be made. We have already drawn some tentative conclusions with respect to the comparative behavior of the three guanidine derivatives. Assuming the other constants in table 50 to be approximately correct, some additional tentative conclusions may be drawn:

(1) $PyH^+ \ldots Py$ is much more stable in *o*-dichlorobenzene than in nitrobenzene.

(2) It is more stable than $Bu_3NH^+ \ldots NBu_3$ in this solvent, but less stable than $Bu_3NOH^+ \ldots ONBu_3$.

(3) $(Bu_3NH^+NBu_3)Pi^-$ appears to form more extensively in *o*-dichlorobenzene than does $(PyH^+Py)Pi^-$ (see eq 55). (NOTE: In reporting the equilibrium constant for the reaction of $PyH^+ \ldots Pi^-$ with Py as being $\ll 1$, we made an approximation; the actual conclusion of Ralph and Gilkerson was that this equilibrium constant *multiplied by* [Py] is $\ll 1$, Py_2H^+ being the only complex formed to a significant extent in this system [448].)

By far the most comprehensive study of homoconjugate cation formation to date is a potentiometric investigation by Coetzee and Padmanabhan, using *acetonitrile* as the solvent [445, 446], which supplemented a conductimetric study by Muney and Coetzee [444]. The solutions contained varying amounts of free base together with a fixed concentration of its perchlorate or picrate. A wide assortment of amines was included, so as to determine how their tendencies toward homoconjugation vary with such factors as basic strength, steric hindrance, and the number of cationic protons available for hydrogen bonding. 1,3-Diphenylguanidine and pyridine were also included, as well as some diamines. Results obtained with monoamines are summarized in table 51. The next to last column in table 51 contains values determined for K_{BH^+B} (eq 56), and the last column contains values for $K_{BH^+B_2}$ (eq 57).

$$BH^+ \ldots B + B \rightleftharpoons BH^+ \ldots B_2. \qquad (57)$$

Formation of $BH^+ \ldots B_2$ is expected only when at least two cationic protons are available for hydrogen bonding to B.

The results given in table 51 clearly fulfill expectations. To begin with, the K_{BH^+B} values for aliphatic amines indicate a marked tendency for 1:1 bonding to their conjugate acids. In contrast, pyridine, a much weaker base, exhibits less tendency toward homoconjugation, and the still weaker bases, aniline and *p*-toluidine, none at all.

Secondly, it is apparent that homoconjugation is impeded when bulky groups are attached to amine nitrogen. Of the tertiary aliphatic amines studied, only Me_3N showed a measurable tendency toward homoconjugation. Homoconjugation of secondary aliphatic amines, also, is impeded noticeably by substituents larger than Me, except for cyclic amines (such as pyrrolidine, piperidine, and morpholine), where the substituent groups are "tied back," leaving the amino nitrogen relatively exposed. A cyclic *tertiary diamine*, triethylenediamine, was observed to form a 1:1 complex. (It would be interesting to study the behavior of the cyclic tertiary *monoamine*, quinuclidine.) The authors calculated [445] that a K_{BH^+B} value near 30 (which seems typical for unhindered aliphatic amines) corresponds to $\Delta G = -2$ kcal/mole.

As for diphenylguanidine, although it can bond 1:1 to its conjugate acid in benzene containing bromophthalein magenta E (table 50), as well as in acetonitrile without added acid (table 51), no K_{BH^+B} value was obtained in the potentiometric studies.

TABLE 51. *Approximate formation constants (25°) of some homoconjugate cations in acetonitrile* [a]

Base	pK_a in water	Anion	K_{BH^+B} [b]	$K_{BH^+B_2}$ [b]
NH_3	9.21	ClO_4^-	11	2
$MeNH_2$	10.62	ClO_4^-	35	2
$EtNH_2$	10.63	ClO_4^-	25	2
n-$PrNH_2$	10.53	ClO_4^-	19	2
n-$BuNH_2$	10.59	ClO_4^-	26	2.5
t-$BuNH_2$	10.45	Pi^-	20	1
$PhCH_2NH_2$	9.34	Pi^-	15	....
$HOCH_2CH_2NH_2$	9.50	Pi^-	24	1.5
$PhNH_2$	4.58	ClO_4^-; Pi^-	None	....
p-$MeC_6H_4NH_2$	5.07	ClO_4^-	None	....
Me_2NH	10.64	ClO_4^-	31	0.5
Et_2NH	10.98	ClO_4^-	3	....
Et_2NH	10.98	Pi^-	1	....
n-Bu_2NH	11.25	ClO_4^-: Pi^-	None	....
i-Bu_2NH	10.50	Pi^-	None	....
$NH(CH_2)_3CH_2$	11.27	Pi^-	32	2
$NH(CH_2)_4CH_2$	11.22	Pi^-	26	....
$NH(CH_2)_2OCH_2CH_2$	8.36	Pi^-	10	....
Me_3N	9.76	ClO_4^-	6	....
Et_3N	10.65	Pi^-	None	....
n-Pr_3N	10.65	ClO_4^-	None	....
n-Bu_3N	10.89	ClO_4^-: Pi^-	None	....
i-Am_3N	....	Pi^-	None	....
$(PhNH)_2C=NH$	10.00	ClO_4^-	None	....
$(PhNH)_2C=NH$	10.00	CH_2CN^-	[c] 20	....
Py	5.17	ClO_4^-	4	....

[a] Formation constants (K_{BH+B}, K_{BH+B_2}) were determined by glass-electrode measurements in buffer solutions consisting of a constant concentration (5×10^{-4} *M*) of the perchlorate or picrate of the base and varying concentrations of free base (usually up to 0.1 *M* or higher). This table is an abridged and rearranged version of Table I of J. F. Coetzee and G. R. Padmanabhan, J. Am. Chem. Soc. **87**, 5005 (1965). (Also see J. F. Coetzee, G. R. Padmanabhan, and G. P. Cunningham, Talanta **11**, 93 (1964).)

[b] $K_{BH+B} = [BHB^+]/[B][BH^+]$; $K_{BH+B_2} = [BH^+B_2]/[B][BHB^+]$.

[c] Obtained in a conductometric study of diphenylguanidine in acetonitrile, by W. S. Muney and J. F. Coetzee, J. Phys. Chem. **66**, 89 (1962), which indicated that at concentrations of the base $> \sim 0.05$ *M* the predominant ionization reaction is representable as: $2B + CH_3CN \rightleftharpoons BH^+B + CH_2CN^-$.

REFERENCES:

[444] W. S. Muney and J. F. Coetzee, J. Phys. Chem. **66**, 89 (1962).

[445] J. F. Coetzee, G. R. Padmanabhan, and G. P. Cunningham, Talanta **11**, 93 (1964).

[446] J. F. Coetzee and G. R. Padmanabhan, J. Am. Chem. Soc. **87**, 5005 (1965).

Thirdly, values of $K_{BH^+B_2}$ could be determined for most of the primary aliphatic amines. As expected, they are smaller than values for K_{BH^+B}. Only two secondary aliphatic amines, dimethylamine and pyrrolidine, reacted measurably according to eq 57. Piperidine formed only BH^+B [445]. With hydrazine, however, there was evidence of BH^+B_4 formation.

Coetzee and associates emphasized the significance of homoconjugation of bases in potentiometric and conductimetric titrations, as well as in studies of the relative strengths of bases [444–446].

They also emphasized that MeCN itself, although a much weaker base than H_2O, appears to solvate ammonium ions to a significant extent. We shall see presently (sec. 4.4.4) that others have reached the same conclusion.

b. Studies of solid salts of N-oxides. A number of recent studies have been concerned with homoconjugation of bases in their solid salts. Interest in this topic began with work by Hadži [390, 450], who measured the IR spectrum of solid $(PicO)_2HBr$ (where PicO signifies 2-picoline 1-oxide). On finding a resemblance to the spectra of potassium acid maleate and certain other acid salts having *homoconjugate anions* $(A\ldots H\ldots A)^-$, believed to contain a *symmetrical* hydrogen bond (see sec. 4.5.3a), he suggested that the similarity can be explained by postulating the presence of a *symmetrical homoconjugate cation* in $(PicO)_2HBr$, as indicated by (LXXVI):

$$(PicO\ldots H\ldots OPic)^+\ Br^-$$

(LXXVI)

Inspired by Hadži's discovery, several other investigators have measured the IR spectra of salts of PicO with other monoprotic acids, as well as various salts of related *N*-oxides. Examples of such salts are listed in table 52.

In the course of these studies, various *N*-oxides (for instance, 2-, 3-, and 4-picoline 1-oxides, acridine 1-oxide) have been found to form two series of salts with monoprotic acids: (1) A "*normal*" series, containing 1 equivalent of base to 1 of acid; and (2) an "*abnormal*" series, containing 2 equivalents of base to 1 of acid. In most *normal* salts of *N*-oxides the cation $(BO\ldots H)^+$ is thought to be hydrogen bonded to the anion, since the $\nu(OH)$ frequencies have been found to vary with the proton affinity of the anion (compare 4.3.5a). For example, Szafran reported [454] that in *normal* salts of acridine 1-oxide with HCl, HBr, HI, and $HClO_4$ the $\nu(OH)$ band shifts increasingly toward lower frequencies with increasing basicity of the anion—that is, the $\nu(OH)$ shifts follow the order

$$Cl^- > Br^- > I^- > ClO_4^-.$$

In contrast, the $\nu(OH)$ band does not appear in the customary position (3700–1700 cm^{-1}) in the spectrum of *abnormal* salts, and all IR spectra are

TABLE 52. *Examples of normal and abnormal salts of pyridine 1-oxide and related N-oxides* [a, b]

Base	Normal salts		Abnormal salts	
	Acid	References	Acid	References
Pyridine 1-oxide	HCl	[390]	$HAsF_6$	[451]
	HBr	[390]	$HSbF_6$	[451]
	HNO_3	[450]		
	CCl_3COOH	[390]		
2-Picoline 1-oxide	HCl	[390]	HBr[c]	[390, 452]
			$HAsF_6$[d]	[451]
			$HClO_4$[d]	[453]
			HPF_6	[451]
2,6-Lutidine 1-oxide	HCl	[453]	HI	[453]
	HBr	[453]	$HClO_4$	[453]
			$HSbCl_6$	[453]
Isoquinoline 1-oxide	HCl	[453]	HBr[e]	[453]
	HBr	[453]	$HClO_4$	[453]
			$HSbCl_6$	[453]
2-Quinaldine 1-oxide	HCl	[453]	HBr	[453]
	HBr	[453]	HI	[453]
	HI	[453]	$HClO_4$	[453]
	CCl_3COOH[f]	[454]	$HSbCl_6$	[453]
Acridine 1-oxide	HCl	[454]	HBr	[454]
	HBr	[454]	HI	[454]
	HI	[454]	$HClO_4$	[454]
Acridine 1-oxide	$HClO_4$	[454]	HBF_4	[454]
	CCl_3COOH[f]	[454]	$HSbCl_6$	[454]
2,2′-Bipyridine 1,1′-Dioxide[g]	....	[455]	HCl	[455]
			HBr	[455]
			$HClO_4$	[455]
			$HSbCl_6$	[455]

[a] Examined as solids, by IR spectroscopy except as indicated otherwise. In some cases deuterium analogs were also studied.

[b] *Normal* salts are defined [453] as those containing 1 equivalent of base to 1 equivalent of a monoprotic acid, while *abnormal* salts are those containing 2 equivalents of base to 1 of acid.

[c] X-ray results [452] support the conclusions from IR data [390].

[d] The corresponding salts of 3- and 4-picoline 1-oxide were also studied.

[e] Isolated as the monohydrate.

[f] This salt has an IR spectrum resembling that of abnormal salts, and is thought to have the structure $(BO\ldots H\ldots OB)^+(A\ldots H\ldots A)^-$.

[g] Even though 2,2′-bipyridine 1,1′-dioxide contains *two* basic groups, all of the salts isolated contained *only one* equivalent of acid.

REFERENCES:

[390] D. Hadži, J. Chem. Soc., p. 5128 (1962).
[450] D. Hadži, Boll. Sci. Fac. Chim. Ind. Bologna **21,** 23 (1963).
[451] D. Cook, Chem. Ind. (London), p. 607 (1963).
[452] H. H. Mills and J. C. Speakman, Proc. Chem. Soc., p. 216 (1963).
[453] M. Szafran, Bull. Acad. Polon. Sci. Ser. Sci. Chim. **11,** 111, 169, 497, 503 (1963).
[454] M. Szafran, Bull. Acad. Polon. Sci. Ser. Sci. Chim. **12,** 289, 383 (1964).
[455] M. Szafran, Spectrochim. Acta **19,** 2132 (1963).

practically alike, whatever the anion present (except, of course, for bands characteristic of anions) [453]. Still further, replacing hydrogen by deuterium (for example, in the abnormal iodide or perchlorate of 2,6-lutidine 1-oxide [453]) does not cause any change in the IR spectrum. For such reasons, the abnormal salts are believed to contain a homoconjugate cation analogous to (LXXVI) [390, 450–455]. It is also believed that the homoconjugate cation contains a *symmetrical* hydrogen bond. Mills and Speakman, who studied $(\mathrm{PicO})_2\mathrm{HBr}$ by x-ray diffraction at Hadži's suggestion, agree with this and other conclusions reached by him [452].

It should also be mentioned that the spectrum of abnormal salts of 2,6-lutidine 1-oxide was found by Szafran to revert to the normal spectrum upon solution of the salts in methyl sulfoxide [453]. From this he concluded that the homoconjugate cation had been destroyed, by conversion to the solvated cation, as indicated in eq 58:

$$(\mathrm{LutO...H...OLut})^+ + \mathrm{Me_2SO} \rightleftharpoons (\mathrm{LutOH...OSMe_2})^+ + \mathrm{LutO}. \qquad (58)$$

He represents $(\mathrm{LutOH...OSMe_2})^+$ as being a resonant cation. Szafran concluded that the homoconjugate cation is stable toward chloroform.

The concept of homoconjugate cation formation can be seen to provide a reasonable explanation for the existence of stable "abnormal" salts of *N*-oxides, and for their characteristic properties. This explanation is further strengthened by Szafran's discovery [455] of the apparent inability of 2,2′-bipyridine 1,1′-dioxide (2,2′-dipyridyl 1,1′-dioxide) to form "normal" salts (see last item in table 52). Several structures are conceivable for the homoconjugate cation of this *N*-oxide [455]; it should be especially stable if it has a cyclic, intramolecularly hydrogen-bonded structure.

The postulate that the hydrogen bond in such cations is symmetrical also seems reasonable, but so far there does not appear to be any rigorous proof of symmetry.

Quinaldine 1-oxide and acridine 1-oxide both form stable 1 : 1 trichloroacetates, but the IR spectra of these salts are abnormal [454]. In fact, they are similar to the spectrum of a 1 : 1 mull of $\mathrm{KH(CCl_3COO)_2}$ and $(\mathrm{quinO})_2\mathrm{HBr}$, as well as to spectra obtained from mulls in which the latter salt is replaced by $(\mathrm{quinO})_2\mathrm{HClO_4}$ or a corresponding salt of acridine 1-oxide. Szafran therefore thinks it likely that the structures of the 1 : 1 trichloroacetates are as indicated by (LXXVII):

$$\left[\mathrm{BO...H...OB}\right]^+ \left[\mathrm{CCl_3C({=}O)O...H...OC({=}O)CCl_3}\right]^-$$

(LXXVII)

These results with solid salts of *N*-oxides are in harmony with the finding (see last item in table 50) that *n*-$\mathrm{Bu_3NO}$ forms an extremely stable complex with its conjugate acid in *o*-dichlorobenzene.

4.4.4. Miscellaneous Heteroconjugate Cations

In section 4.4.1 we noted that *hetero*conjugate cations, $\mathrm{B{-}H^+...B'}$, include the special category known as "solvated" cations. Examples of the latter were discussed in section 4.2.2. This section may be regarded as a continuation of that discussion.

The heteroconjugate cations now to be discussed are listed in table 53, which emphasizes cases in which B′ is a base with a measurable pK_a value. Values of $K_{\mathrm{BH^+B'}}$ (eq 59) are included where available. *Solvated* cations in

$$\mathrm{BH^+ + B' \rightleftharpoons BH^+...B'} \qquad (59)$$

which B′ was EtOH, MeOH, MeCN, or $\mathrm{H_2O}$ are also included to show analogies in behavior. The solvents principally used were *benzene*, two halogenated aromatic hydrocarbons (*chlorobenzene*, *o-dichlorobenzene*), and *nitrobenzene*. Only limited use could be made of the halogenated *aliphatic* hydrocarbon, *1,2-dichloroethane*, because of its reactivity with free aliphatic amines. It will be noted that in most of the systems studied the anion present was $\mathrm{Pi^-}$.

In all of the examples given the investigators were convinced that association of neutral molecules with cations involved hydrogen bonding, from evidence similar to instances previously cited. It was found, for example, in conductance investigations that adding Py or MeCN to $\mathrm{Bu_3NHPi}$ in *o*-dichlorobenzene greatly increased the conductivity, whereas such additions to a solution of $\mathrm{Bu_4NPi}$ had only a minor effect [448].

Furthermore, a comparison of the results cited in table 50 with those in table 53 provides evidence that cations $\mathrm{BH^+}$ which bond readily to their *conjugate* bases (B) also bond readily to *other* bases (B′). For example, the visual appearance and absorption spectrum of the diphenylguanidinium salt of bromophthalein magenta E in benzene solutions are altered similarly by ethanol, pyridine, and an excess of diphenylguanidine [5]. In a different type of experiment, the conductance of tri-*n*-butylammonium picrate in *o*-dichlorobenzene was found to be augmented by adding acetonitrile, pyridine, 4-cyanopyridine, 4-picoline, or free tributylamine [448].

A third strong argument in support of the hydrogen bonding concept is provided by the comparative values of $K_{\mathrm{BH^+...B'}}$ (see table 53, 5th column) determined in experiments in which three pyridine-type bases of known pK_a values were added to *n*-$\mathrm{Bu_3NHPi}$ in *o*-dichlorobenzene: a clear-cut parallelism between the strength of B′ and the stability of $\mathrm{BH^+B'}$ was revealed. Although the stability of $\mathrm{Bu_3NH^+NBu_3}$ (table 50) is less than expected from the basic strength of $\mathrm{Bu_3N}$, this irregularity is attributable to steric hindrance. It is noteworthy that MeCN, though regarded as a far weaker base than $\mathrm{H_2O}$, shows an appreciable tendency to associate 1 : 1 with $\mathrm{Bu_3NH^+}$.

TABLE 53. *Examples of heteroconjugate cations* (B–H$^+$...B′)[a]

B	Solvent	Anion	B' [b]	Estimated $K_{BH^+...B'}$ [c]	References
$(PhNH)_2C{=}NH$	C_6H_6	(BPM–E)$^-$ [d]	EtOH	....	[5]
		(BPM–E)$^-$ [d]	Py (5.17)	....	[5]
NH_3	$PhNO_2$	Pi$^-$	Py (5.17)	....	[24]
n-Bu_3N	$PhNO_2$	Pi$^-$	Py (5.17)	[e] 6.2	[24, 448]
n-Bu_3N	PhCl	Pi$^-$	Py (5.17)	820	[448]
		Pi$^-$	4-MePy (6.02)	1830	[448]
n-Bu_3N	o-$C_6H_4Cl_2$	Br$^-$	Py (5.17)	1450	[448]
	o-$C_6H_4Cl_2$	Pi$^-$	4-CNPy (1.90)	40	[448]
		Pi$^-$	MeCN	212	[448]
		Pi$^-$	Py (5.17)	1370	[448]
		Pi$^-$	4-MePy (6.02)	3240	[448]
n-Bu_3N	$C_2H_4Cl_2$ [f]	Pi$^-$	MeOH	41	[448]
Me_3NO [g]	$PhNO_2$	Pi$^-$	H_2O	....	[24]
		Pi$^-$	Py (5.17)	....	[24]
		Pi$^-$	Et_3N (10.65)	....	[24]
		Pi$^-$	$C_5H_{10}NH$ (11.22)	....	[24]
$PhN(Me_2)O$	$PhNO_2$	Pi$^-$	Py (5.17)	....	[24]
n-Bu_3NO	o-$C_6H_4Cl_2$	Pi$^-$	Py (5.17)	1.2×10^5	[449]

[a] In the first two examples the physical method used was absorbance in the visible region; in all other cases it was conductance.

[b] pK_a values from the literature are given in parentheses.

[c] $K_{BH^+...B'}$ corresponds to $BH^+ + B' \rightleftharpoons BH^+...B'$ (25°); the values cited appear to be in molar units.

[d] (BPM—E)$^-$ signifies the anion of bromophthalein magenta E.

[e] Calculated by Ralph and Gilkerson [448] from data of Witschonke and Kraus [24].

[f] Reaction of free amines with 1,2-$C_2H_4Cl_2$ prevented their use as examples of B′.

[g] Bases B′ are listed in the order of increasing effectiveness is promoting ion-pair dissociation (as indicated by increased conductivity).

REFERENCES:

[5] M. M. Davis and H. B. Hetzer, J. Res. NBS **46**, 496 (1951).
[24] C. R. Witschonke and C. A. Kraus, J. Am. Chem. Soc. **69**, 2472 (1947).

[448] E. K. Ralph, III, and W. R. Gilkerson, J. Am. Chem. Soc. **86**, 4783 (1964).

[449] W. R. Gilkerson and E. K. Ralph, III, J. Am. Chem. Soc. **87**, 175 (1965).

Evidence of a similar kind came from Witschonke and Kraus's conductance experiments, referred to earlier (see table 35), in which four different bases were added to Me_3NOHPi in nitrobenzene. The four bases—H_2O, Py, Et_3N, and $C_5H_{10}NH$—were increasingly effective in the order listed in promoting the ion pair dissociation of Me_3NOHPi, showing that effectiveness is proportional to proton affinity.

As yet, too few such studies have been performed to permit many additional conclusions about homo- and heteroconjugation of cations. However, the following tentative conclusions seem justified by the evidence given here: (1) n-Bu_3NOH^+ forms more stable conjugate cations than n-Bu_3N. (2) Both Bu_3NH^+...Py and Bu_3NH^+...4-MePy form more extensively in o-dichlorobenzene than in chlorobenzene. (3) Bu_3NH^+...Py forms much less extensively in nitrobenzene than in either of the solvents just mentioned. It might also be thought than Bu_3NH^+ associates a little more extensively with Py when the anion is Br$^-$ than when it is Pi$^-$ judging from a difference in values for $K_{BH^+B'}$ (table 53); however, Ralph and Gilkerson do not regard the difference as exceeding the experimental uncertainty [448].

4.5. Hydrogen Bonding of Anions to Neutral Proton Donors

4.5.1. Introduction

We have just seen that homo- and heteroconjugate cations, B–H$^+$...B and B–H$^+$...B′, exist very commonly in aqueous and nonaqueous systems. Proton bonds between anions, A$^-$...H–A or

A⁻...H–A′, would be expected to form still more readily. Experimental evidence of the correctness of this view is much too extensive for complete coverage here. However, numerous examples will be presented to illustrate the widespread occurrence of homo- and heteroconjugate anions in aprotic and dipolar aprotic solvents. Examples will also be given of anion conjugation in solids.

The principal subtopics, in the order of presentation, will be: (a) Homo- and heteroconjugation of OH^- ions; (b) homoconjugation of aliphatic and aromatic carboxylates, phenolates, halides, and miscellaneous other types of anions; and (c) heteroconjugation.

Illustrations will be given of the significance of anion conjugation in some practical chemical situations—for example, in performing conductimetric, photometric, and potentiometric titrations; interpreting IR spectra; and controlling the rates of synthetic reactions.

Conjugate anions, like conjugate cations, usually seem to consist of 1:1 aggregates. It should be emphasized, however, that some anions form more complex aggregates when environmental conditions are favorable.

4.5.2. Homo- and Heteroconjugation of OH^- Ions

In work briefly reviewed in section 4.4.2a [430–435], Diamond and associates concluded that the hydronium ion tends to be extracted into aprotic solvents from aqueous solutions of acids either as the homoconjugate cation, $H_3O^+(H_2O)_3$, or as a heteroconjugate cation. Agarwal and Diamond [456] believe that the OH^- ion parallels H_3O^+ in its hydrogen-bonding ability. This conclusion is based on experiments in which a tetraalkylammonium hydroxide was extracted from water into benzene or nitrobenzene containing an alcohol, with the hydroxide at constant concentration and the alcohol at varying concentrations, or vice versa. Extraction into *benzene* appeared to proceed according to eq 60, with triply alcoholated ion pairs as the extracted species, while with *nitrobenzene* the results were similar except that in this solvent of much higher dielectric constant the solvated hydroxide is present as separate ions (eq 61).

$$R_4N^+_{aq} + OH^-_{aq} + 3R'OH_{org} \rightleftharpoons R_4N^+ \cdot {}^-OH \cdot 3R'OH_{org} \qquad (60)$$

$$R_4N^+_{aq} + OH^-_{aq} + 3R'OH_{org} \rightleftharpoons R_4N^+_{org} + OH^- \cdot 3R'OH_{org}. \qquad (61)$$

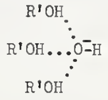
The extraction experiments are summarized in table 54.

The suggested structure for triply alcoholated OH^- ions is indicated by (LXXVIII):

TABLE 54. *Summary of extractions of quaternary ammonium hydroxides* (R_4NOH) *from water into alcohol* ($R'OH$)—*containing benzene or nitrobenzene* [a]

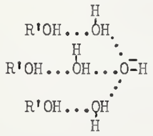
Solvent	R′	R	Composition of extracted species
Benzene	Benzyl or decyl	Pentyl or hexyl	$R_4N^+ \cdot OH^-(HOR')_3$
Nitrobenzene	Benzyl or 4-methyl-cyclohexyl.	Propyl or butyl	R_4N^+ *plus* $OH^-(HOR')_3$

[a] From B. R. Agarwal and R. M. Diamond, J. Phys. Chem. **67**, 2785 (1963) [456].



(LXXVIII)

It is also believed that H_2O molecules may form bridges between OH^- ions and $R'OH$ molecules, as indicated in (LXXIX):



(LXXIX)

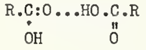
Structures (LXXVIII) and (LXXIX) are analogous to (LXXII) and (LXXIII), respectively.

From these results Agarwal and Diamond think it probable that in aqueous solutions the OH^- ion holds a primary shell of three H_2O molecules, by very strong hydrogen bonds; thus agreeing with conclusions of other investigators.

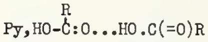
4.5.3. Homoconjugate Aliphatic and Aromatic Carboxylate Ions

a. *Solid acid carboxylates. Ammonium, potassium,* and *sodium* acid carboxylates have been prepared and studied as solids for well over a century. For example, they are said [457] to have been referred to in textbooks by Berzelius ("Lehrbuch der Chemie," 1847) and Gmelin ("Handbook of Chemistry," 4th edition, 1853). By 1914, according to Pfeiffer's estimate [458] some 60 to 70 acid salts of aliphatic and aromatic carboxylic acids had been described.

Pfeiffer himself reported the preparation of both normal and acid salts of *pyridine* with 17 mono- or dicarboxylic acids. The general method for preparing the *normal salts* consisted of dissolving the acid in pyridine and then evaporating off all or part of the excess of pyridine. Normal salts were converted into the *acid salts* on crystallization from alcohol. Pfeiffer's work predated recognition of the general importance of hydrogen bonding. Nevertheless, reasoning from the well-known tendency for RCOOH to form dimers, for which he postulated the general structure (LXXX) (or, alternatively, the cyclic structure accepted nowadays), he believed the pyridinium acid salts to be representable as (LXXXI):


$\mathrm{R.\underset{\overset{\cdot}{OH}}{C}:O\ldots HO.\underset{\overset{\|}{O}}{C}.R}$

(LXXX)


$\mathrm{Py,HO{-}\overset{R}{\overset{|}{C}}:O\ldots HO.C(=O)R}$

(LXXXI)

Smith and Speakman [457] investigated the acid potassium salts of benzoic and phenylacetic acids as possible *p*H standards. Since the late 1940's solid acid carboxylates have been studied extensively by infrared and x-ray spectroscopy, and occasionally by newer techniques, mainly to ascertain whether or not the $RCOO^-$...HOCOR hydrogen bond in a given crystalline salt is symmetrical. The principal acid carboxylates so studied are listed in table 55, together with a few examples from Pfeiffer's work. Although strong indications of homoconjugation of anions in solid species do not necessarily signify that $RCOO^-$...HOCOR bonds will be stable enough to persist in aprotic and dipolar aprotic organic solvents, it will be seen presently that such bonds are generally very stable. In fact, at least one such bond, $PhCOO^-$...HOCOPh, appears to persist even in aqueous solutions [471, 472, 472a].

TABLE 55. *Examples of carboxylate homoconjugation,* $RC(=O)O^-$...HOC(=O)R, *in solids* [a]

Carboxylic acid	Cation present	Type of measurement [b]	References
Acetic	Na^+	X-ray	[462, 466]
Benzoic	K^+	X-ray; IR; NMR	[461, 463]
4-Chlorobenzoic	NH_4^+, K^+, or Rb^+	X-ray	[468]
Cinnamic	NH_4^+ or K^+	X-ray	[467]
Dibromohydrocinnamic	PyH^+	Chem	[458]
Glycolic	K^+ or Rb^+	X-ray	[469]
2-Nitrobenzoic	PyH^+, K^+, or Rb^+	Chem; x-ray	[458, 465]
3-Nitrobenzoic	PyH^+	Chem	[458]
4-Nitrobenzoic	PyH^+, K^+, Na^+, or Rb^+	Chem; x-ray; IR; NMR	[458, 465, 463]
Phenylacetic	K^+ or Rb^+	X-ray; IR; ND; NMR	'[459, 460, 463, 464]
Trichloroacetic [c]	$(BO...H...OB)^+$	IR	[454]
Trifluoroacetic	Cs^+, K^+, or Rb^+	X-ray	[470]

[a] In part of the examples cited a *symmetrical* hydrogen bond is believed by some authors to be present.

[b] Meaning of symbols: Chem, chemical analysis; IR, infrared absorption spectroscopy; ND, neutron diffraction; NMR, nuclear magnetic resonance spectroscopy; x-ray, x-ray diffraction.

[c] See table 52, footnote f.

REFERENCES:

[454] M. Szafran, Bull. Acad. Polon. Sci. Ser. Sci. Chim. **12**, 289, 383 (1964).
[458] P. Pfeiffer, Chem. Ber. **47**, 1580 (1914).
[459] J. C. Speakman, J. Chem. Soc., p. 3357 (1949).
[460] M. Davies and W. J. Orville Thomas, J. Chem. Soc., p. 2858 (1951).
[461] J. M. Skinner, G. M. D. Stewart, and J. C. Speakman, J. Chem. Soc., p. 180 (1954).
[462] J. C. Speakman, Proc. Chem. Soc., p. 316 (1959).
[463] R. Blinc and D. Hadži, Spectrochim. Acta **16**, 853 (1960).
[464] G. E. Bacon and N. A. Curry, Acta Cryst. **13**, 717 (1960).
[465] H. N. Shrivastava and J. C. Speakman, J. Chem. Soc., p. 1151 (1961).
[466] J. C. Speakman and H. H. Mills, J. Chem. Soc., p. 1164 (1961).
[467] R. F. Bryan, H. H. Mills, and J. C. Speakman, J. Chem. Soc., p. 4350 (1963).
[468] H. H. Mills and J. C. Speakman, J. Chem. Soc., p. 4355 (1963).
[469] L. Golič and J. C. Speakman, J. Chem. Soc., p. 2521 (1965).
[470] L. Golič and J. C. Speakman, J. Chem. Soc., p. 2530 (1965).

Not all of the carboxylic acids tested by Pfeiffer yielded stable pyridinium salts at ordinary temperatures. For example, *o*-bromobenzoic acid, cinnamic acid, and the isomeric toluic acids were recovered unchanged from pyridine, and the pyridinium salt of benzoic acid was recovered from ethanol as the free acid. The products clearly depend in large measure on the extent of competing hydrogen bonding reactions, such as chelation and bonding to the solvent.

The reader is referred to original papers for conclusions with respect to the symmetry of hydrogen bonds in salts listed in table 55.

b. Homoconjugation of carboxylates in solutions. Experimental evidence of homoconjugation of a carboxylate ion in solution seems to have been obtained first for the *benzoate ion*, in *water.* In the early 1930's, the formation of anions corresponding to double molecules of benzoic acid was postulated to account for the "salting in" of benzoic acid by sodium benzoate [471, 472]. The same conclusion was reached in a recent determination of the distribution of benzoic acid between water and toluene in the presence of sodium or potassium benzoate [472a], in which the equilibrium constant for homoconjugation (eq 62) was found to be 1.0 (molar units, 25°).

$$C_6H_5COO^- + C_6H_5COOH \rightleftharpoons C_6H_5COO^- \ldots HOCOC_6H_5. \qquad (62)$$

This value is fairly close to an earlier estimate (0.45 to 0.77) of Kolthoff and Bosch [472].

Indirect evidence of acid carboxylate formation in benzene was provided by cryoscopic data for mixtures of representative tertiary aliphatic amines with acetic or myristic acid in benzene. Two species—$R_3N(R'COOH)_2$ and $R_3N(R'COOH)_4$—were believed to be formed [473].

We have already had occasion (sec. 4.3.5b) to discuss direct evidence, supplied by infrared spectroscopy, that $CH_3COO^- \ldots HOCOCH_3$ is a product of the half-neutralization of acetic acid by Et_3N, Et_2NH, or n-$BuNH_2$ in carbon tetrachloride or chloroform [392–394], as well as evidence that the acid carboxylates are intermediate products in the neutralization of CCl_3COOH and CF_3COOH by pyridine in chloroform [395]. Still another infrared study was concerned with the acid potassium salts of 4-chloro- and 4-nitrobenzoic acids in methyl sulfoxide [477].

Furthermore, in the titration of benzyl-*N*,*N*-dimethylamine with CCl_3COOH in benzene by the differential vapor pressure (DVP) method [352] the shape of the titration curve disclosed that formation of the acid carboxylate had occurred (see sec. 4.3.3b).

The above and additional examples of carboxylate homoconjugation are listed in table 56 or table 57. Table 56 is concerned with *aliphatic* and substituted aliphatic acids, whereas table 57 deals with *benzoic* and related acids.

In 1947 Maryott published an account of experimental conductimetric titrations of acids (picric, *dl*-camphorsulfonic, and trichloroacetic) and aliphatic amines (triethyl-, di-*n*-butyl, and *n*-heptyl-) in three solvents, namely, *benzene*, *dioxane*, and *benzene containing 1 percent of methanol* [341]. Both "forward" and "reverse" titrations were performed, but we shall concern ourselves only with forward titrations, which by definition were those in which the amine (~ 0.2 *M*) was added to the acid (~ 0.01 *M*). Representative titration curves are presented in figures 19 to 21.

Acids and amines of the types used would be expected to have negligibly low conductances in dilute aprotic solvents like benzene. However, as preceding discussion has shown (see tables 32 and 33 and context), partly substituted ammonium salts (e.g., picrates, chlorides) are measurably conducting in such media, even though only a tiny fraction of the salt (a millionth of a percent or so) is dissociated into free ions. Consequently, in the 1 : 1 reaction of an acid with an amine the conductance could be expected to rise gradually until the end-point and remain approximately constant thereafter. Examples of this simple pattern of behavior were obtained in titrating *picric acid* with n-Bu_2NH or Et_3N (see fig. 19). It will be noted that the titration curves in benzene and dioxane were almost identical when dibutylamine was the titrant, and that the curve for benzene-methanol had practically the same shape, although the conductance values were higher throughout the titration. It is not certain what caused drifts in the conductance during neutralization of picric acid with *triethylamine* in benzene or dioxane [341], but air was not excluded from the solutions and it therefore seems possible that the anomalies resulted from the presence of a little Et_3NO [31, 403].

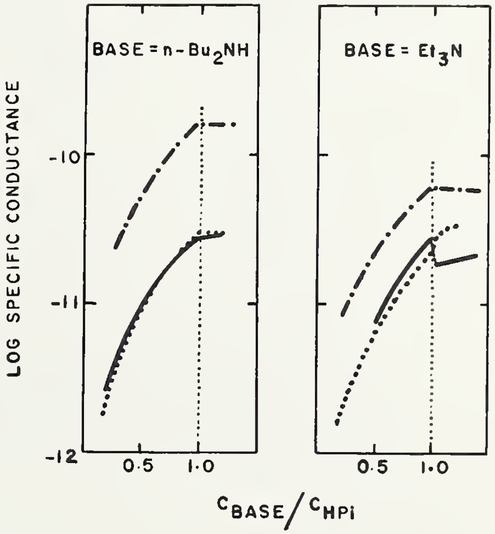


FIGURE 19. *Conductance titrations in benzene (solid lines), dioxane (dotted lines), and benzene containing 1 percent of methanol (dot-dash lines); ~ 0.2* M *di-*n*-butylamine or triethylamine was added to ~ 0.01* M *picric acid.*

Adapted by permission from figures 2 and 3 of A. A. Maryott, J. Res. NBS **38**, 527 (1947). (Ref. No. 341.)

The curves for conductance titrations of *trichloroacetic acid* in benzene are strikingly different

TABLE 56. *Examples of 1 : homoconjugate anion formation from* RCOOH, *deduced in studies of solutions* [a]

Solvent	Identity of R	Base or cation added	Method [b]	References
Acetone	CH_3	R_4NOH in Py	EMF	[475]
	CH_2Cl	Et_3N	C	[474]
	$CHCl_2$	Et_3N or *n*-Bu_3N	C	[474]
	CCl_3	Et_3N or *n*-Bu_3N	C	[474]
Acetonitrile	CH_2Cl	Et_3N	C	[474]
	$CHCl_2$	Et_3N	C	[474]
	CCl_3	Et_3N	C	[474]
Benzene	CH_3	*i*-Am_3N	CRY	[473]
	CCl_3	R_3N, Bu_2NH, or $HpNH_2$	C, VPL	[341, 352]
	$C_{13}H_{27}$	R_3N	CRY	[473]
	$C_6H_5OCH_2$	TDPNB [c]	VIS	[482]
	$C_6H_5C{\equiv}C$	TDPNB [c]	VIS	[482]
Carbon tetrachloride	CH_3	Et_3N, Et_2NH, or $BuNH_2$	IR	[392–394]
Chloroform	CH_3	Et_3N, Et_2NH, or $BuNH_2$	IR	[392–394]
	CCl_3	Py	IR	[395]
	CF_3	Py	IR	[395]
Dioxane	CCl_3	Et_3N or Bu_2NH	C	[341]
Methyl sulfoxide	$C_6H_5CH_2$	K^+	IR	[477]
Toluene	H	Bu_4NOH in *i*-PrOH	EMF	[476]
	CH_3	Bu_4NOH in *i*-PrOH	EMF	[476]
	CCl_3	Bu_4NOH in *i*-PrOH	EMF	[476]

[a] RCOOH signifies an aliphatic or substituted aliphatic acid. See table 57 for examples of $ArCOO^-...HOCOAr$.

[b] Meaning of symbols: C, conductance; CRY, cryoscopy; VPL, vapor pressure lowering; EMF, IR, VIS, usual meanings.

[c] TDPNB symbolizes the indicator base "p-Tolyl Di-*n*-propyl Nile Blue" (LXXXIV).

REFERENCES:

[341] A. A. Maryott, J. Res. NBS **38**, 527 (1947).
[352] S. Bruckenstein and A. Saito, J. Am. Chem. Soc. **87**, 698 (1965).
[392] G. M. Barrow and E. A. Yerger, J. Am. Chem. Soc. **76**, 5211 (1954).
[393] E. A. Yerger and G. M. Barrow, J. Am. Chem. Soc. **77**, 4474 (1955).
[394] E. A. Yerger and G. M. Barrow, J. Am. Chem. Soc. **77**, 6206 (1955).
[395] G. M. Barrow, J. Am. Chem. Soc. **78**, 5802 (1956).
[473] S. Kaufman and C. R. Singleterry, J. Phys. Chem. **56**, 604 (1952).
[474] P. J. R. Bryant and A. W. H. Wardrop, J. Chem. Soc., p. 895 (1957).
[475] H. B. van der Heijde, Anal. Chim. Acta **16**, 392 (1957).
[476] G. A. Harlow and D. B. Bruss, Anal. Chem. **30**, 1833 (1958).
[477] D. Hadži and A. Novak, Spectrochim. Acta **18**, 1059 (1962).
[482] M. M. Davis and H. B. Hetzer, Anal. Chem. **38**, 451 (1966).

TABLE 57. *Examples of 1 : 1 homoconjugate anion formation from* ArCOOH, deduced in studies of solutions[a]

Solvent	Substituent in C_6H_5	Base or cation added	Method[b]	References
Acetone	2-NO_2	Et_3N	C	[474]
	3-NO_2	Et_3N	C	[474]
	4-NO_2	Et_3N	C	[474]
	3,5-$(NO_2)_2$	Et_3N	C	[474]
Acetonitrile	None	Anion-exchange resin	DR	[478]
	None	Et_4N^+	EMF	[481]
	4-CH_3	Anion-exchange resin	DR	[478]
	3-Br	Et_4N^+	EMF	[481]
	3-Cl	Anion-exchange resin	DR	[478]
	2-OH	Bu_2NH, Bu_3N, Na^+, or Et_4N^+	C, S, EMF	[407, 481]
	4-OH	Et_4N^+	EMF	[481]
	4-OCH_3	Anion-exchange resin	DR	[478]
	4-NO_2	Anion-exchange resin	DR	[478]
	4-NO_2	Et_4N^+	EMF	[481]
	3,5-$(NO_2)_2$	R_3N, R_4N^+, K^+, Py-type	C, S, EMF	[479–481]
Benzene	None	R_3N, R_2NH, or RNH_2	CRY, P	[347]
	2-OH	TDPNB[c]	VIS	[482]
	3-NO_2	TDPNB[c]	VIS	[482]
Methyl sulfoxide	4-Cl	K^+	IR	[477]
	4-NO_2	K^+	IR	[477]
Water	None	Na^+	S	[471, 472]
	None	K^+ or Na^+	D	[472a]

[a] ArCOOH signifies an aromatic or substituted aromatic acid. See table 56 for examples of $RCOO^-...HOCOR$.

[b] Meaning of symbols: DR, distribution of ArCOOH between its salt with an anion-exchange resin and the solvent; P, dielectric polarization; S, solubility of ArCOOH in the presence of its Na or K salt; other symbols as explained in footnote b of table 56.

[c] See table 56, footnote c.

REFERENCES:

[347] E. N. Gur'yanova and I. G. Beskina, J. Gen. Chem. USSR Eng. Transl. **33,** 914 (1963).
[407] J. F. Coetzee and G. P. Cunningham, J. Am. Chem. Soc. **87,** 2534 (1965).
[471] E. Larsson, Z. Physik. Chem. Leipzig **153,** 466 (1931).
[472] I. M. Kolthoff and W. Bosch, J. Phys. Chem. **36,** 1685 (1932).
[474] P. J. R. Bryant and A. W. H. Wardrop, J. Chem. Soc., p. 895 (1957).
[477] D. Hadži and A. Novak, Spectrochim. Acta **18,** 1059 (1962).
[478] J. E. Gordon, J. Phys. Chem. **67,** 19 (1963).
[479] I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc. **85,** 426 (1963).
[480] I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc. **87,** 1004 (1965).
[481] I. M. Kolthoff and M. K. Chantooni, Jr., J. Phys. Chem. **70,** 856 (1966).
[482] M. M. Davis and H. B. Hetzer, Anal. Chem. **38,** 451 (1966).
[472a] A. Brändström, Acta Chem. Scand. **20,** 1335 (1966).

from those for picric acid (see fig. 20, *solid* lines). After an initial steep rise, which reaches a maximum a little beyond half neutralization of the acid, the conductance drops sharply until the end-point, after which there is a more gradual rise or a tendency to level off. The maximum is especially pronounced in the curve for titration with triethylamine in benzene.

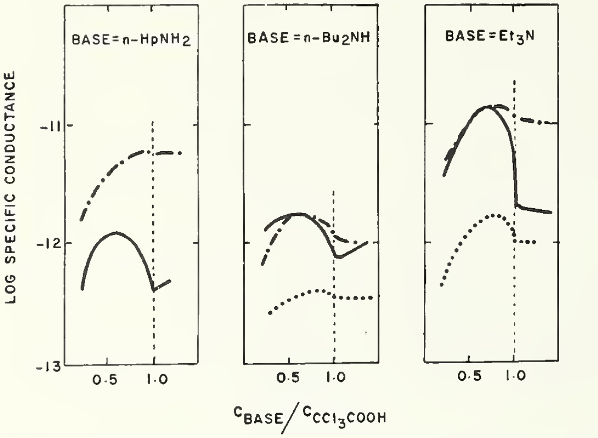


FIGURE 20. *Conductance titrations in benzene (solid lines), dioxane (dotted lines), and benzene containing 1 percent of methanol (dot-dash lines).* ~ *0.2* M n-*Heptylamine, di-n-butylamine, or triethylamine was added to* ~ *0.01* M *trichloroacetic acid.*

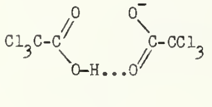
Adapted by permission from figures 4 to 6 of A. A. Maryott, J. Res. NBS **38**, 527 (1947). (Ref. No. 341.)

Analogous, though less pronounced, maxima were also obtained with dioxane as the solvent (*dotted* lines), and even in the benzene-methanol mixture (*dot-dash* lines), some evidence of the mid-titration maximum remained.

From the abnormally high conductance of solutions containing free acid as well as salt, Maryott concluded that an acid salt forms as an intermediate product in such titrations (eq 63):

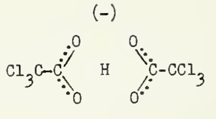
$$BH^+...A^- + H\text{-}A \rightleftharpoons BH^+...A^-...H\text{-}A. \qquad (63)$$

Obviously, the cation-anion interaction will be weaker in the acid salt than in $BH^+...A^-$, thus explaining the marked difference in conductance of the two salt species. One way of representing the acid anion is indicated by (LXXXII):



(LXXXII)

However, Maryott pointed out that an acid carboxylate ion must have exceptional stability to exist in dioxane, a medium in which carboxylic acid dimers do not seem to be stable, and he prefers the alternative resonant structure indicated by (LXXXIII), in which the proton is assumed to occupy a position such that it is shared by all four oxygen atoms, which are located *tetrahedrally* around it.



(LXXXIII)

It is apparent from figure 20 that substitution of Bu_2NH for Et_3N results in smaller increases in conductance during the titration of trichloroacetic acid in benzene or dioxane. This finding is in harmony with various results, cited in section 4.3, which indicated that dimers of secondary ammonium carboxylates are quite stable in aprotic media. Similar indications of salt dimerization are apparent in the conductance curve obtained by titrating trichloroacetic acid with n-$HpNH_2$ in benzene (fig. 20) and comparative results obtained on titrating camphorsulfonic acid with Et_3N and Bu_2NH in dioxane (fig. 21).

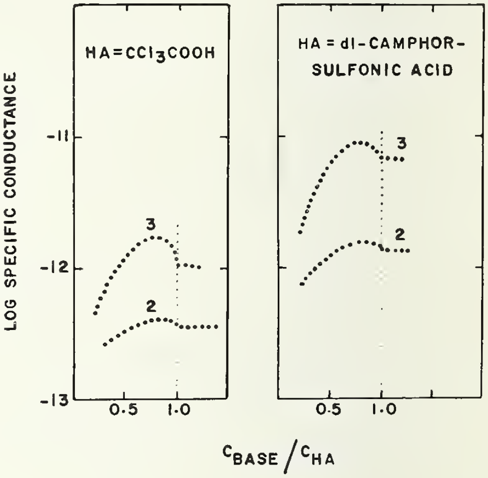


FIGURE 21. *Conductance titrations in dioxane:* ~ 0.02 M *Di-*n-*butylamine (see curves marked "2") or triethylamine (curves marked "3") was added to* ~ 0.01 M *trichloroacetic acid or* dl-*camphorsulfonic acid.*

Adapted by permission from figures 4 to 6 of A. A. Maryott, J. Res. NBS **38**, 527 (1947). (Ref. No. 341.)

These exploratory studies not only demonstrated the feasibility of performing conductance titrations in solvents of very low dielectric constant, but also showed that homoconjugation of a carboxylate or sulfonate ion is valuable in foreseeing an approaching end-point and locating it precisely. Furthermore, they have inspired other systematic investigations of conductance titrations of carboxylic acids in such solvents as acetone [474] and acetonitrile [474, 407, 479–481].

In a particularly noteworthy investigation [474] Bryant and Wardrop showed that similar sharply defined mid-titration maxima are obtained in two aprotic solvents of much higher dielectric constant than benzene, namely, *acetone* and *acetonitrile*. Using acetone as solvent for the most part, and a tertiary amine (Et_3N or n-Bu_3N) as the titrant, they obtained pronounced conductance maxima for the following carboxylic acids:

CCl_3COOH, $CHCl_2COOH$, $CH_2ClCOOH$;

2-, 3-, and 4-$NO_2C_6H_4COOH$;

3,5-$(NO_2)_2C_6H_3COOH$.

In agreement with Maryott, they attributed the maxima to homoconjugation of anions. The maxima disappear in *ethanol*, and the conductance titration curves then have the same shape as for picric acid. In further agreement with Maryott, the authors concluded that homoconjugate carboxylate ions must be exceptionally stable, since they are formed in solvents in which the carboxylic acids are known to be monomeric.

Although results obtained by titrations in acetone and acetonitrile were similar, the conductivities were higher in the latter solvent.

Acetic acid proved to be too weak for satisfactory titration. Some results with nitrophenols will be referred to in section 4.5.4.

At about the time Bryant and Wardrop's work was published it was also shown that reproducible potential rises sometimes occur in the region of half neutralization in *potentiometric titration curves* for carboxylic acids and other acidic compounds, in solvents like *acetone* and *toluene* (see table 56). Such mid-titration inflections are believed to result from anion homoconjugation [475, 476].

Anion homoconjugation in *acetonitrile* has been studied systematically by Kolthoff and Chantooni [479–481] and Coetzee and Cunningham [407], employing conductance titrimetry and in some cases solubility measurements and potentiometry as well. Using the combined data and making certain reasonable assumptions, they were able to estimate values of equilibrium constants for various competing reactions, such as:

$$\mathrm{BHA} \rightleftharpoons \mathrm{BH}^+ + \mathrm{A}^- \qquad (17)$$

$$\mathrm{BHA} \rightleftharpoons \mathrm{B} + \mathrm{HA} \qquad (18)$$

$$\mathrm{BH}^+ + \mathrm{B} \rightleftharpoons \mathrm{BH}^+\mathrm{B} \qquad (56)$$

$$\mathrm{BH}^+\mathrm{AHA}^- \rightleftharpoons \mathrm{BH}^+ + \mathrm{AHA}^- \qquad (64)$$

$$\mathrm{A}^- + \mathrm{HA} \rightleftharpoons \mathrm{A}^-\ldots\mathrm{HA}. \qquad (65)$$

In this way they arrived at approximate values for the equilibrium constant $K_{\mathrm{A}^-\ldots\mathrm{HA}}$ (eq 65). This constant has been variously referred to as a "homoconjugation," "formation," or "stability" constant. They also applied the overall results in calculating conductimetric titration curves, which agreed well with actual titration curves.

In a related type of study, Gordon determined the comparative stabilities of the homoconjugate anions of benzoic and four substituted benzoic acids by measuring the distribution of each acid between its salt with an *anion-exchange resin* and the solvent *acetonitrile* (eq 66) [478]:

$$\mathrm{ArCOOH\,(in\ MeCN)} + \mathrm{ArCOO^-Res^+} \rightleftharpoons \mathrm{(ArCOO\ldots HOCOAr)}, \mathrm{Res}^+. \qquad (66)$$

He found that his log K values are linearly related to the pK_a values of the acids within the experimental uncertainty:

$$\log K = 3.48 - 0.200\,pK_a. \qquad (67)$$

Gordon's five equilibrium constants are given in table 58 (column 6), along with the $K_{\mathrm{A}^-\ldots\mathrm{H-A}}$ values obtained by Kolthoff and Chantooni and Coetzee and Cunningham; the pK_a values of the acids are included (column 2). It is appropriate not only to intercompare these values but also to compare them with corresponding dimerization constants (see table 24 and context). The following tentative conclusions seem warranted:

(1) The stronger an acid of type ArCOOH, the more stable its homoconjugate anion.

(2) The statement just made has to be modified for acids in which there is strong intramolecular hydrogen bonding. For example, anion homoconjugation was found to be less extensive for 2-hydroxybenzoic (salicylic) acid than for three much weaker acids, and was too small to measure in the case of 2,6-dihydroxybenzoic (γ-resorcylic) acid.

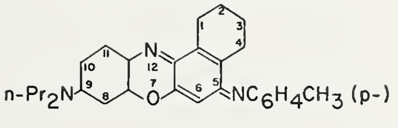
(3) Stabilities of homoconjugate anions of the type $\mathrm{ArCOO^-\ldots HOCOAr}$ (in MeCN) vary *inversely* with the stabilities of the corresponding acid dimers, $(\mathrm{ArCOOH})_2$, in benzene.

(4) Conjugate *anions* of the type

$$\mathrm{ArCOO^-\ldots HOCOAr}$$

are considerably more stable than homoconjugate *cations* of the ammonium type (compare table 51).

Our final examples of apparent carboxylate homoconjugation are from spectrophotometric titrations of an indicator base known as "p-*Tolyl di-n-propyl Nile Blue*" ("TDPNB") with several types of acids in benzene [482]. The acids included *o*-chlorobenzoic, *m*-nitrobenzoic, phenoxyacetic, phenylpropiolic, salicylic, and trichloroacetic acids. The structure of the indicator base is represented by (LXXXIV). This indicator is related to Nile Blue A anhydro-base, and its systematic name is "5-*p*-tolylimino-9-(di-*n*-propylamino)-benzo[*a*]phenoxazine" [482, 483]. The proton-acceptor atom is considered to be the nitrogen atom attached to carbon No. 5.



(LXXXIV)

Examples of spectrophotometric titration curves are given in figure 22, A and B. It will be seen that

TABLE 58. *Comparative homoconjugation constants of some aromatic carboxylate ions in acetonitrile*[a]

Carboxylic acid	pK_a in water	C[b]	S[c]	EMF[d]	DR[e]	References
4-Hydroxybenzoic	4.58	....	....	1,000	....	[481]
4-Methoxybenzoic	4.47	....	....	....	383	[478]
4-Toluic	4.37	....	....	....	409	[478]
Benzoic	4.20	....	....	4,000	427	[481, 478]
3-Chlorobenzoic	3.83	....	....	....	528	[478]
3-Bromobenzoic	3.81	....	....	6,000	....	[481]
4-Nitrobenzoic	3.43	....	....	7,000	609	[481, 478]
Salicylic	3.00	[f]800–1500	2,000	2,000	....	[407, 481]
3,5-Dinitrobenzoic	2.82	....	17,000	10,000	....	[481, 479]
2,6-Dihydroxybenzoic	1.0	Very small	....	....	....	[407]

[a] At 25°. Equation 65 applies except in method DR; that is, $A^- + HA \rightleftharpoons A^-...HA$.

[b] The acids were titrated conductimetrically with Bu_3N, Bu_2NH, and $n\text{-}BuNH_2$.

[c] Calculated from effects of added ArCOOH on the solubility of ArCOONa or ArCOOK.

[d] From EMF data for mixtures of ArCOOH and $ArCOONEt_4$. This method is considered more reliable than the solubility method [481].

[e] In this method the equilibrium constant is for distribution of ArCOOH between acetonitrile and its salt with an anion-exchange resin. That is: ArCOOH(in MeCN) + $ArCOO^-Res^+ \rightleftharpoons (ArCOO^-...HOCOAr), Res^+$

[f] Values of $K_{A^-...HA}$ varied with the titrant and the concentration of HA: Two titrations with Bu_2NH gave 800 and 900, and two with Bu_3N gave 1500 and 1000.

REFERENCES:

[407] J. F. Coetzee and G. P. Cunningham, J. Am. Chem. Soc. **87**, 2534 (1965).
[478] J. E. Gordon, J. Phys. Chem **67**, 19 (1963).
[479] I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc. **85**, 426 (1963).
[481] I. M. Kolthoff and M. K. Chantooni, Jr., J. Phys. Chem. **70**, 856 (1966).

some curves (such as that for *trichloroacetic acid* in fig. 22A) show a continuous increase in absorbance at the beginning, followed by a gradual leveling off. Such "simple" titration curves are obtained when B and HA associate in 1:1 ratio (eq 44):

$$B + H{-}A \rightleftharpoons B{-}H^+...A^-. \qquad (44)$$

The acids in this group are all *strong*. In contrast, the titration curves obtained with *moderately strong* carboxylic acids—for example, *phenoxyacetic acid*—tend to have an S-shape (see fig. 22B). (The S-shape would be much more apparent, of course, if the horizontal scale in fig. 22B were not so highly compressed.) Although the investigations were not continued beyond exploratory stages, it seems probable that such S-shaped curves result when there is overlapping production of BHA and $B(HA)_2$, with the former product predominating at very low acid concentrations, and the latter, at high acid concentrations [482].

For $B{-}H^+...A^-$ to be formed to an important extent, a carboxylic acid must be reacting as the monomer, and B must be a much better proton acceptor than A^-. When A^- and B are equally good proton acceptors or A^- is the better acceptor, and HA forms a stable dimer, formation of $B(HA)_2$ can be predicted. Probably $B(HA)_2$ is sometimes formed by direct interaction of B and $(HA)_2$ (eq 68), as postulated by Kaufman and Singleterry when interpreting cryoscopic data for amine-carboxylic acid systems in benzene; a further association of $B(HA)_2$ with $(HA)_2$ was also thought to occur (eq 69) [473]:

$$B + (HA)_2 \rightleftharpoons B(HA)_2 \qquad (68)$$

$$B(HA)_2 + (HA)_2 \rightleftharpoons B(HA)_4. \qquad (69)$$

On the other hand, when the part of the carboxylic acid is present as monomer, or as monomer loosely bound to solvent molecules, eq 63 may be a preferable formulation:

$$BH^+...A^- + H{-}A \rightleftharpoons BH^+...A^-...H{-}A. \qquad (63)$$

While emphasizing homoconjugation in 1:1 ratio as the most frequently observed type, we should not ignore occasional indications of conjugation in other ratios—for instance, there have been reports of adsorption of carboxylic acids in excessive amounts on ion-exchange resins. No detailed structures can be offered to explain such behavior. However, it should be possible for extra molecules of R′–COOH to hydrogen bond to a

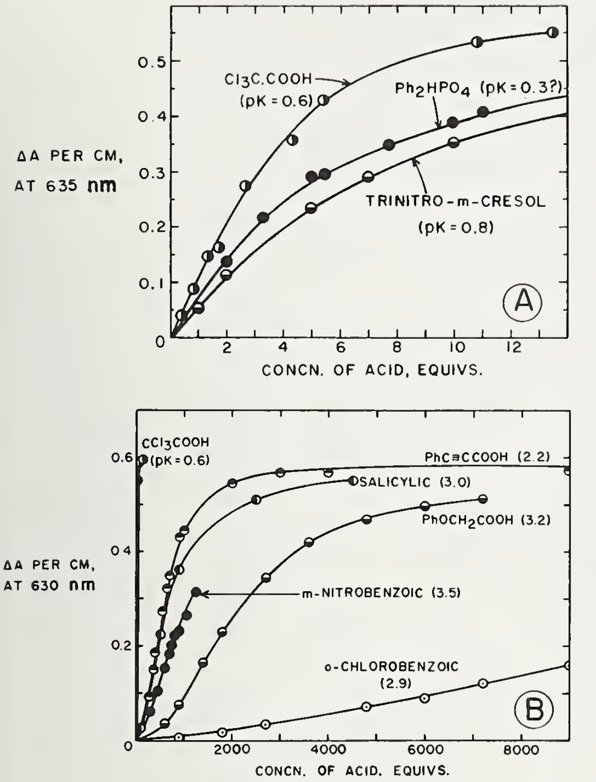
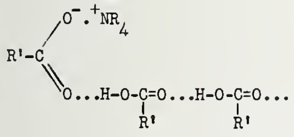


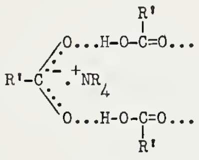
FIGURE 22. *Spectrophotometric titration curves obtained on titrating tolyl dipropyl Nile Blue base with some strong (A) and moderately strong (B) acids in benzene.*

Reproduced from figures 9 and 10 of M. M. Davis and H. B. Hetzer, Anal. Chem. 38, 451 (1966). (Ref. No. 482.)

carboxylate, for example, $R'-COO^- \cdot {}^+NR_4$, to yield aggregates like those suggested by (LXXXV) and (LXXXVI):



(LXXXV)



(LXXXVI)

From the examples listed in tables 55 to 58 it is evident that carboxylate homoconjugates are stable enough to form under widely varying conditions. As an illustration, the homoconjugate of $C_6H_5COO^-$ forms in solvents as different as benzene and water and in the absence of any solvent. Furthermore, the homoconjugates form in the presence of varied types of cations: R_4N^+, R_3NH^+, $R_2NH_2^+$, PyH^+, K^+, Na^+, and others. It was pointed out in section 4.4.2a that Diamond and associates used perchloric acid as the source of protons in studies of homo- and heteroconjugation of the *hydronium ion* [430–435], their reason being that this acid yields an anion with exceptionally low proton affinity. Analogously, should one wish to maximize anion homoconjugation, the cation present ought to be one with minimal affinity for proton acceptors; that is, it should belong to type R_4N^+ rather than to a type of cation (R_3NH^+, etc.) whose interaction with anions is strengthened by hydrogen bonding, and K^+ should be used if feasible, in preference to Na^+.

4.5.4. Homoconjugate Phenolate Ions

We have seen that Maryott's conductance titration curves for picric acid in benzene and dioxane (fig. 19), unlike the curves for trichloroacetic and camphorsulfonic acids (figs. 20 and 21), showed no indications of anion homoconjugation. Extending Maryott's work to a larger group of carboxylic acids and nitrophenols, with acetone or acetonitrile as the solvent, Bryant and Wardrop [474] perceived that the exceptional behavior of picric acid is shared by 2,6-dinitrophenol, and must be the result of strong *chelation*. As readers will have foreseen, a second impediment to homoconjugation is the presence of a *bulky substituent* in one or both *ortho* positions.

Tables 59 and 60 contain substantial documentation of these statements, and additional evidence will be discussed briefly. Investigations yielding *positive evidence* of phenolate homoconjugation are summarized in table 59. Table 60 summarizes experiments in which *little or no tendency* toward homoconjugation was observed.

a. Examples of homoconjugation. The formation of homoconjugate phenolate ions (usually 1:1 complexes) has been inferred in the following types of measurement:

(1) *Conductance titrations* of phenols in *aprotic* solvents (benzene, toluene, xylene, carbon tetrachloride), in certain *dipolar aprotic* solvents (acetone, methyl isobutyl ketone), and in the *weakly basic* solvent, pyridine. The evidence of homoconjugation was a maximum, usually quite pronounced, in conductance near the titration midpoint [474, 484].

(2) *Potentiometric titrations* of phenols (or, alternatively, determinations of EMF values for series of buffered phenol solutions) in a similar range of solvents (benzene, toluene, gasoline, pyridine, ethylenediamine, acetonitrile) [475, 476, 486, 487]. Here, the indication of homoconjugation was an additional potential rise near half-neutralization, which seems to have been reported first in work by van der Heijde [475]. He noted, for example, a close parallelism in the shapes of titration curves for *acetic acid* (in acetone) and *phenol* (in pyridine) when titrating with $Bu_3N(Me)OH$ (in pyridine), using a glass-calomel electrode combination. A notable investigation of analytical aspects of such titrations has been performed by Harlow and Bruss [476]; several examples from their results are included in tables 59 and 60. Special mention should also be made of the use of potentiometric data in calculating $K_{A^-\ldots HA}$ values for several phenols in ethylenediamine [486] and acetonitrile [487] (see table 59).

Table 59. *Examples of homoconjugate phenolate ions* $(\mathrm{ArO^-\ldots HOAr})$[a]

Substituents in C_6H_5OH	Solvents	Type of measurement[b, c]	Estimated value of $K_{A^-\ldots HA}$[d]	References
None	Acetone	C	....	[484]
	Acetonitrile[e]	EMF	....	[487]
	Benzene[f]	UV	....	[485]
	Ethylenediamine	EMF	15	[486]
	i-Propyl Alcohol	UV	....	[485]
	Pyridine	EMF, C[e]	....	[475, 484]
	Toluene[f]	EMF, C	....	[476, 484]
2,4-Me_2	Toluene[f]	C	....	[484]
2,3,5-Me_3	Toluene[f]	C	....	[484]
2-Et	Pyridine	C	....	[484]
3,5-Et_2	Toluene[f]	C	....	[484]
5-Me-2-*i*-Pr[g]	Ethylenediamine	EMF	7	[486]
4-Me-2-*t*-Bu	Pyridine	EMF	....	[475]
	Toluene[f]	EMF	....	[476]
2-Ph	Ethylenediamine	EMF	40	[486]
4-Ph	Ethylenediamine	EMF	46	[486]
2-Cl	Toluene[f]	EMF	....	[476]
4-Br, 4-Cl	*i*-Propyl Alcohol	UV	....	[485]
4-Cl	Pyridine	C	....	[484]
2-NO_2	Acetonitrile	EMF	110	[487]
3-NO_2	*i*-Propyl Alcohol	VIS	....	[485]
3-NO_2	Pyridine	C	....	[484]
	Toluene[f]	EMF, C	....	[476, 484]
4-NO_2	Acetonitrile	EMF	1400	[487]
	Methyl sulfoxide	IR	....	[391]
	i-Propyl Alcohol	VIS	....	[485]
2,4-$(NO_2)_2$	Acetonitrile	EMF	100	[487]
3,5-$(NO_2)_2$	Acetone	C	....	[474]

[a] Usually the cation present was R_4N^+, but in a few cases it was K^+, Na^+, or Et_3NH^+.

[b] Meaning of symbols is the same as in the preceding tables.

[c] Some experiments utilized a series of buffered solutions; in other cases, titrations were performed.

[d] $K_{A^-\ldots H\text{-}A}$ applies to the reaction: $A^- + H{-}A \rightleftharpoons A^-\ldots H{-}A$.

[e] The anion $PhO^-(HOPh)_2$ was also thought to form.

[f] A small amount of *i*-PrOH was present.

[g] Thymol.

References:

[391] D. Hadži, A. Novak, and J. E. Gordon, J. Phys. Chem. **67**, 1118 (1963).
[474] P. J. R. Bryant and A. W. H. Wardrop, J. Chem. Soc., p. 895 (1957).
[475] H. B. van der Heijde, Anal. Chim. Acta **16**, 392 (1957).
[476] G. A. Harlow and D. B. Bruss, Anal. Chem. **30**, 1833 (1958).
[484] D. B. Bruss and G. A. Harlow, Anal. Chem. **30**, 1836 (1958).
[485] L. E. I. Hummelstedt and D. N. Hume, Anal. Chem. **32**, 1792 (1960).
[486] S. Bruckenstein and L. M. Mukherjee, J. Phys. Chem. **66**, 2228 (1962).
[487] J. F. Coetzee and G. R. Padmanabhan, J. Phys. Chem. **69**, 3193 (1965).

TABLE 60. *Examples of phenols having little or no tendency to form homoconjugate anions*[a]

Substituents in C_6H_5OH	Solvents	Cation present	Type of measurement[b]	References
2-NO_2[c]	Benzene[d]	$n\text{-Bu}_4\text{N}^+$	VIS	[485]
	Toluene[d]	$n\text{-Bu}_4\text{N}^+$	EMF	[476]
$2,6\text{-(NO}_2)_2$	Acetone	Et_3NH^+	C	[474]
$2,4,6\text{-(NO}_2)_3$	Acetone	Et_3NH^+	C	[474]
	Acetonitrile	Et_4N^+	EMF[e]	[487]
	Acetonitrile	Et_4N^+	EMF[f]	[488]
	Benzene	Bu_2NH_2^+	C	[341]
$3\text{-Me-}2,4,6\text{-(NO}_2)_3$	Benzene	TDPNB[g]	VIS	[482]
$2,6\text{-Me}_2$	Pyridine	Na^+ or K^+	C	[484]
$2,4,6\text{-Me}_3$	Pyridine	Na^+ or K^+	C	[484]
	Toluene[d]	$n\text{-Bu}_4\text{N}^+$	C	[484]
2-Me-6-*t*-Bu	Toluene[d]	$n\text{-Bu}_4\text{N}^+$	EMF	[476]
4-Me-2,6-*t*-Bu	Pyridine	Bu_3NMe^+	EMF	[475]
	Pyridine	Na^+ or K^+	C	[484]
2,4,6-*t*-Bu	Toluene[d]	$n\text{-Bu}_4\text{N}^+$	EMF	[476]
Thiophenol	Acetonitrile	Bu_3NMe^+	EMF	[475]
	Toluene[d]	$n\text{-Bu}_4\text{N}^+$	EMF	[476]

[a] Except as stated otherwise, no indications of homoconjugation were detected.
[b] Meaning of symbols is the same as in the preceding tables.
[c] Compare with the result for an acetonitrile solution, cited in table 59.
[d] A small amount of *i*-PrOH was present.
[e] This was an exploratory study.
[f] "Very slight homoconjugation" was detected, with $K_{A^- \ldots H\text{-}A}$ estimated as being about 2.
[g] TDPNB symbolizes the indicator base "*p*-Tolyl di-*n*-propyl Nile Blue" (LXXXIV).

REFERENCES:

[341] A. A. Maryott, J. Res. NBS **38**, 527 (1947).
[474] P. J. R. Bryant and A. W. H. Wardrop, J. Chem. Soc., p. 895 (1957).
[475] H. B. van der Heijde, Anal. Chim. Acta **16**, 392 (1957).
[476] G. A. Harlow and D. B. Bruss, Anal. Chem. **30**, 1833 (1958).
[482] M. M. Davis and H. B. Hetzer, Anal. Chem. **38**, 451 (1966).
[484] D. B. Bruss and G. A. Harlow, Anal. Chem. **30**, 1836 (1958).
[487] J. F. Coetzee and G. R. Padmanabhan, J. Phys. Chem. **69**, 3193 (1965).
[488] I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc. **87**, 4428 (1965).
[485] L. E. I. Hummelstedt and D. N. Hume, Anal. Chem. **32**, 1792 (1960).

(3) *Photometric titrations of phenols.* Phenolates absorb at longer wavelengths than the corresponding phenols, and a wavelength region can usually be found in the near-ultraviolet or visible where the absorbance of the *phenolate* increases sharply with concentration, and where the *phenol* contributes little or nothing to the absorbance. Taking advantage of this situation, a number of investigators have successfully determined 1:1 *acid-base association constants* in aprotic solvents like *benzene* (for examples see refs. 14, 20, 32, 254a, 482) and *chlorobenzene* [354, 364, 441, 85]. The phenols selected for such work (bromophthalein magenta E, bromophenol blue, 2,4- and 2,6-dinitrophenol) were very unlikely to form homoconjugates, especially under the conditions used.

Phenolate homoconjugation was very evident, however, in a different type of investigation by

Hummelstedt and Hume, whose objective was to explore analytical possibilities of photometric titrations [485]. They titrated some 16 different phenols (phenol itself, 1- and 2-naphthols, and halo- or nitro-derivatives of phenol), usually 0.01 M in isopropyl alcohol, with n-Bu_4NOH (~ 0.4 M) in the same solvent. In part of the experiments the isopropyl alcohol was largely replaced by benzene. With isopropyl alcohol as the sole solvent, the titration curves for phenol, unchelated phenols, and non-hindered phenols tended to have an *S*-shape resembling that illustrated earlier for certain carboxylic acids (fig. 22B). However, as would be expected, an anomalous curve shape was most pronounced when most of the isopropyl alcohol was replaced by benzene. Agreeing with other investigators, Hummelstedt and Hume concluded that $ArO^-...HOAr$ formation occurs at the beginning of such titrations. An additional reasonable postulate was that $ArO^-...HOAr$ has spectral absorption characteristics intermediate between those of ArOH and ArO^-. As they pointed out, undesirable spectral shifts occur during a photometric titration when using a mixture of solvents (for example, benzene-*iso*propyl alcohol) whose composition does not remain constant.

Hummelstedt and Hume also stressed the sensitivity of the photometric method as a detector of homoconjugation: Whereas in toluene containing more than 1 percent of isopropyl alcohol neither the conductimetric [484] nor the potentiometric [476] method supplies indications of phenolate homoconjugation, phenol homoconjugates are detectable photometrically even in pure isopropyl alcohol. In their opinion the photometric method offers unique advantages in analytical applications (including differentiating titrations of up to four weak acids), as well as for investigating complex formation.

(4) *Infrared spectroscopy.* Hadži, Novak, and Gordon [391] isolated several acid phenolates, including the sodium and the potassium acid salt of 4-nitrophenol, and measured their infrared absorption spectra as mulls, as undercooled melts, and as solutions in methyl sulfoxide. Indications of $ArO^-...HOAr$ were the *absence* of a band in the region of the stretching vibration of free O–H, and the *presence* of an extremely broad absorption band whose location and other characteristics were considered consistent with its assignment to a hydrogen-bonded group, O...H...O. These authors were concerned with the symmetry or asymmetry of such hydrogen bonds. For our discussion, it is sufficient to note that homoconjugation was inferred for specimens examined as solutions in *methyl sulfoxide*, as well as for those examined as mulls or melts. However, the hydrogen bonds thought to be *symmetrical* in certain intermolecular homoconjugates in the absence of a solvent became *asymmetrical* on solution in methyl sulfoxide.

2,2′-Dihydroxybiphenyl and bis-(2-hydroxyphenyl)-methane, as well as some of their phenyl-substituted derivatives, show marked readiness to form conjugate anions [391, 476, 494]. For example, the infrared spectra of the sodium acid salt of 2,2′-dihydroxybiphenyl ($NaOC_6H_4C_6H_4OH$)—whether as crystals, as an undercooled melt, or as a solution in methyl sulfoxide—are all very similar, and the same holds true for the sodium acid salt of 2,2′-methylenebis-(4-chlorophenol), $NaOC_6H_3(Cl)$-CH_2-$C_6H_3(Cl)OH$ [391]. This similarity and other characteristics of the spectra are considered to indicate that these salts contain a very stable $A^-...H{-}A$ bond. The stability is understandable, since the $A^-...H{-}A$ bonds, in all probability, form part of a *cyclic* structure—a 7-membered ring in the first-mentioned salt, and an 8-membered ring in the latter. Salts of these types display exceptional titrimetric behavior. As an illustration, when titrating various alkyl-substituted bis-(2-hydroxyphenyl)methanes in *benzene-i-PrOH*, Sprengling observed [494] that one of the phenolic groups is much more acidic than a single phenolic group, whereas the second phenolic group is abnormally weak. Harlow and Bruss [476] confirmed Sprengling's observations, finding one phenolic OH group to be easily titratable, while the second OH could not be titrated at all.

Table 59 contains estimates of $K_{A^-...H\text{-}A}$ for phenol and three phenol derivatives in *ethylenediamine* [486], and for three nitro derivatives of phenol in *acetonitrile* [487]. While these results are obviously too few to support any broad generalizations, the values for the four phenol derivatives in ethylenediamine suggest that, paralleling carboxylate homoconjugation, the stronger the conjugate acid ArOH, the more stable the homoconjugate $ArO^-...HOAr$. The other three $K_{A^-...H\text{-}A}$ values will be discussed briefly in the next section.

b. Examples of non-homoconjugation. As mentioned a little earlier, homoconjugation is markedly impeded when the phenol in question either (1) contains a stable chelate ring, or (2) is an appreciably "hindered" phenol. At this point we shall elaborate somewhat on these two topics.

Chelated Phenols. The role of chelation is well illustrated by the differing *conductance titration curves* obtained for 3,5-dinitrophenol (listed in table 59) and its 2,6-isomer (see table 60) in *acetone* solutions: A mid-titration maximum appeared in the curve for 3,5-dinitrophenol, but was absent in that for 2,6-dinitrophenol [474].

It is also instructive to compare the *homoconjugation constants* estimated from *EMF data* for 2- and 4-nitrophenols and 2,4-dinitrophenol in *acetonitrile* (table 59) [487]: Although 2-nitrophenol ($pK_a = 7.23$) and 4-nitrophenol (pK_a 7.15) are about equally strong acids in water, it is plain that in the experiments cited homoconjugation was much more extensive for the *para*- than for the *ortho*-isomer. The *ortho*-isomer is, undoubtedly, the example most frequently cited—with extensive documentation—in discussions of chelate ring formation in aprotic solvents. Homoconjugation of 2,4-dinitrophenol appears, likewise, to be strongly inhibited by chelation: In spite of its much greater pK_a value (4.11), its homoconjugation constant is much smaller than that of 4-nitrophenol, being, instead, about the same as that of 2-nitrophenol.

Readers will probably have noticed that 2-nitrophenol is listed both in table 59 and 60. Its inclusion in the latter table arises from the fact that even a slight indication of homoconjugation seems to have been lacking in *photometric titrations* of this acid in *benzene containing a little isopropyl alcohol* [485], and also in *EMF titrations* in a similar medium (namely, *toluene containing a little isopropyl alcohol)* [476]. Picric acid, likewise, might have been listed in both tables, since "very slight homoconjugation", with $K_{A^-\ldots HA} \approx 2$, was inferred in EMF measurements employing acetonitrile as the solvent [488].

Tables such as these, while not to be regarded as rigorous classifications, have predictive value. We are not surprised, for example, to learn that in *photometric titrations* of tolyl dipropyl Nile Blue base with trinitro-*m*-cresol (3-methylpicric acid) in *benzene*, homoconjugation of this phenol derivative was not discernible. The absence of homoconjugation is indicated in figure 22A, as well as in figure 23. The latter figure shows representative absorption curves for the indicator base before and after adding trinitro-*m*-cresol in amounts ranging from 1 to 1600 equivalents. Not only is there a well-defined isosbestic point (near 556 nm), but there is also excellent agreement between a *calculated* (dotted line) and *experimental* limiting curve. Data such as these yielded a precise value (log $K_{BHA} = 4.13$, molar units, 25°) of the 1:1 acid-base association constant [482].

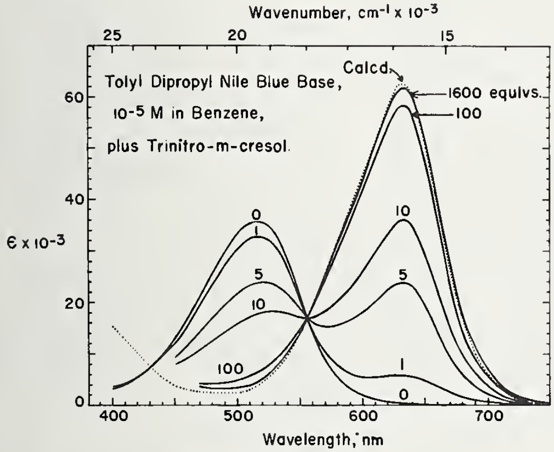


FIGURE 23. *Spectral absorption curves of mixtures of tolyl dipropyl Nile Blue base (LXXXIV) with trinitro-m-cresol (methylpicric acid) in benzene; used in determining the equilibrium constant* (K_{BHA}) *for the 1:1 acid-base association at 25°.*

Reproduced from figure 7 of M. M. Davis and H. B. Hetzer, Anal. Chem. **38**, 451 (1966). (Ref. No. 482.)

Furthermore, with the benefit of our recently acquired understanding of homoconjugation in carboxylates and phenolates, it is now possible to offer reasonable explanations of some puzzling results in early studies of acid-base behavior in aprotic solvents. For example, Brønsted and Bell's finding [491] that the velocity of the addition of phenol to ethyl diazoacetate in *benzene* is strongly catalyzed by carboxylic acids is perhaps attributable to enhancement of acidity by *hetero*conjugation (see later discussion in section 4.5.7b). In another study, concerned with the acid-catalyzed rearrangement of *N*-bromoacetanilide in *chlorobenzene*, Bell [492] derived a simple equation correlating the *catalytic effects in this solvent* and the *aqueous ionization constants* of 2,4,6-trichlorophenol, pentachlorophenol, and the following eight carboxylic acids: acetic; 2-chloropropionic; cinnamic; phenoxyacetic; phenylpropiolic; and mono-, di-, and trichloroacetic acids. Astonishingly, picric acid was far too poor a catalyst to fit into this relation. Picric acid was again a misfit in investigations by Bell and Caldin [493] of the acid-catalyzed inversion of *l*-menthone in chlorobenzene (99.4°); that is, its catalytic activity in this reaction was anomalously low. Such results are in keeping with the failure of picric acid to undergo self-association or to readily form homoconjugate anions. It is evident that the comparatively great strength of picric acid in water ($pK_a = 0.33$, according to recent spectrophotometric data [362]) is a misleading clue to its behavior in nonleveling solvents like benzene and chlorobenzene. Although, as we saw earlier (fig. 19), picric acid is quantitatively titratable in such media with relatively strong organic bases like di-*n*-butylamine and triethylamine, apparently the O–H bond to an *ortho* nitro oxygen is too strong for there to have been extensive intermolecular hydrogen bonding of picric acid to the weak organic bases involved in the catalytic experiments just mentioned.

Hindered phenols [475, 476, 484]. A well-known example of a hindered phenol is 6-methyl-2-*tert.*-butylphenol (table 60). This phenol gave a "normal" potentiometric titration curve in toluene, whereas the curve for a less hindered isomer, 4-methyl-2-*tert.*butylphenol, showed an inflection at the midpoint of the titration [476]. Most of the phenols listed in table 60 are substituted in both the 2- and 6-positions, but this does not mean that there is *no* inhibition of homoconjugation with only one bulky *ortho* substituent. An illustration of this point can be found in Harlow and Bruss's paper [476], where comparative potentiometric titration curves show decreasing evidence of homoconjugation with increasing shielding of the –OH group in the following series of phenols:

$$C_6H_5OH > 2\text{-}t\text{-Bu-4-Me}C_6H_3OH$$

$$> 2\text{-}t\text{-Bu-6-Me}C_6H_3OH > 2,4,6\text{-}(t\text{-Bu})_3C_6H_2OH.$$

Further comparisons of potentiometric or conductance titration curves for unhindered, hindered, and partially hindered phenols are to be found in the three papers cited.

Thiophenol [475, 476, 484]. In the same three investigations thiophenol exhibited no tendency toward homoconjugation in spite of its having a distinctly more acid character than phenol. That is, it was found to give "normal" curves in potentiometric or conductance titrations employing such solvents as acetonitrile [475], pyridine [484], and toluene containing a minute amount of isopropyl alcohol [476]. This difference in the behavior of phenol and thiophenol is attributed to the fact that sulfur is less able than oxygen to bond to hydrogen. Possibly weak homoconjugation would be detected in more favorable environments, that is, where alternative hydrogen bonding reactions are more completely excluded. This suggestion is supported by a number of examples, summarized by Pimentel and McClellan [102], in which mercaptans and other sulfur compounds have been found capable of forming hydrogen-bonded complexes. Moreover, thiophenol is now regarded as being somewhat dimerized (or otherwise aggregated) in aprotic media, although once considered to be incapable of self-association. For example, Spurr and Byers, employing infrared spectroscopy, deduced a dimerization constant ($K_{1,2}$) of about 0.02 (CCl_4, molar units, 24°) [489], and Marcus and Miller, under closely comparable conditions (PhCl, 28°), obtained the value 0.011 by PMR spectroscopy [490]. These are smaller than corresponding values reported for phenol (see table 18).

4.5.5. Homoconjugation of Halide Ions

At one period homoconjugation of halides was thought to be limited to the acid fluoride ion, HF_2^-, but more recent work has shown that all four of the common halide ions are capable of homoconjugation. Examples will be given of halide homoconjugation in aprotic and dipolar aprotic solvents, and following that, some results with solid specimens will be summarized.

a. Homoconjugation in Solutions. It seems likely that Meerwein was the first to become aware of chloride homoconjugation. In an article bearing the title (in translation), "Enhancement of the Ionizability of Weak Electrolytes by Complex Formation and Its Significance for the Catalytic Process," he referred to "dimolecular acids, like dihydrochloric acid, $[HCl_2]H$" as being, in common with "dimolecular organic acids," more strongly ionized than the "monomolecular acids" [495]. (Ethyl ether seems to have been the solvent used.)

In a major contribution appearing in 1954 [496], Herbrandson and associates reported several reasons for postulating the existence of HCl_2^- in *nitrobenzene* containing *both* HCl and Et_4NCl. For example, in the mixtures the solubility of Et_4NCl was substantially greater than in the absence of HCl, the vapor pressure of HCl from the solution was less than in the absence of Et_4NCl, and the H–Cl stretching frequency at 2703 cm^{-1} was replaced by a broad absorption band at lower frequencies. Results for acid-catalyzed reactions also pointed to the same conclusion, yielding for the homoconjugation constant (see eq 70) the value 500 ($PhNO_2$, molar units, 25°).

$$Cl^- + H{-}Cl \rightleftharpoons HCl_2^- . \qquad (70)$$

Furthermore, they isolated the acid salts Me_4NHCl_2 and Et_4NHCl_2 from nitrobenzene solutions.

During an investigation of triple ion formation in *benzene*, Hughes, Ingold, and co-workers [497] measured the conductance of solutions containing HCl alone and in mixtures with Bu_4NCl, Bu_4NNO_3, and Bu_4NClO_4, obtaining the results shown in table 61. Numbers in the last column indicate the extent to which the conductance (30°) of any mixture

TABLE 61. *Relative stabilities in benzene of* $(ClHCl)^-$, $(ClHNO_3)^-$, *and* $(ClHClO_4)^-$, *from conductance measurements (30°)*[a]

Molar concentration		Conductance[b]			
HCl	n-Bu_4NA	HCl only	n-Bu_4NA only	Mixture	Δ[c]
		$A^- = Cl^-$			
0.40×10^{-4}	1.92×10^{-4}	0.02	0.17	0.33	0.14
3.0	4.55	0.10	0.55	2.08	1.43
3.3	3.84	0.10	0.41	2.00	1.49
3.4	3.57	0.11	0.38	1.87	1.38
3.6	3.33	0.11	0.36	1.74	1.27
3.8	3.12	0.11	0.34	1.60	1.15
4.0	2.00	0.12	0.18	0.93	0.63
		$A^- = NO_3^-$			
....	10.0	....	2.55	2.55	....
0.25	9.7	0.01	2.5	2.63	0.12
0.50	9.5	0.02	2.4	2.83	0.41
		$A^- = ClO_4^-$			
....	10.0	....	4.5	4.5	....
0.60	9.4	0.02	4.2	4.1	−0.12
1.00	8.8	0.03	3.7	3.8	0.07

[a] See Table 4 of Hughes, Ingold, et al. [497]. The criterion of stability is the magnitude of Δ; see accompanying discussion.

[b] The conductance (reciprocal resistance, 10^8 ohm^{-1}) was measured before and after adding various amounts of HCl to solutions containing n-Bu_4NA, where A^- was Cl^-, NO_3^-, or ClO_4^-.

[c] Δ = The conductance of the mixture minus the sum of the conductances of the separate components.

REFERENCE

[497] E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker, J. Chem. Soc., p. 1206 (1957).

TABLE 62. *Examples of homoconjugate anion* ($X^-...H-X$) *formation, deduced in studies of solutions* [a]

Solvent	X^-	Class of base or cation	Method [b]	Estimated value of $K_{X^-...H-X}$ [c]	References
Acetonitrile	Br^-	In [d]	VIS	250	[500]
	Br^-	R_4N^+	IR, UV, PMR	....	[502]
	Cl^-	In [d]	VIS	200	[500]
	Cl^-	R_4N^+	IR, UV, PMR	....	[502]
	Cl^-	R_4N^+	IR, Raman	....	[504]
Benzene	Br^-	R_4N^+	IR	....	[503]
	Cl^-	R_4N^+	C, VPL, RATE	....	[497, 498]
	Cl^-	R_4N^+ [f]	IR, Raman	....	[503, 504]
Carbon tetrachloride	F^-	R_3N [f]	IR	....	[381]
Chloroform	Br^-	R_3N	D	....	[409]
	Cl^-	R_3N	D	....	[409]
	F^-	R_3N	D	....	[409]
Dichloromethane	Cl^-	R_4N^+	IR, Raman	....	[504]
Ethyl ether	Cl^-	N.S. [e]	RATE	....	[495]
Methyl sulfoxide	Br^-	R_4N^+ [f]	IR, PMR	....	[502]
	Cl^-	R_4N^+	IR, PMR	....	[502]
Nitrobenzene	Br^-	Py	C	....	[501]
	Cl^-	R_4N^+ [f]	IR, RATE, S, VPL	500	[496]
	Cl^-	Py	C	....	[501]
Nitromethane	Cl^-	R_4N^+	VIS	....	[499]

[a] In some cases $X^-...D-X$ was studied as well.

[b] Significance of symbols: RATE, enhancement of acid strength by homoconjugation caused an increase in the rate of an acid-catalyzed reaction; other symbols are used as in the preceding tables.

[c] At 25° in molar units. $K_{X^-...H-X}$ corresponds to $X^- + HX \rightleftharpoons X^-...H-X$. Activity coefficients are assumed to cancel or approximate 1.

[d] In this table "In" signifies a nitroaniline-type ("Hammett") indicator. Also see table 65.

[e] Not specified.

[f] The salt used in experiments had been isolated and identified as $B(HX)_2$. See table 63 for additional examples of solid species of the composition $B(HX)_2$.

REFERENCES:

[381] A. A. Lipovskii and S. A. Nikitina, Russ. J. Inorg. Chem. Engl. Transl. **10**, 93 (1965).

[409] J. I. Bullock, S. S. Choi, D. A. Goodrick, D. G. Tuck, and E. J. Woodhouse, J. Phys. Chem. **68**, 2687 (1964).

[495] H. Meerwein, Ann. Chem. **455**, 227 (1927).

[496] H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, J. Am. Chem. Soc. **76**, 4046 (1954).

[497] E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker, J. Chem. Soc., p. 1206 (1957).

[498] S. F. Mok, cited in ref. [497], p. 1216.

[499] Y. Pocker, J. Chem. Soc., p. 240 (1958).

[500] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., J. Am. Chem. Soc. **83**, 3927 (1961).

[501] I. R. Beattie and G. J. Leigh, J. Chem. Soc., p. 4726 (1962).

[502] D. G. Tuck and E. J. Woodhouse, Proc. Chem. Soc., p. 53 (1963).

[503] J. C. Evans and G. Y-S. Lo, J. Phys. Chem. **69**, 3223 (1965).

[504] J. C. Evans and G. Y-S. Lo, J. Phys. Chem. **70**, 11 (1966).

exceeded the sum of the conductances of the separate components. From these results it was concluded that $(ClHCl)^-$ is very stable in benzene, $(ClHNO_3)^-$ is moderately stable, and $(ClHClO_4)^-$ does not exist.

In harmony with these results, S. F. Mok [498] found the vapor pressure of HCl (~ 0.001 *M*) from benzene to be strongly depressed on the addition of *n*-Bu_4NCl in a comparable amount. Moreover, she observed that the catalytic effect of HCl on the methyl-alcoholysis of triphenylmethyl (trityl) chloride in benzene is largely destroyed by adding an equivalent of Bu_4NCl, whereas HCl and *n*-Bu_4NClO_4 act additively as catalysts in this reaction.

The examples just cited, along with numerous others, are listed in table 62, where nine solvents are represented. It will be seen that homoconjugation has been detected for F^-, Cl^-, and Br^-, employing numerous types of physical measurements (conductance; distribution; kinetics; IR, UV, visible, PMR, and Raman spectroscopy; solubility measurements; and vapor pressure lowering). Indications of homoconjugation need not all be discussed in detail, since they are very much like those for homoconjugates already discussed. For instance, in conductance titrations of HCl (0.01 *M* or 0.05 *M*) in nitrobenzene the titration curves show a pronounced maximum near the mid-point, and similar results are obtained in titrating HBr [501].

Naturally, there has been much speculation as to the manner in which acids like HCl exert their catalytic function in aprotic media. A pertinent example is the interaction of phenol with trityl chloride in *o-dichlorobenzene* to form *p*-tritylphenol. Hart and Cassis, who studied this reaction and the corresponding reaction of *o*-cresol with trityl chloride, yielding *p*-trityl-*o*-cresol, concluded that the most likely role of HCl is in facilitating the ionization of trityl chloride, as represented by the following equation [505]:

$$Ph_3C{-}Cl + HCl \rightleftharpoons Ph_3C^+Cl^-...H{-}Cl. \qquad (71)$$

b. Homoconjugation of X^- in solids [190b, 381, 502–504, 506–511]. During the past ten years a number of investigators have examined acid fluorides, chlorides, bromides, and iodides as the solids, and they have unanimously inferred the presence of $X^-...H{-}X$ (or, in some cases, $X^-...D{-}X$). The nature of such studies is briefly indicated in table 63.

Mixed conjugates have also been detected in solids—for example, $(ClHNO_3)^-$, $(ClDNO_3)^-$, $(BrDCl)^-$, $(IDCl)^-$ [507], and $(BrHCl)^-$ [508].

There is wide agreement that FHF^- is the most stable of all hydrogen-bonded species, and that, moreover, its hydrogen bond is symmetrical. In other words, it is thought that the proton in $F^-H^+F^-$ is located in a single potential minimum, intermediate between the F^- ions [see fig. 24(d)]. Westrum and Pitzer [506] believe this conclusion to have been established with certainty by their own careful investigations of the system $KHF_2-KF-HF$, in which thermodynamic and dielectric data were obtained, as well as by infrared spectral data from the literature. Another indication of the exceptional stability of HF_2^- is found in Waddington's calculated value, 58 ± 5 kcal/mole, for the enthalpy change in the following reaction [510]:

$$HF_2^-(g) \rightleftharpoons HF(g) + F^-(g). \qquad (72)$$

McDaniel and co-workers ascertained the comparative stabilities of HI_2^-, HBr_2^-, HCl_2^-, and HF_2^- in "systems designed to minimize lattice energy effects and specific cation-anion interaction" [508, 511]. The reactions studied are representable by the following equation:

$$R_4NX(s) + HX(g) \rightleftharpoons R_4NXHX(s). \qquad (73)$$

For these four homoconjugates, in the order listed, the respective values found for ΔH are: −12.4, −12.8, −14.2, and −37 kcal/mole. The corresponding value obtained for the mixed species $(BrHCl)^-$ is −9.1 kcal/mole; in the adoption of this value the proton was presumed to be closer to Cl^- than to Br^-.

TABLE 63. *Studies of homoconjugation of halide ions[a] in solids*

X^-	Types of cations present	Method[b]	References
F^-	K^+, R_4N^+, R_3NH^+	THERM, P, IR	[506, 510, 190b, 511, 381]
Cl^-	Cs^+, R_4N^+	IR, Raman, THERM	[509, 503, 504, 507, 508]
Br^-	R_4N^+	THERM, IR	[508, 502, 507]
I^-	R_4N^+	THERM, IR	[508, 507]

[a] $X^-...H{-}X$ or $X^-...D{-}X$.

[b] "THERM" signifies the measurement of one or more thermodynamic properties such as heat capacity, entropy, and lattice energy.

REFERENCES:

[190b] L. Pauling, The Nature of the Chemical Bond, 3d ed. (Cornell Univ. Press, Ithaca, N.Y., 1960).

[381] A. A. Lipovskii and S. A. Nikitina, Russ. J. Inorg. Chem. Engl. Transl. **10**, 93 (1965).

[502] D. G. Tuck and E. J. Woodhouse, Proc. Chem. Soc., p. 53 (1963).

[503] J. C. Evans and G. Y-S. Lo, J. Phys. Chem. **69**, 3223 (1965).

[504] J. C. Evans and G. Y-S. Lo, J. Phys. Chem. **70**, 11 (1966).

[506] E. F. Westrum, Jr. and K. S. Pitzer, J. Am. Chem. Soc. **71**, 1940 (1949).

[507] J. A. Salthouse and T. C. Waddington, J. Chem. Soc. (A), p. 28 (1966).

[508] D. H. McDaniel and R. E. Valleé, Inorg. Chem. **2**, 996 (1963).

[509] T. C. Waddington, J. Chem. Soc., p. 1708 (1958).

[510] T. C. Waddington, Trans. Faraday Soc. **54**, 25 (1958).

[511] S. A. Harrell and D. H. McDaniel, J. Am. Chem. Soc. **86**, 4497 (1964).

4.5.6. Homoconjugation of Other Organic and Inorganic Acids

a. Perchloric acid. In work previously reviewed ClO_4^- was found to have little if any tendency to become hydrogen bonded to cations R_3NH^+ (see sec. 4.3.5c) or to HCl (sec. 4.5.5a) in aprotic media. Consequently, it is not surprising that extraction experiments have supplied no evidence of an ability to form a homoconjugate anion. Such experiments have shown that when concentrated aqueous mineral acids (HCl, HNO_3, and certain others) are equilibrated with an R_3N-containing aprotic solvent the organic layer acquires more than one HA molecule per molecule of R_3N. However, after extractions of aqueous perchloric acid by a *chloroform* solution of methyldioctylamine, Bullock and associates [409] concluded that essentially no AHA^- was present in the organic layer.

Similarly, Bucher and Diamond found that *benzene*, *o-dichlorobenzene*, and *nitrobenzene* solutions of trilaurylamine, following their use as extracting media, contained only the 1:1 perchlorate [442]. Their experimental results are summarized in table 64.

TABLE 64. *Molar ratio* $HClO_4$*/trilaurylamine in the organic phase* (22°) [a]

Molarity of aq. $HClO_4$	Molar ratio $HClO_4/(C_{12}H_{25})_3N$ in		
	Benzene	*o*-Dichlorobenzene	Nitrobenzene [b]
0.495	1.00	1.00	1.00
0.991	1.00	....	1.00
3.92	1.00	....	1.00
6.37	1.00	1.00	1.03
10.00	1.10	....	1.07

[a] From Table I of J. J. Bucher and R. M. Diamond, J. Phys. Chem. **69**, 1565 (1965). The ratio was determined by appropriate analytical procedures after benzene, *o*-dichlorobenzene, and nitrobenzene solutions of trilaurylamine (~0.1 *M*) had been equilibrated with aqueous perchloric acid of various concentrations by shaking for an hour.

[b] Corrected for $HClO_4$ extracted by the pure solvent.

REFERENCE:

[442] J. J. Bucher and R. M. Diamond, J. Phys. Chem. **69**, 1565 (1965).

b. Other acids. Table 65 lists conditions under which the homoconjugate anions of several common mineral acids (HBr, HCl, HNO_3, H_2SO_4) and some related organic acids (camphor- and methanesulfonic acids) have been observed to form. [Also see table 62.]

The di-(2-ethylhexyl) ester of orthophosphoric acid is also believed to form a homoconjugate anion in toluene [513, 514]. After an x-ray examination of *crystalline* di-*p*-chlorophenyl hydrogen phosphate [517], Calleri and Speakman formed the opinion that the hydrogen bond linking a molecule of this acid with the anion of a second molecule may be "genuinely symmetrical" (and probably, therefore, comparatively strong). No corresponding studies seem to have been made for a related acid salt.

Estimates of $K_{A^{-}\cdots H\text{-}A}$ for HBr, HCl, HNO_3, and H_2SO_4 in *acetonitrile* solutions [500, 516] are included in table 65. Apparently the first three of these acids are moderately, and about equally, homoconjugated in this solvent, and H_2SO_4 is considerably more so.

The work reviewed has made clear that anion homoconjugation is to be expected in solvents of little or no proton-donor ability, the dielectric constant having, at most, a minor role, and it has also extended our understanding of the role of water and alcohols as ionizing media. These conclusions were aptly expressed by Hammett [515], following a study of sulfuric acid-indicator reactions in *nitromethane:* "The clear implication is that the reaction of one molecule of acid with one molecule of base as it is observed in waterlike solvents requires as an indispensable factor the solvation of the anion, presumably by hydrogen bonding between the acidic hydrogen of the solvent and the unshared electrons of the anion. In the absence of solvent molecules with the necessary properties the transfer of the proton from the acid to the base may require the drafting of an additional molecule or molecules of the acid to perform the function fulfilled by the solvent in waterlike systems."

4.5.7. Heteroconjugate Anions

The conclusions just quoted are documented still more strongly and directly by systematic investigations of heteroconjugation of anions. The majority of such studies have been concerned with hydrogen bonding to X^- (halide) ions, especially Br^- (see tables 66 to 69). A much smaller number (see table 70) have dealt with bonding to carboxylate, nitrate, or bisulfate.

a. Chemical behavior. The earliest observations were made without the aid of instruments. Using a method devised by Hantzsch [18], in which the comparative strengths of acids are determined by ascertaining how much ether must be added to red salts of the indicator base, methyl yellow, before the color reverts to yellow, Meerwein observed [495] that for the hydrochloride this point was reached on dilution to about 0.02 *N*. However, with benzoic acid (or another organic acid), even in its saturated ether solutions, the indicator remained yellow. Meerwein then mixed the two yellow solutions, whereupon the color instantly became red, and considerably more ether had to be added before the color was again yellow. He concluded that the intensified acid reaction was caused by the formation of a complex of HCl and RCOOH, which he represented as $[HCl \cdot OCOR]H$.

Dietzel and Paul [540] discovered that in titrations of alkaloids with *p*-toluenesulfonic acid in *chloro-*

TABLE 65. *Homoconjugate anion formation from miscellaneous organic and inorganic acids, deduced in studies of solutions*

Solvent	Acid	Base or cation present	Method[a]	$K_{A^- \ldots HA}$	References
Acetonitrile	Hydrobromic	In[c]	VIS	[b] 280	[500, 516]
	Hydrochloric	In[c]	VIS	[b] 170	[500, 516]
	Nitric	In[c]	VIS	200	[500]
	Sulfuric	In[c]	VIS	1,150	[500]
	Sulfuric	Na^+	S	1,000	[516]
	Sulfuric	n-$BuNH_2$	C	....	[479]
Chloroform	Hydrocyanic	R_3N	D	....	[409]
	Nitric	R_3N	D	....	[409]
Dioxane	*dl*-Camphorsulfonic	Et_3N or Bu_2NH	C	....	[341]
Nitrobenzene	Methanesulfonic	Py-type	ΔH	....	[512]
Nitromethane	Sulfuric	In[c, d]	VIS	....	[515]
Toluene	Di-(2-ethylhexyl) phosphate	La^{+3}	D, CRY	....	[513, 514]

[a] ΔH signifies heat of reaction. Other symbols have the same significance as in the preceding tables.

[b] Note that these values are slightly different from those cited in table 62.

[c] In this table "In" signifies an indicator of the nitroaniline ("Hammett") type.

[d] In >0.1 M H_2SO_4 solutions an indicator salt of the composition $InH^+ \ldots OS(OH)(O \ldots HOSO_3H)_2$ was thought to be formed.

REFERENCES:

[341] A. A. Maryott, J. Res. NBS **38**, 527 (1947).
[479] I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc. **85**, 426 (1963).
[500] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., J. Am. Chem. Soc. **83**, 3927 (1961).
[512] H. C. Brown and R. R. Holmes, J. Am. Chem. Soc. **77**, 1727 (1955).
[513] D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoll, J. Inorg. Nucl. Chem **4**, 334 (1957).
[514] D. F. Peppard, J. R. Ferraro, and G. W. Mason, J. Inorg. Nucl. Chem. **4**, 371 (1957).
[515] H. Van Looy and L. P. Hammett, J. Am. Chem. Soc. **81**, 3872 (1959).
[516] I. M. Kolthoff and M. K. Chantooni, Jr., J. Phys. Chem. **66**, 1675 (1962).
[409] J. I. Bullock, S. S. Choi, D. A. Goodrick, D. G. Tuck, and E. J. Woodhouse, J. Phys. Chem. **68**, 2687 (1964).

form, with methyl yellow as the indicator, the endpoint could be made sharper by adding about 1 percent of phenol, but did not suggest an explanation. Here, it seems reasonable to postulate hydrogen bonding of phenol to one or more sulfonate oxygens, with consequent enhanced strength of the sulfonic acid.

Later, intensified acid reactions were attributed *by their discoverers* to hydrogen bonding. For instance, Bartlett and Dauben [518] found that the strength of HCl in *dioxane*, measured by an indicator method, is increased on adding any of the following proton-donor molecules: Methanol, ethanol, isopropyl alcohol; phenol, *o*- and *p*-cresol, *o*- and *p*-chlorophenol; 2,4,6-trichlorophenol; *p*-cyanophenol; acetic acid. They ascribed the enhanced strength of HCl to bonding of Cl to the proton donor, and remarked that "hydrogen bond formation appears to run parallel to the acid strength in the series of phenols except for phenols with ortho-substituents capable of intramolecular hydrogen bonding, which are far less efficient 'acceptors' than would be expected from their acid strength."

Similar reasoning has been used in explaining results of reaction rate studies. As an illustration, Swain [537] found that the conversion of trityl chloride or bromide to trityl methyl ether by reaction with MeOH in *benzene* (a base such as Py or Et_3N being present to combine with HX, the by-product) is greatly accelerated by adding phenol, and even more so by adding *p*-nitrophenol. After eliminating other possible explanations, Swain concluded that the increased rates are a consequence of hydrogen bonding to the halogen of trityl chloride to form $Ph_3C{-}X \ldots HOAr$, thereby weakening the attachment of HX to the methane carbon and facilitating its replacement by OMe (compare eq 71).

Analogously, in the reaction of *tert.*-butyl bromide in *nitromethane* with various OH derivatives (water,

TABLE 66. *Examples of heteroconjugate halide ion* ($X^-...H-A$) *formation in several aprotic solvents* [a]

Solvent	HA [b]	X^-	References
Acetonitrile [c]	HCl, DCl	Br^-	[529]
Benzene	HCl, DCl [c]	Br^-	[529]
	HNO_3 [d]	Cl^-	[497]
	ROH [d]	Br^-	[519]
	ROH	Br^-, Cl^-	[521, 522]
	$CH_3CONHCH_3$	Br^-	[521, 522]
Carbon tetrachloride	HOH [e]	Br^-, Cl^-, F^-, I^-	[528]
	ROH	Br^-, Cl^-, F^-, I^-	[520, 524, 525]
	ROH	I^- [f]	[526]
	ArOH	Br^-, Cl^-	[520, 525]
	CDX_3	Br^-, Cl^-	[525]
	$HC{\equiv}C \cdot CH_2Br$	Br^-, I^-	[525]
	R_2NH, RNHAr, or Ar_2NH	Br^-	[520]
Chloroform	ArOH	Br^-, Cl^-, I^-	[520]
Dichloromethane	HCl, DCl [c]	Br^-	[529]
	ROH	Br^-, Cl^-, F^-, I^-	[525]
	ROH	I^- [g]	[527]
Dioxane [h]	ROH, ArOH, RCOOH	Cl^-	[518]
Ethyl ether [h]	RCOOH	Cl^-	[495]
Nitrobenzene [d]	ROH	Br^-	[47]
Nitromethane [d]	ROH	Br^-	[519]

[a] Except when indicated otherwise, solutions contained a mixture of $R_4N^+X^-$ and HA, and $X^-...H-A$ formation was deduced from shifted $\nu(H-A)$.

[b] R denotes an alkyl group and Ar, an aryl group.

[c] Both IR and Raman spectra were measured.

[d] Formation of $X^-...H-A$ was deduced from conductance data.

[e] Bu_3NH^+ and $Bu_2NH_2^+$, also, were used as cations.

[f] Both IR and UV absorption were measured, the IR data showing the effect of $I^-...HOR$ formation on $\nu(O-H)$ and the UV data showing its effect on absorption by I^-.

[g] From UV absorption data only.

[h] Enhancement of acid strength resulting from $Cl^-...H-A$ formation caused the indicator base methyl yellow to turn red.

REFERENCES:

[47] H. Sadek and R. M. Fuoss, J. Am. Chem. Soc. **72**, 301 (1950).
[495] H. Meerwein, Ann. Chem. **455**, 227 (1927).
[497] E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker, J. Chem. Soc., p. 1206 (1957).
[518] P. D. Bartlett and H. J. Dauben, Jr., J. Am. Chem. Soc. **62**, 1339 (1940).
[519] R. C. Miller and R. M. Fuoss, J. Am. Chem. Soc. **75**, 3076 (1953).
[520] H. Lund, Acta Chem. Scand. **12**, 298 (1958).
[521] J. Bufalini and K. H. Stern, Science **130**, 1249 (1959).
[522] J. Bufalini and K. H. Stern, J. Am. Chem. Soc. **83**, 4362 (1961).
[524] J. B. Hyne and R. M. Levy, Can. J. Chem. **40**, 692 (1962).
[525] A. Allerhand and P. von R. Schleyer, J. Am. Chem. Soc. **85**, 1233 (1963).
[526] M. J. Blandamer, T. E. Gough, and M. C. R. Symons, Trans. Faraday Soc. **60**, 488 (1964).
[527] M. J. Blandamer, T. E. Gough, and M. C. R. Symons, Trans. Faraday Soc. **62**, 296 (1966).
[528] S. C. Mohr, W. D. Wilk, and G. M. Barrow, J. Am. Chem. Soc. **87**, 3048 (1965).
[529] J. C. Evans and G. Y-S. Lo, J. Phys. Chem. **70**, 20 (1966).

alcohols, phenols, carboxylic acids) the latter are considered to assist the ionization of the bromide. Gelles, Hughes, and Ingold [538] found the effectiveness of phenol, water, and ethanol to decrease in the order named. Subsequently, Pocker [539] extended these results, using a variety of alcohols and phenols, and also acetic and benzoic acids. For *alcohols*, the catalytic order proved to be:

$$\mathrm{PhCH_2OH} > \mathrm{MeOH} > \mathrm{EtOH} > n\text{-}\mathrm{PrOH} > n\text{-}\mathrm{BuOH} > i\text{-}\mathrm{PrOH} > s\text{-}\mathrm{BuOH} > t\text{-}\mathrm{BuOH}.$$

The catalytic order found for *phenols* was as indicated by the following list of substituents (pK_a values in parentheses):

$$p\text{-}\mathrm{NO_2}\ (7.15) > p\text{-}\mathrm{CN}\ (7.97) > p\text{-}\mathrm{I}\ (9.30) > p\text{-}\mathrm{Br}\ (9.36) > p\text{-}\mathrm{Cl}\ (9.42) > \mathrm{None}\ (10.00) > m\text{-}\mathrm{Me}\ (10.09) > p\text{-}\mathrm{Me}\ (10.26) > p\text{-}t\text{-}\mathrm{Bu} > p\text{-}\mathrm{MeO}\ (10.21).$$

To explain the comparatively low ability of the two carboxylic acids to assist the ionization of *t*-BuBr in nitromethane it was suggested that in this solvent they are largely present as the dimers.

b. Physical measurements. The remaining examples of anion heteroconjugation were studied with the aid of physical methods, principally conductance and infrared or ultraviolet absorption spectroscopy.

Table 66 is a listing of examples in which F^-, Cl^-, Br^-, or I^- is arbitrarily regarded as being the proton acceptor, and the proton donor is one of the following chemical types (all of which are known to be weaker acids than HX): Water, alcohols, phenols, carboxylic acids, an acetylene derivative (propargyl bromide), chloroform-d, an amide, or a secondary amine (specifically, Bu_2NH, PhNHMe, Ph_2NH, or indole). In addition there are examples of bonding of HCl or DCl to Br^-. Another inclusion—the bonding of HNO_3 to Cl^-—was mentioned previously in the discussion of table 61.

Continued study of such systems has been inspired in part by *conductance data* indicating solute-solvent interaction. In two early examples, the results for Bu_4NBr and related salts in *mixtures* of *methanol* with *nitrobenzene* [47], *nitromethane* [519], or *benzene* [519] (supplemented by other pertinent data, such as dielectric constants, viscosities, and spectral absorption) were not consistent with a "continuum theory." Instead, the solute was ". . . seen to behave like two or three different substances, depending on whether it is in solvent A, solvent B, or a mixture of the two . . .," and the authors concluded that ". . . this seeming absurdity can only be accounted for by postulating that the actual solute particles are different in the three cases; this can only occur if there is specific interaction between solute and solvent" [519]. In a preceding paper [47] the specific suggestion was made that in $MeOH-PhNO_2$ mixtures the anion associates with MeOH and the cation, with $PhNO_2$, as represented by (LXXXVII):

$$\mathrm{Bu_4N^+.(^-O_2N^+C_6H_5).Br^-(^+HO^-CH_3)}$$

(LXXXVII)

Several papers dealing with infrared studies soon demonstrated that conductance behavior of the sort just mentioned is indeed caused in part by hydrogen bonding of proton-donor molecules to anions. In the first of these papers, Lund [520] listed shifts in ν(O–H) values for a number of proton donors caused by adding anions to their solutions in carbon tetrachloride or chloroform. For example, table 67 shows comparative ν(O–H) shifts for *p*-cresol in *chloroform* when the anion was varied. Lund pointed out that the spectral shifts vary inversely with the apparent molar volumes of the anions (in cc per mole), as computed by Fajans and Johnson [530] for infinitely dilute solutions in water. Of the anions listed, ClO_4^-, the anion of lowest electron density, is clearly the poorest proton acceptor, the best proton acceptor being Cl^-, the anion of highest electron density.

Table 68, also based on results of Lund, compares the effects of added Br^- on ν(O–H) for a series of proton donors, the solvent in this experiment being

TABLE 67. *Comparative shifts of* ν(O–H) *of* p-cresol, *0.10* M *in* $CHCl_3$, *produced by adding different anions as* R_4N^+ *salts* [a, b, c]

Anion (0.031 *M*)	Apparent molar vol. of anion [d]	Δν, cm⁻¹
ClO_4^-	44.5	−180
I^-	36.7	−340
NO_3^-	29.4	−400
Br^-	25.1	−405
Pi^-	………………	−405
Cl^-	18.0	−445

[a] Adapted from Table 2 of H. Lund, Acta Chem. Scand. **12**, 298 (1958).

[b] In the chloride R_4N^+ was $(Bu_3NCH_2Ph)^+$, but in all the other salts it was Bu_4N^+.

[c] Chloroform was used as solvent because of the low solubilities of some of the salts in CCl_4; it was recognized as being a competing proton donor.

[d] The values cited are from ref. [530]. Units are cc per mole.

REFERENCES:

[520] H. Lund, Acta Chem. Scand. **12**, 298 (1958).

[530] K. Fajans and O. Johnson, J. Am. Chem. Soc. **64**, 668 (1942).

TABLE 68. *Shifts in* ν(O–H) *for some alcohols and phenols in* CCl_4, *produced by adding 0.031* M Bu_4NBr[a]

Proton donor	$pK_a(H_2O)$ [b]	$\Delta\nu$, cm^{-1}
tert-Butyl alcohol	....	−275
iso-Propyl alcohol	....	−275
Ethanol	[c] 16	−285
2,2,2-Trichloroethanol	[c] 12.24	−330
2,4,6-Trimethylphenol	[d] 10.89	−365
o-Cresol	10.29	−400
p-Cresol	10.26	−402
Phenol	10.00	−405
2,4-Dibromophenol	[e] 7.79	[f] −420
2,4-Dichlorophenol	7.85	[f] −450
2,4,6-Tribromophenol	[g] 5.9 [h] 6.24	−505
2,4,6-Trichlorophenol	[g] 5.5 [h] 6.48 [i] 6.46	−535

[a] Adapted from Table 1 of H. Lund [520].

[b] Except as noted otherwise, pK_a values are from ref. [271], Appendix 12.1, Table 5.

[c] Ref. [531]. The pK_a value for ethanol was obtained by an extrapolation.

[d] Ref. [532].

[e] Communicated by R. A. Robinson [533].

[f] It will be recalled (see fig. 8 and related discussion) that the ν(O–H) bands of various monomeric, mono-*o*-halophenols in CCl_4 have been found to have two peaks, one of which has been assigned to the *cis* (intramolecularly hydrogen-bonded) isomer and the other, to the *trans* isomer. The ν(O–H) shift cited here is the one assigned [209] to the *cis* isomer.

[g] Ref. [534].

[h] Calculated from pK_a values for the related monosubstituted phenols [535] on the assumption of additivity of substituent effects.

[i] Ref. [536].

REFERENCES:

[209] N. A. Puttnam, J. Chem. Soc., p. 486, 5100 (1960).
[520] H. Lund, Acta Chem. Scand. **12**, 298 (1958).
[531] F. A. Long and P. Balinger, *in* Electrolytes (Trieste Symposium, 1959, B. Pesce, ed.), p. 152 (Pergamon Press, New York, N.Y., 1962).
[532] H. C. Ko, W. F. O'Hara, T. Hu, and L. G. Hepler, J. Am. Chem. Soc. **86**, 1003 (1964).
[533] R. A. Robinson, unpublished work.
[534] A. G. Ogston, J. Chem. Soc., p. 1713 (1936).
[535] A. I. Biggs and R. A. Robinson, J. Chem. Soc., p. 388 (1961).
[536] G. T. Tiessens, Rec. Trav. Chim. **50**, 112 (1931).

carbon tetrachloride. Unmistakably, $\Delta\nu$ increases with increased strength of the proton donor. Recalling that some of the proton donors are chelated or hindered, we would not anticipate a perfect correlation. Lund's results for secondary amines as proton donors were not included in this table; they ranged from 130 cm^{-1} (for dibutylamine) to about 285 cm^{-1} (for indole).

Lund called attention to an analytical application of these findings: A band near 3μ in the spectra of quaternary ammonium halides in chloroform indicates the presence of ethanol, added as a stabilizer. No such band appears in the spectrum when the solvent is pure chloroform or chloroform stabilized with hexane.

Infrared results of Bufalini and Stern for *benzene* solutions [521, 522] added strong support to the overall conclusions of Lund. Moreover, when combined with dielectric data of Richardson and Stern [523] they indicated convincingly that in eq 74 the value of *n* is 1.

$$Bu_4N^+Br^- + nHOMe \rightleftharpoons Bu_4N^+Br^-\ldots nHOMe. \qquad (74)$$

The equilibrium constant obtained for this reaction (expressed as *log K*, molar units, 25°) is 1.81. Values approximating −6.6 and −14 were obtained for ΔH(kcal/mole) and ΔS (cal/mole deg), respectively.

Like Lund, they tested the effect of varying the proton acceptor (using Pi^-, NO_3^-, Br^-, or Cl^-) and the proton donor (MeOH, *n*-BuOH, *t*-BuOH, $CH_3CONHMe$), reaching the same overall conclusions almost *in toto.* Some conclusions of special interest are:

(1) Anion "solvation demand" in benzene-alcohol systems increases in the order:

$$Pi^- \ll NO_3^- < Br^- < Cl^-.$$

In fact, Pi^- did not seem to be solvated at all. This conclusion may appear at variance with Lund's result (table 67), but we must bear in mind that Lund used a much more active proton donor in his comparisons.

(2) A steric factor is very apparent in the comparative behavior of *n*- and *t*-butyl alcohols.

(3) The interaction of MeOH with $PhN(Me_2)HCl$ is much less than with Bu_4NCl. The reduced hydrogen bonding of Cl^- to HOMe is believed to be the results of strong hydrogen bonding to $PhN(Me_2)H^+$.

(4) Although not shifted by added Bu_4NClO_4, ν(O–H) for methanol *is* shifted by $AgClO_4$.

(5) The shift caused by adding *N*-methylacetamide indicates that anion solvation is not limited to the O–H group, and "the effect of even dilute electrolyte solutions on biologically important materials which exhibit hydrogen bonding may be quite significant."

Observations of Hyne and Levy, who studied the interaction of *n*-Bu_4NBr with *t*-BuOH in *carbon tetrachloride* [524], are in general agreement with those of the above-named authors. Minor respects in which their results differ from those of Bufalini and Stern are ascribed to the use of carbon tetrachloride as solvent instead of benzene.

Another investigation of similar character but greater scope was performed by Allerhand and Schleyer [525]. Here, the inert diluent was *carbon tetrachloride* or *dichloromethane.* Besides tetra-*n*-butylammonium fluoride, chloride, and bromide and tetraheptylammonium iodide, the salts studied included other kinds of "onium" compounds—for example, *N*-hexadecylpyridinium chloride, bromide, and iodide, *N*-methylquinolinium iodide, and tetraphenylarsonium chloride. The types of proton donors were also extended to include propargyl bromide and three deuterohaloforms. Very briefly summarized, the main conclusions were:

(1) The infrared spectral shifts observed for proton donors are caused by hydrogen bonding to anions;

(2) the magnitudes of the shifts depend strongly on the nature of the anion X^-, being in the order

$$Cl^- > F^- > Br^- > I^-;$$

(3) variations in the cation strongly affect the spectral shifts when the anion is Cl^-, but not when it is Br^- or I^-;

(4) covalently bound halogen atoms are very much weaker proton acceptors than X^-, and the order of spectral shifts found is the reverse of that in (2).

A noteworthy aspect of investigations by Blandamer, Gough, and Symons [526, 527] is that bonding of I^- to HOR was studied with respect to the effect on I^- (measured in the ultraviolet region) as well as the effect on ν(O–H). In the first of these papers, which dealt with the interaction of tetra-*n*-hexylammonium iodide with methanol in *carbon tetrachloride*, equilibrium constants were calculated from both the ultraviolet and the infrared data. Regarding the system as involving an equilibrium between "contact ion pairs" and "modified contact ion pairs" corresponding to eq 74, they derived values for n and K. From the *ultraviolet* data, $n=0.93$ and log K (molar units, 20° to 23°) $=1.199$, and from the *infrared* data, $n=1$ and log $K=1.137$. The ultraviolet absorption curves for different mixtures of methanol and carbon tetrachloride with a fixed concentration of the salt showed sharply defined isosbestic points.

In the second paper, ultraviolet spectra were determined for solutions in *dichloromethane*, with analogous results. Both methanol and *tert.*-pentyl alcohol were used as proton donors. Being hindered, the latter alcohol solvated I^- less completely than methanol.

Barrow and students [528] studied the association of *water* with F^-, Cl^-, Br^-, and I^- in *carbon tetrachloride*. Like their predecessors, they concluded that the spectral shifts observed indicate hydrogen bonding of the proton-donor molecule to X^-. Part of their experimental data are given in table 69. It will be seen that the order of anion effects indicated is

$$F^- \approx Cl^- > Br^- > I^-,$$

which is a little different from the anion order found by Allerhand and Schleyer. Table 69 also shows that values of $\Delta\bar{\nu}$ become smaller when Bu_4N^+ is replaced by Bu_3NH^+ or $Bu_2NH_2^+$, once again demonstrating that X^- is less easily bonded to a neutral proton donor when already hydrogen bonded to a cation.

Table 69. *Shifts in* ν(O–H) *of water on hydrogen bonding to* X^- *of* R_4NX, R_3NHX, *or* R_2NH_2X *in carbon tetrachloride* [a]

Identity of salt [b]	$\bar{\nu}$ (free)	$\bar{\nu}$ (bonded)	$\Delta\bar{\nu}$ [c]
Bu_4NF	3679	3307	372
Bu_4NCl	3678	3308	370
Bu_4NBr	3676	3376	300
Hp_4NI	3677	3422	255
Bu_3NHF	3682	3405	277
Bu_3NHCl	3679	3405	274
Bu_2NH_2Cl	3678	3447	231
Bu_3NHBr	3678	3429	249

[a] From Table II of S. C. Mohr, W. D. Wilk, and G. M. Barrow, J. Am. Chem. Soc. **87**, 3048 (1965). The temperature was not specified.

[b] 0.033 *M*.

[c] $\bar{\nu}$ (free) minus $\bar{\nu}$ (bonded).

Reference:

[528] S. C. Mohr, W. D. Wilk, and G. M. Barrow, J. Am. Chem. Soc. **87**, 3048 (1965).

Although the salt-water complex is believed to be representable by $Bu_4NX...HOH$ at low salt concentrations, hydrogen bonding to a second molecule of Bu_4NX is considered probable at high salt concentrations. Barrow also thinks two molecules of HOH can hydrogen bond to F^-.

This investigation also included a study of hydrogen bonding of some neutral bases B to water. The bases included acetone, acetonitrile, dimethylformamide, dioxane, ethyl acetate, ethyl ether, 4-picoline *N*-oxide, pyridazine, and pyridine. Conclusions were that B...HOH is formed at low concentrations of such bases, and B...HOH...B, at higher concentrations.

In a very recent publication [529] Evans and Lo reported a detailed study of quaternary ammonium salts containing the anion $(ClHBr)^-$ or $(ClDBr)^-$. *Acetonitrile*, *benzene*, and *dichloromethane* were used as solvents. Among other findings they concluded that in the mixed anion $(ClHBr)^-$ the H–Cl bond is stronger, and the H–Br bond is weaker, than in the respective homoconjugate anions.

There has been relatively little systematic investigation of heteroconjugation involving anions other than the halides. In the most complete such investigation, Kolthoff and Chantooni [429] studied the conjugation of $3,5\text{-}(NO_2)_2C_6H_3COO^-$ with *p*-bromophenol and with resorcinol in the solvent *acetonitrile*. The conjugation of HSO_4^- with resorcinol was studied less completely. The conditions of the experiments are outlined in Table 70, which also lists examples of conjugation of CH_3COO^- with *chloroform* in the same solvent (already discussed at length in sec. 4.3.5b) and conjugation of $HCOO^-$ and NO_3^- with methanol in *benzene* (in-

TABLE 70. *Miscellaneous other examples of heteroconjugate anions* ($A^-\ldots H{-}A'$), *studied in solution*

Anion, A^-	Proton donor, HA'	Solvent	Base or cation present	Method	References
Acetate	$CHCl_3$	$CHCl_3$	Et_3N	IR	[392]
	$CHCl_3$	$CHCl_3$	Et_2NH	IR	[393]
	$CHCl_3$	$CHCl_3$	n-$BuNH_2$	IR	[394]
Formate	CH_3OH	C_6H_6	Bu_4N^+	IR	[521, 522]
3,5-Dinitrobenzoate	[a] ArOH	CH_3CN	Et_3N	C	[429]
	[a] ArOH	CH_3CN	K^+	S	[429]
	[a] ArOH	CH_3CN	Et_4N^+	IR	[429]
Nitrate	CH_3OH	C_6H_6	Bu_4N^+	IR	[521, 522]
Bisulfate	[b] ArOH	CH_3CN	Py	C	[429]

[a] ArOH = p-Bromophenol or resorcinol. See accompanying discussion of heteroconjugate species formed under differing conditions.

[b] ArOH = resorcinol.

REFERENCES:

[392] G. M. Barrow and E. A. Yerger, J. Am. Chem. Soc. **76**, 5211 (1954).
[393] E. A. Yerger and G. M. Barrow, J. Am. Chem. Soc. **77**, 4474 (1955).
[394] E. A. Yerger and G. M. Barrow, J. Am. Chem. Soc. **77**, 6206 (1955).
[429] I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc. **85**, 2195 (1963).
[521] J. Bufalini and K. H. Stern, Science **130**, 1249 (1959).
[522] J. Bufalini and K. H. Stern, J. Am. Chem. Soc. **83**, 4362 (1961).

cluded in the studies of Bufalini and Stern). In all of the examples cited the authors concluded, from IR spectral shifts, that heteroconjugation involves hydrogen bonding of the proton donor to the anion.

In the studies of Kolthoff and Chantooni a number of simultaneous equilibria had to be taken into account, including homo- and heteroconjugation constants of anions and ion pair dissociation constants of homo- and heteroconjugate species of salts. The experimental work involved conductance titrations, infrared absorption measurements, and determinations of increases in the solubility of potassium 3,5-dinitrobenzoate on additions of p-bromophenol or resorcinol. Some of the principal conclusions were:

(1) In acetonitrile heteroconjugation of the 3,5-dinitrobenzoate ion with p-bromophenol occurs both in 1:1 ratio ($K_{A^-\ldots HA'}=360$) and 1:2 ratio ($K_{A^-\ldots 2HA'}=3900$).

(2) Heteroconjugation with resorcinol likewise occurs in 1:1 ratio ($K_{A^-\ldots HA'}=340$) and 1:2 ratio ($K_{A^-\ldots 2HA'}=5100$).

(3) The presence of two OH groups in resorcinol makes possible the formation of a 2:1 complex, also. The estimated value of $K_{A^-\ldots HOC_6H_4OH\ldots A^-}$ is 500. The 2:1 complex is thought to form when the molar concentration of dinitrobenzoate exceeds that of resorcinol.

(4) By using the stability constants cited, in conjunction with other data and reasonable assumptions, conductance titration curves can be calculated that are in satisfactory agreement with experimental titration curves.

(5) Heteroconjugation, like homoconjugation, greatly increases ion pair dissociation of a salt BH^+A^-, and consequently, the conductance. Heteroconjugation is not necessarily beneficial, however, from an analytical viewpoint. In contrast to homoconjugation, which causes a sharp maximum to appear in conductance titration curves near half-neutralization of an acid, thus aiding in location of the end-point, heteroconjugation may cause this maximum to be eliminated and the end-point to become obscured.

However, heteroconjugation is probably sometimes beneficial in analytical titrations. For example, Dietzel and Paul [540] and also Trautner and Shaw [541], when titrating various amines and alkaloids with 0.05 M toluenesulfonic acid in *chloroform*, with methyl yellow as the indicator (an application of Vorländer's "aminometric" method [542–544]), found that the addition of 1 percent of phenol by volume led to a sharper color change. As remarked earlier, hydrogen bonding of phenol to the sulfonate ion seems a reasonable explanation.

Kolthoff and associates have commented on the comparative behavior of *acetic acid* and *acetonitrile* as solvents [500]. In spite of having a far lower dielectric constant than acetonitrile, acetic acid is a much better medium for ion pair dissociation, undoubtedly because it hydrogen bonds to anions such as HSO_4^- and Cl^-, while acetonitrile cannot do so.

As a final example of probable heteroconjugation through hydrogen bonding, mention may be made of spectrophotometric studies by Steigman and Lorenz [545], using mixtures of a phenolic indicator (2,4-dinitrophenol or bromophthalein magenta E) with dialkylammonium or quaternary ammonium salts in benzene. The authors ascribed spectral evidence of increased acid-base interactions to the formation of "unsymmetrical anionic triple ions." Their interpretation of results was made somewhat difficult by a competing hydrogen bonding reaction (dimerization of secondary ammonium salts) and interaction of quaternary ammonium salts with the glass container. Such a reaction with glass has been attributed to ion-exchange [546].

4.6. Concluding Discussion of Hydrogen Bonding

4.6.1. Definition of a Hydrogen Bond. Systems Which Form Hydrogen Bonds

It may seem illogical to have postponed defining a hydrogen bond until the end of this lengthy discussion, but it has been assumed that readers already have some knowledge of hydrogen bonding. Moreover, as recently as 1957, at the Ljubljana Symposium on Hydrogen Bonding, the assembled experts considered it worthwhile to devote their final discussion to a possible clarification or reframing of the definition of a hydrogen bond. For example, it was suggested that it might be well to distinguish between hydrogen bonding to an *n*-electron donor and bonding to a π-electron donor. However, there seemed to be a consensus in favor of Pimentel's "operational definition," according to which a hydrogen bond is said to exist when the following two criteria have been met:

(1) there is evidence of molecular association; and

(2) there is evidence that this association involves bonding to a hydrogen atom already bonded to another atom [102, 547].

An alternative definition based on such arbitrary criteria as a minimum energy of interaction or the magnitudes of spectral shifts would obviously not be satisfactory.

If Pimentel's definition is adopted, it is clear that his dual criteria are met in the systems given special emphasis here—symbolized by $B{-}H^+ \ldots A^-$, $B{-}H^+ \ldots B$, $B{-}H^+ \ldots B'$, $A^- \ldots H{-}A$, and $A^- \ldots H{-}A'$—and from one standpoint this review can be regarded as a supplement to Pimentel and McClellan's compendium [102] on hydrogen bonding, which deals mainly with bonding of type $B \ldots H{-}A$. Correspondingly, their book has been regarded as a supplement to our discussion, and it has not been thought necessary or desirable to discuss formally examples of hydrogen bonding given thorough treatment by them—for example, self-aggregation of alcohols and amines, and the bonding of alcoholic OH to the oxygen of esters, ethers, and ketones.

The adoption of Pimentel's operational definition of the hydrogen bond implies a simultaneous acquiescence in the view that hydrogen bonding is of far wider occurrence than was formerly supposed. For example, one accepts the view that H–C in haloforms and mono-substituted acetylenes is a proton-donor group, and that π-electron donors should be grouped with *n*-electron donors.

The evidence regarding hydrogen bonding that has been brought together in this review, in combination with the evidence compiled by Pimentel and McClellan, may be likened to an assembled jigsaw puzzle. There can no longer be doubt that hydrogen bonding plays an extremely vital role in acid-base behavior, leading to the formation of many types of aggregates, that vary widely in stability. Moreover, it seems quite probable that some of these aggregates exist in water, as well as in aprotic solvents. However, water is not a suitable solvent for determining their characteristics because it is involved so actively in hydrogen bonding reactions. Thus, as Brønsted foresaw [13], systematic investigations of individual acid-base systems in aprotic solvents have yielded a more eomprehensive and deeper insight into acid-base behavior than that resulting from studies employing water and waterlike solvents.

Clearly, the overall composition of systems consisting of aprotic diluents mixed with a variety of proton-acceptor and proton-donor species will depend on such factors as the *number* of interacting species, their relative *concentrations*, the relative proton donor-acceptor *affinities*, and particle *shapes* and *sizes*. To attain desired results in practical situations it is advisable not to add solvents and reactants when they are not known to be essential or beneficial.

Numerous values of hydrogen bonding equilibrium constants have already been given—mostly in the tables, but also, in some cases, in the text. Section 5 will contain tables of values for log K_{BHA} in which a variety of bases, acids, and aprotic solvents are represented. When available, values of ΔH and ΔS will also be given. It will be seen that these results represent merely a good start toward the accumulation of hydrogen bonding equilibrium constants. More, as well as better, data are much needed. Interesting possibilities for additional studies of hydrogen bonding in aprotic solvents are suggested by Leffler and Grunwald's brief discussion of "lifetimes of solvation complexes" [548]. Examples referred to are a benzene-picric acid complex with a lifetime greater than 5×10^{-11} sec (20°) and determinations of rate constants for the dissociation of dimeric benzoic acid in carbon tetrachloride and toluene.

4.6.2. Some Recent Concepts of Hydrogen Bonding

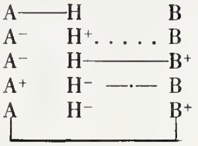
The theory of hydrogen bonding is certainly relevant to our discussion—in fact, it was necessary in section 4.3.5b to anticipate some of the discussion of this section. However, there is agreement among theoreticians that a theory accounting satisfactorily for all hydrogen bonding phenomena has not yet been developed. Writing on this subject around 1960, Pimentel said [102]: "Today the theory remains a subject of considerable controversy, its qualitative predictive power is limited, and it has almost no quantitative predictive power. It seems certain that the full impact of the H bond upon our general theory of the chemical bond has not yet been realized."

There is a need for improved communications between theoreticians and those concerned with chemical and physical manifestations of hydrogen bonding. Not infrequently, theoreticians seem to have based their attempts to develop a theory on a too restrictive concept of the scope of hydrogen bonding interactions and the range of energy changes involved, whereas experimentalists have sometimes been over-ready to adopt a theoretical explanation without eliminating alternative explanations. It is hoped that theoreticians will be aided by the foregoing summary of experimental results. Our remaining discussion will represent an attempt to aid experimentalists wishing to have a brief outline of some modifications which the theory has undergone and to be directed to more extensive and authoritative reviews.

Since the formal presentation of Latimer and Rodebush's theory in 1920 the theory of the hydrogen bond has undergone considerable alteration. Their conception of a weak hydrogen bond was a "hydrogen nucleus held between 2 octets," and they believed there could be continuous gradations in hydrogen bonding, ranging from the case of associated water molecules, where the bonding hydrogen was thought to be "held quite firmly to the original water molecule," to ammonium chloride, where complete transfer of hydrogen from chlorine to ammonia was considered to occur [549].

Before long, however, Pauling pointed out that the hydrogen atom, having only one stable orbital (the 1*s* orbital) can form only one covalent bond; hence, in an aggregate of the type B...H–A the hydrogen bond to B must be largely electrostatic in character [190b].

As time passed, more and more theoreticians expressed the view that, while electrostatic attraction must be a factor in hydrogen bonding, it does not account for all hydrogen bonding phenomena. For example, if it were the sole factor, there should be a correlation between the dipole moment of the electron donor and the strength of a hydrogen bond, whereas Gordy and Stanford found there to be a complete absence of such a correlation in their infrared studies of the interaction of CH_3OD with electron-donor liquids of varied types [550, 551, 102]. Furthermore, increases in the intensity of the ν(O–H) absorption band on hydrogen bond formation are sometimes far in excess of the increase expected for a purely electrostatic model [551, 102]. In Coulson's opinion [551], the excessively large increases "imply that during the motion of the proton there are larger fluctuations of charge when the hydrogen bond is formed than when it is not formed. This seems to be possible only if charge can move on to and away from the farther atom (e.g., O_2 in O_1–H...O_2) during the vibrations of H. Thus effects due to the enhanced intensity of vibrational transitions in the infrared and the change of vibration frequency on compression seem to require what is now often referred to as a delocalization of electrons away from and on to the O_1–H region from the O_2 region . . ." Attempts have been made to estimate the relative importance of electrostatic and covalent contributions in hydrogen bonding interactions (for examples, see refs. [27, 551, 552, 102, 375, 376]), on the assumption of contributing *valence bond* structures analogous to those shown below [102]:



A——H B (Covalent A–H bond)
A^- H^+. . . . . B (Ionic; no charge transfer)
A^- H————B^+ (Covalent H–B bond with charge transfer)
A^+ H^- —·— B (Ionic; no charge transfer)
A H^- B^+ (Covalent A–B bond with charge transfer).

Pimentel has commented on some defects of this approach, and foresees a probable "turn toward the molecular orbital approach [102]."

Mulliken's ideas about hydrogen bonding, mentioned in a recent very concise review [553], will undoubtedly be enlarged on in a book said to be in preparation.

A continuing divergence of opinion is indicated by comments by Longuet-Higgins [554] and Ubbelohde [555] at a "Symposium on Molecular Interactions in the Liquid Phase" (during which Mulliken's paper [553] was presented). Longuet-Higgins expressed the view that "broadly speaking one may distinguish weak hydrogen bonds, which occur very widely, from strong hydrogen bonds, which are much less common . . . ." On the other hand, Ubbelohde, who believes that resonance effects become progressively more prominent as hydrogen bonds become shorter and stronger, regards it as "unlikely that a really sharp distinction can be made between weak and strong hydrogen bonds in the sense suggested by Longuet-Higgins . . . ." Instead, he thinks "a whole spectrum of hydrogen bonds appears to exist."

In the last decade or two, increasing emphasis has been placed on the *mobility of the proton within* hydrogen bonds (for example, see refs. [102, 25, 395, 396, 450, 551–552, 556–567] and additional references cited therein). This is well illustrated by Zimmermann's discussion of "Protonic States in Chemistry" [562]. He begins with a reminder that any elementary particle may be described as a wave or as a corpuscle, adding that the wave picture has been used to advantage by chemists in describing the behavior of electrons, whereas the proton, with more than 1800 times the mass of the electron, is generally represented as a corpuscle located in a more or less fixed position in a molecule. He then points out that the proton is smaller than other atoms by about five orders of magnitude, concluding that "it therefore seems reasonable to base the description of protons in chemistry on the wave picture as well. According to this view, states are supposed to exist for protons, much as in the case of electrons, in which protons are delocalized" [562].

Applying this idea to intermolecular hydrogen bonding, Zimmermann states that a hydrogen bond represents the joining of a Brønsted acid-base pair to give $B\ldots H{-}A$, and it is reasonable to presume that there can be proton transfer within the bond to yield a polar form, $B^+{-}H\ldots A^-$. Some *limiting conditions* which can be visualized for the potential energy and for protonic states in hydrogen bonds are indicated by the four *hypothetical* potential energy curves in figure 24. The different situations represented are as follows:

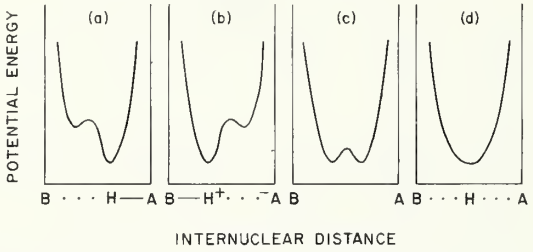


FIGURE 24. *Hypothetical potential energy curves for four classes of hydrogen bonding, indicating limiting conditions for proton states; suggested by Fig. 5 of H. Zimmermann, Angew. Chem. Intern. Ed. Engl.* **3**, *157 (1964).* (Ref. No. 562)

(a) A weak proton donor HA is bonded to a weak proton acceptor B. The proton remains near A in its *ground* state. The complex, $B\ldots H{-}A$, is referred to as a "hydrogen-bonded complex."

(b) The proton donor and acceptor are both strong. The proton shifts from A toward B. The product, symbolized by $B{-}H^+\ldots A^-$, is now commonly called "a hydrogen-bonded ion pair."

(c) The proton donor and acceptor are both intermediate in strength. The proton is about equally likely to be located at a covalent bond length from B and a covalent bond length from A. The potential energy troughs are about the same in depth, and the barrier separating them is low, hence the proton can shift toward B or toward A by "leaping over" the barrier or "tunneling through." This means that $B\ldots H{-}A$ will be in equilibrium with $B{-}H^+\ldots A^-$.

(d) B and A are both extremely good electron donors, and the hydrogen bond is very short. In its ground state the proton stays about mid-way between B and A. The homoconjugate anion HF_2^- is considered the prime example (recall sec. 4.5.5).

The "tunnel effect," not possible according to classical theory but quite plausible according to the quantum-mechanical picture, has become an important concept of modern chemistry. It is thought to have been demonstrated experimentally in studies of the infrared and Raman spectra of imidazole [187, 562]. It has provided an explanation for the "inversion" of the ammonia molecule, is frequently invoked in discussions of the kinetics of proton transfer processes (for illustrations, see refs. [559, 563, 567]), and it may have major biological implications [561].

The concept represented by figure 24(c), which Zimmermann refers to as "protomerism" [562], seems to have been suitably applied in his studies of the imidazole spectrum. As we saw in section 4.3.5b, Barrow and Bell [395, 396] interpreted infrared and electronic spectral absorbance data as demonstrating that triethylammonium *p*-nitrophenolate and pyridinium dichloroacetate are authentic examples of salts which exist in aprotic solvents as equilibrium mixtures of the two protomers, $B\ldots H{-}A$ and $B{-}H^+\ldots A^-$. Furthermore, they believe that many other salts probably belong in the same category. The writer has given a few specific reasons for unwillingness to accept these particular conclusions, and believes that the point at issue is too important for final acceptance of Barrow's interpretation without more extensive experimental documentation and systematic elimination of alternative explanations. Appropriate additional information would include acid-base equilibrium constants and conductance data.

It is appropriate to note here that since 1960 proton transfer reactions of *excited* molecules have received increasing attention. Weller and his associates [568, 571] and Mataga, Kawasaki, and Torihashi [569, 570] are prominent among those pioneering in the field. Solvents used in the investigations include acetonitrile [569, 571], benzene [569], *n*-butyl chloride [571], chlorobenzene [569], *o*-chlorotoluene [571], ethylene chloride [569], methylcyclohexane [568, 571], toluene [571] and water [568].

5. Acidity and Basicity Scales in Aprotic Organic Solvents

5.1. Early Attempts to Determine Relative Acidities

New ideas about acid-base behavior which were propounded by Hantzsch and by Brønsted, starting in the early 1920's, made a strong appeal to many young chemists of that period. With the widening recognition that the presence of water is not a prerequisite for acid-base behavior there began varied attempts to determine relative strengths of acids dissolved in solvents like benzene, chlorobenzene, chloroform, and ether. Hantzsch and his associates, using two kinetic methods and a static method, demonstrated that acids which appear equally strong in aqueous solutions (including perchloric, hydrochloric, and nitric acids) display markedly different strengths in organic solvents such as those named (for examples and discussion, see refs. [18, 426, 572, 19, 22, 425]). One criterion of relative strength was the effectiveness of an acid in accelerating the decomposition of ethyl diazoacetate. The static method usually employed methyl yellow, which forms fairly stable red salts with the stronger acids. The relative strength of an acid was denoted by the quantity needed for conversion of the original yellow color to red, or, alternatively, by the volume of an "indifferent" solvent that had to be added to effect dissociation of the red salt into the constituent base and acid. Weissberger and Fasold [22] tried to determine the equilibrium constant for 1:1 association of methyl yellow with trichloroacetic acid in benzene and in chloroform (and also studied the influence of addenda on this equilibrium in benzene). The results did not correspond to a simple 1:1 equilibrium. With the benefit of present knowledge, summarized in earlier sections, it is clear that this was not a suitable acid-base system for demonstrating the validity of Hantzsch's basic concepts. Moreover, at the time of the experiments spectrometric equipment enjoyed by present-day chemists was not available.

Investigators of the Brønsted school also performed static experiments using indicators and studied acid-catalyzed reactions in such solvents as benzene and chloroform (for illustrations, see refs. [10, 491, 357, 573, 492, 493, 355]; conductance and potentiometry were also employed in attempts to derive acidity scales [340]. Reference was made in section 4.5.4b to experiments in which the catalytic effects of a series of carboxylic acids and halophenols, dissolved in chlorobenzene, were related to their aqueous strengths by a simple equation (into which, unaccountably, picric acid did not fit). In other experiments, employing 2,6-dinitrophenol and bromophenol blue (the change from colorless to yellow [29]), Griffiths also found [355] that the strengths of a series of carboxylic acids in chlorobenzene closely paralleled their strengths in water.

Somewhat later, Bodforss [574] had the novel idea of using an optically active base (brucine) and measuring the changes in optical rotation on its reaction with a large group of aliphatic and aromatic carboxylic acids in benzene and in chloroform. "Empirical acid constants" indicated a general, though imperfect, parallelism of strengths in the aprotic solvent and in water. Bodforss concluded that the equilibria did not appear to conform to the mass action law.

The first successful demonstration of the correctness of Hantzsch's claim that the fundamental acid-base reaction in an aprotic solvent is an *association* seems to have been obtained in a spectrophotometric investigation of reactions of the indicator acid bromophthalein magenta E in benzene with bases such as triethylamine or 1,3-diphenylguanidine [14]. Equilibrium constants were calculated for the 1 : 1 association of B with HA to give BHA. Shortly thereafter, similar equilibrium constants were obtained for the reaction of tribenzylamine with picric acid [23, 20] and with trinitro-*m*-cresol [20] in benzene. The equilibrium involving tribenzylamine, picric acid, and tribenzylammonium picrate was studied both dielectrometrically [23] and spectrophotometrically [20], with results in excellent concordance. One reason why these systems were suitable for testing Hantzsch's postulate is that the reference acids are *monomeric* in an aprotic solvent. There are no competing hydrogen bonding reactions of significance at the concentrations employed; moreover, any dissociation of the salt into ions is negligible in extent.

Other examples soon followed. Among the first was Bell and Bayles' survey [354] of the reactivities of various aliphatic and aromatic amines with 2,6-dinitrophenol or bromophenol blue (first step, colorless to yellow) in chlorobenzene.

5.2. Log K_{BHA} Scales of Acidity and Basicity

Let us remind ourselves that the reason why *p*H values can be determined for aqueous solutions is that water can function both as a proton donor and as a proton acceptor and interacts in the appropriate capacity with dissolved acids and bases. Although chemists have been known to inquire about the "*p*H of an oil" it becomes clear, on reflection, that there is no such thing as the *p*H ($-\log aH^+$) of, say, a benzene solution, and neither can there be pK_a and pK_b values in the same sense as in water. In fact, in a solvent of this type self-association of acids and bases is more likely to assume significance than their ionic dissociation.

Since the only way to determine the strength of an acid is by ascertaining its readiness to react with a base, a suitable reference base must, obviously, be added when the solvent is of an aprotic type. Similarly, a suitable reference acid is required for determining the strength of a base.

The simplest kind of acidity or basicity scale consists of a series of equilibrium constants corresponding to the reaction

$$\underset{\text{base}}{\mathrm{B}} + \underset{\text{acid}}{\mathrm{HA}} \rightleftharpoons \underset{\text{salt}}{\mathrm{BHA}}, \tag{30}$$

with B or HA constituting the reference compound as the case may be. Then

$$K_{\mathrm{BHA}} = [\mathrm{BHA}]/([\mathrm{B}][\mathrm{HA}]). \tag{75}$$

In the tables of 1:1 acid-base association constants to be introduced presently, the values of K_{BHA} will be seen to fall mostly in the range 10^2 to 10^7; hence, log K_{BHA} is generally in the range 2 to 7.

The relation of such an acidity scale to the aqueous pK_a scale is easily comprehended by supposing the interaction of an acid HA with water to be representable as a two-stage reaction (eqs 20 and 76):

$$\underset{\text{base}}{H_2O} + \underset{\text{acid}}{HA} \rightleftharpoons H_2OH^+ \ldots A^- \qquad (20)$$

$$H_2OH^+ \ldots A^- + 2H_2O \rightleftharpoons H_2OH^+ \ldots OH_2 + A^- \ldots HOH. \qquad (76)$$

(It will be understood, of course, that eqs 20 and 76 are intended to represent the hydrogen bonding role of water in the simplest possible terms.) A crude representation of the overall equilibrium is

$$HA_{aq} + aq \rightleftharpoons H_2OH^+_{aq} + A^-_{aq}. \qquad (77)$$

As we know, aqueous ionization constants for organic acids are commonly in the range 10^{-2} to 10^{-7}, and the symbol pK_a ($-\log K_a$) has been adopted to eliminate the inconvenience of having to use exponents and negative signs. A *low* aqueous pK_a value will therefore correspond to a *high* log K_{BHA} value. It will be obvious that various log K_{BHA} scales for acids and bases in any aprotic solvent cannot be merged into a single scale corresponding to the aqueous pK_a scale.

The symbols "pK" (as in "pK_{rel}") and "p" (as in pHClO$_4$, pRNH$_2$, etc.) are sometimes encountered in discussions of acidity and basicity scales in aprotic solvents [575–579]. For example, Trémillon and associates [575–578] refer to numbers here called "log K_{BHA}" values as "pK" values, arriving at their terminology in the following manner:

(1) The acid-base reaction (in chloroform, let us say) is formulated as an *association:*

$$B\ (\text{base}) + HA\ (\text{acid}) \rightleftharpoons BHA\ (\text{salt}). \qquad (30)$$

(2) Next, the equilibrium constant for the acid-base reaction is formulated as a *dissociation:*

$$K = (B)(HA)/(BHA) \qquad (78)$$

(3) Finally, $K_{dissocn.}$, calculated according to eq 78, is converted into its *negative* logarithm, or pK value.

We do not see any advantage in extending the use of the symbol "p" except when by so doing a negative coefficient can be avoided. In fact, its use for both aprotic and amphiprotic solvents is likely to lead to confusion, because the "pK" (that is, log K_{BHA}) values in an aprotic solvent become larger with increasing acidic strength instead of smaller, as in water. A more serious objection is the likelihood that the fundamental relationship between 1:1 acid-base *association constants* in aprotic solvents and *ionic dissociation constants* in water and like solvents will become obscured. A further argument in favor of using log K_{BHA} for aprotic solutions is that proton donor-acceptor interactions involving *strong* acids and bases are thereby placed in a proper relationship with *weak hydrogen bonding interactions*, and also with *electron donor-Lewis acid interactions.*

A complication encountered in solution chemistry is that in the computation of equilibrium constants the units of concentration vary with the preference of the investigator. One worker may employ *molar* units, a second may use *molal* units, while a third may adopt the *mole-fractional* system. To differentiate the three sets of equilibrium constants, the symbols K_c, K_m and K_x (or K_N) are ordinarily used. (See sec. 4.1 for useful approximate relations between the three equilibrium constants.) For measurements involving aprotic solvents the molar scale is by far the most popular.

Substitution of the expression "equilibrium *quotient*" for "equilibrium *constant*" has occasionally been advocated for systems in aprotic solvents, because activity coefficients are not incorporated in the equations. However, few workers have adopted this recommendation. For one thing, the solutions studied are very often much more dilute than aqueous solutions characterized as "dilute," and it is considered justifiable to regard the activity coefficients as not differing measurably from 1. It should also be emphasized that under proper experimental conditions acid-base equilibrium "quotients" have been found to be satisfactorily "constant" over a substantial range of concentrations (for examples, see refs. 32 and 254a). An extrapolation procedure is not used. (Among conditions essential in "properly performed" experiments are care to exclude impurities and maintain a constant temperature, selection of reactants having neither very great nor very low affinity for each other, and avoidance of a large imbalance in molar ratios of reactants.) See further discussion of this topic in ref. 254a.

Izmailov has determined the relative strengths of acids in such solvents as benzene, chlorobenzene, carbon tetrachloride, and ethylene chloride potentiometrically [579], according to a procedure devised by LaMer and Downes [340]. The relative strengths are indicated by numerical values of "pK_{rel}", where $pK_{rel} = -\log(K_{HA/HA°})$. The identity of HA° is not always the same—for example, in some experiments it was picric acid, and in others, benzoic acid. It should be noted that such experiments sometimes employ solvents which, though referred to as "aprotic," actually contain significant quantities of other types of solvents.

5.3. Methods Used in Determining Values of Log K_{BHA}

Whereas infrared absorption spectroscopy has provided the principal means for studying weak hydrogen bonding interactions, absorption spectroscopy in the visible and ultraviolet has been the principal method for studying interactions of strong or moderately strong acids and bases. Figure 23 (introduced earlier) shows some of the absorption curves obtained during determination of log K_{BHA} for the association involving trinitro-*m*-cresol and tolyl dipropyl Nile Blue base in benzene. In these experiments successively larger amounts of trinitro-*m*-cresol were added to tolyl dipropyl Nile Blue (which was 10^{-5} *M* in each mixture), until there was no further change in the absorption curve. The experimental curve for a mixture containing 1600 equivalents of the acid was very similar to the calculated "limiting curve." Moreover, there was a well-defined isosbestic point, supporting the assumption that only two deeply colored species were present [482].

A related example is shown in figure 25, in which the reference compound was the acid (*p*-nitrophenol). Here again, the experimental and theoretical limiting curves were the same, and there was a sharply defined isosbestic point, Some other indicators also used as reference acids in benzene are represented in figures introduced earlier: For example, bromocresol green (fig. 13); bromophthalein magenta E (fig. 14); picric acid (fig. 15); and 2,4-dinitrophenol (fig. 17).

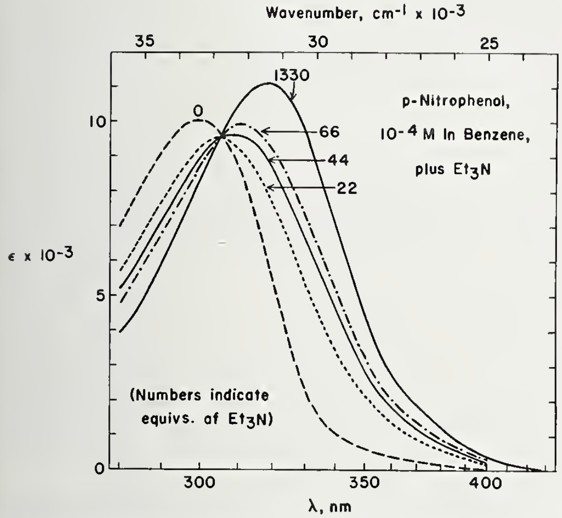


FIGURE 25. *Spectral absorption curves of mixtures of* p-nitrophenol (10^{-4} M) *with triethylamine in benzene; used in determining the equilibrium constant* (K_{BHA}) *for the 1:1 amine-phenol association* (25°) [17].

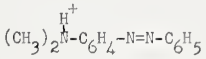
A well-defined isosbestic point cannot be regarded as proof that a solution contains only two colored species. In some instances, a more extensive study of the system will indicate that secondary changes are occurring which have little effect on the spectrum except when one of the reactants is present at a high concentration. The case of *methyl yellow* deserves special mention, since this indicator (LXXXVIII) has probably been used more extensively than any other indicator in studying acid-base equilibria. The yellow color of the base is attributed to the azo structure, and the red color seen on the addition of acids can be explained by the resonance hypothesis, as indicated by (LXXXIX, *a* and *b*). If a proton should add to the amino nitrogen (XC) the yellow color would not be affected.

$(CH_3)_2N\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_5$

(LXXXVIII)

$(CH_3)_2N\text{-}C_6H_4\text{-}N{=}\overset{H^+}{N}\text{-}C_6H_5 \longleftrightarrow (CH_3)_2\overset{+}{N}{=}C_6H_4{=}N\text{-}\overset{H}{N}\text{-}C_6H_5$

(LXXXIXa) (LXXXIXb)



$(CH_3)_2\overset{H^+}{N}\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_5$

(XC)

Through systematic investigations of Brode and co-workers [582, 583] it has become well established that in solvents like benzene the stable *trans* form of methyl yellow is partly converted to the *cis* form in light. Moreover, there is extensive experimental evidence that Hantzsch and Burawoy were correct when, in 1930, they asserted that the red *and* yellow species of salts both form when an acid is added to methyl yellow [584–586].

Davis and Hetzer [632] studied the interaction of methyl yellow with diphenyl phosphate in benzene, obtaining the system of curves shown in figure 26.

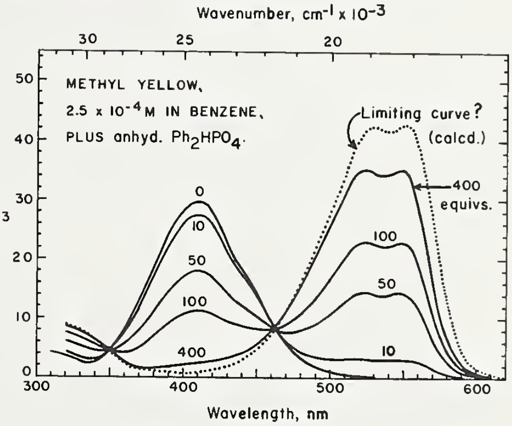


FIGURE 26. *Spectral absorption curves of mixtures of methyl yellow* (2.5×10^{-4} M) *with anhydrous diphenyl phosphate in benzene* [632].

Great pains were taken to exclude daylight, and it seemed evident that the intensity of the spectrophotometer source was too low to cause measurable isomerism to the *cis* form. Although two seemingly very sharp isosbestic points were obtained, and a value for log K_{BHA} (1.57) was calculated by assuming the double-peaked band near 540 nm to be due solely to a red salt, irregular changes in the absorbance near 400 nm indicated that part of the indicator was probably converted to the yellow salt. In short, this indicator shows complicated behavior and does not seem well suited for exact work when used in an aprotic solvent. Moreover, methyl yellow is not a very strong base, and with most organic acids an extremely large excess is required for a measurable change towards red. Dimerization and homoconjugation of acids may then occur.

Sometimes it is assumed that "electronic spectra are incapable of showing any appreciable difference between free ions, ion-pairs, or any other aggregates containing the same absorbing species" (see ref. [85] and literature cited). Section 4.3.4 presented substantial evidence that this generalization does not hold for aprotic solvents. These were by no means isolated examples, and it should constantly be borne in mind that aprotic solvents are "differentiating" media. Whenever uniformity of salt behavior is assumed, the results will be, at best, only approximately correct, and an opportunity for extending knowledge will be forgone.

Not infrequently the limiting curve for an acid-base association cannot be determined experimentally, because one of the reactants is only sparingly soluble or the association constant is very small. In some of these cases it is useful to apply a method proposed by Rose and Drago [580] for calculating the limiting absorbance and the association constant. Another method, originally devised by Benesi and Hildebrand [72] for determining the formation constant of the 1:1 complex of benzene with iodine, has been widely used for weak complexes, but some applications of this method have been criticized; Trotter and Hanna [581] have contributed one of the most recent discussions of this topic.

Successful use of the dielectrometric method for studying the acid-base dissociation of tribenzylammonium picrate and determining $1/K_{\mathrm{BHA}}$ [23] was mentioned a little earlier. A few other methods occasionally used will be mentioned in discussing the tables of log K_{BHA} values.

5.4. Tables of Log K_{BHA}, ΔH, and ΔS Obtained Using Aprotic Solvents

About twenty tables of values of log K_{BHA} and—when available—values of ΔH and ΔS, constructed after an extensive (but not exhaustive) survey of the literature, will be presented in this section and discussed briefly. Results for only one or a few compounds were not included unless they helped to validate general conclusions. Most of the available values are expressed in molar units, but some values in mole-fractional units are also included. Except when noted otherwise, ΔH and ΔS were calculated from data for log K_{BHA} at two or more temperatures. In all cases ΔH is in kcal/mole and ΔS is in entropy units. In the present state of knowledge the tabulated values should be regarded as approximate, and in some cases, as provisional. However, it seems probable that many of the log K_{BHA} values are as accurate as the available pK_a values for the acid and base concerned.

The numerical magnitude of values of log K_{BHA}, ΔH, and ΔS would be expected to increase with the ability of the reactants to donate or accept protons. Most of the tables include pK_a values for aqueous solutions to facilitate comparisons of acid and base strengths in water and the aprotic solvent concerned.

Examples are included for solutions in benzene, anisole, chlorobenzene, miscellaneous aromatic solvents, heptane, carbon tetrachloride, chloroform, and a few other organic solvents. The tables will be presented according to the sequence of solvents just given.

5.4.1. Aromatic and Substituted Aromatic Hydrocarbons

a. Benzene.

Table 71. The values of log K_{BHA} were obtained using three reference bases: pyridine (Py), 1,3-diphenylguanidine (DPG), and triethylamine (Et_3N). The strengths of the bases in water increase in the order named. The acids represented are phenol, *p*-nitrophenol, the six dinitrophenols, and picric acid.

In part, the stabilities of complexes parallel the aqueous strengths of the constituent bases and acids, but there are noteworthy exceptions. For example, according to Swain and Brown's results (using a dynamic vapor pressure method [588]), 2,4-dinitrophenol has far less ability than *p*-nitrophenol to hydrogen bond to pyridine in benzene, in spite of its much smaller pK_a value. Furthermore, on turning to the last two columns it will be seen that lower constants were obtained with triethylamine as the reference base than with diphenylguanidine, although according to the pK_a values of these bases triethylamine is the stronger base in water.

An investigation of the relative strengths of the isomeric dinitrophenols in benzene in terms of association with triethylamine [16] showed that the log K_{BHA} values are not linearly related to the pK_a values of these acids, probably because internal hydrogen bonding (chelation) in *ortho*-nitrophenols interferes with intermolecular hydrogen bonding. A similar conclusion can be drawn from the parallel investigation in which diphenylguanidine was the reference base [17]. When the log K_{BHA} values for B = diphenylguanidine are plotted (as y) against the corresponding values for B = triethylamine all of the points except that for HA = 2,6-dinitrophenol fall on or very close to a straight line. Excluding the data for 2,6-dinitrophenol, the least squares equation is

$$y = 0.596 + 0.936\ x. \tag{79}$$

The point for 2,6-dinitrophenol would fall on the line if log K_{BHA} for B = Et_3N were greater. This acid is "hindered," and its association with triethylamine seems likely to be obstructed by "F-strain," as in various reactions of triethylamine studied by H. C. Brown and associates [635].

TABLE 71. Log K_{BHA} *for phenol and some related acids in benzene (molar units, 25°)* [a]

Acid (pK_a[b])	Reference Base:		
	Py (5.17)	DPG (10.0)	Et_3N (10.87)
Phenol (10.00[c])	[d] 1.26 [e] 1.56	....	....
p-Nitrophenol (7.15[c])	[d] 2.04	....	[f] 2.46 [g] 2.42
3,5-Dinitrophenol (6.69)	....	[h] 3.49	[i] 3.07
3,4-Dinitrophenol (5.42)	....	[f] 3.92	[i] 3.61
2,5-Dinitrophenol (5.21)	....	[h] 3.06	[i] 2.62
2,3-Dinitrophenol (4.96)	....	[f] 4.28	[i] 3.87
2,4-Dinitrophenol (4.11)	[d] −0.1	[h] 3.83	[g] 3.49 [i] 3.50 [j] 3.47
2,6-Dinitrophenol (3.71)	....	[f] 5.77	[i] 4.94
Picric Acid (0.33[k])	[l] 3.62	....	....

[a] Three reference bases were used, namely, pyridine (Py), 1,3-diphenylguanidine (DPG), and triethylamine. Numbers in parentheses are pK_a values from the literature.

[b] With the exceptions noted, the pK_a values are as given in ref. [587].

[c] From ref. [271].

[d] From ref. [588]; a dynamic vapor pressure method was used.

[e] From ref. [589]; obtained from dielectric data at 25° and 40° which also yielded $\Delta H=-9$ and $\Delta S=-24$.

[f] See ref. [17].

[g] See table 75.

[h] See ref. [590].

[i] See ref. [16].

[j] See ref. [591].

[k] See ref. [362].

[l] See ref. [592].

REFERENCES:

[16] M. M. Davis, J. Am. Chem. Soc. **84**, 3623 (1962).

[17] M. M. Davis, unpublished results.

[271] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2d ed., Academic Press, Inc., New York, N.Y., 1959.

[362] M. M. Davis and M. Paabo, J. Res. NBS **67A**, 241 (1963).

[587] R. A. Robinson, M. M. Davis, M. Paabo, and V. E. Bower, J. Res. NBS **64A**, 347 (1960).

[588] C. G. Swain and J. F. Brown, Jr., J. Am. Chem. Soc. **74**, 2691 (1952).

[589] R. J. Bishop and L. E. Sutton, J. Chem. Soc., p. 6100 (1964).

[590] M. M. Davis, M. Paabo, and N. Matheny, unpublished results.

[591] R. G. Pearson and D. C. Vogelsong, J. Am. Chem. Soc. **80**, 1038 (1958).

[592] T. Jasiński, T. Misiak, and T. Skarżyńska, Roczniki Chem. **39**, 1549 (1965).

In summary, it seems reasonable to assert that strengths of acids and bases in terms of values of log K_{BHA} tend to parallel the strengths in water indicated by pK_a values, but that deviations occur when there is a strongly competing hydrogen bonding reaction such as chelation and when one or both of the reactants is hindered.

Table 72. Having failed to find a suitable *indicator* base for determining relative strengths of aromatic and aliphatic carboxylic acids in benzene Davis and Schuhmann [360] devised an indirect procedure in which diphenyl- or di-*o*-tolylguanidine is the reference base and the carboxylic acid and bromophthalein magenta E are competing proton donors. Davis and Hetzer developed the method further and applied it in determining values of log K_{BHA} for some 40 aromatic carboxylic acids [32], and later the measurements were extended by Davis and Paabo to additional aromatic acids and some aliphatic acids [254a]. The 1:1 complex of bromophthalein magenta E (yellow) and diphenylguanidine (colorless in the visible region) is magenta in benzene solution, with λmax near 540 nm; for this association log $K_{BHA}=5.41$ (see table 73). The color shifts toward yellow, of course, on the addition of a carboxylic acid (colorless in the visible region). From absorbance values for solutions containing the three components in varying, but not greatly different ratios, the log K_{BHA} values given in table 72 were calculated. In some cases a correction was applied for the content of carboxylic acid as the dimer, but for the most part competing hydrogen bonding reactions were thought to be negligible in extent.

Four linear relations emerged when values of log $K_{\text{assocn.}}$ (log K_{BHA}) in benzene were plotted against pK_a in water. These were for *meta-*, *para-*, mono-*ortho-*, and di-*ortho*-substituted benzoic acids. Equations for the first three lines are given below. The equation for di-*ortho*-substituted acids was regarded as only a rough approximation [32].

meta-Substituted acids [254a]: $\text{Log } K_{BHA}=14.37-2.17pK_a$ (80)

ortho-Substituted acids [254a]: $\text{Log } K_{BHA}=10.06-1.30pK_a$ (81)

para-Substituted acids [32]: $\text{Log } K_{BHA}=12.96-1.80pK_a$ (82)

These three linear relations are shown in figure 27.

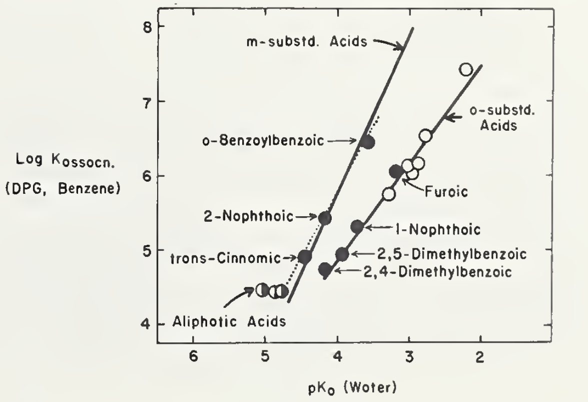


FIGURE 27. *Relative strengths of some carboxylic acids in benzene and water at 25°. The strength in benzene is expressed as the value of log* K_{BHA} *(log* $K_{\text{assocn.}}$*) where B is 1,3-diphenylguanidine. Equations for the three lines are given in the text.* Open *circles, results from ref. 32.* Half-filled *and* filled *circles, results given in ref. 254a.*

The dotted, unlabeled line is the one obtained for *para*-substituted acids. The relation for *meta*-substituted acids is considered "normal," and the existence of separate relations for the isomeric

TABLE 72. *Comparative values of* pK_a *(water, 25°) and log* K_{BHA} *(benzene, B = DPG, molar units, 25°) for some carboxylic acids*[a]

Name of acid	*pK_a*[b]	Log K_{BHA}[c]
Benzoic acid series[d]		
Benzoic	4.20	5.26 (5.32*)
o-Acetoxybenzoic (aspirin)	3.48	5.72
o-Aminobenzoic (anthranilic)	4.95	4.94
m-Aminobenzoic	4.75 (4.35)	4.93
p-Aminobenzoic	4.89 (4.49)	4.45
o-Benzoylbenzoic[e]	3.54	6.44
o-Bromobenzoic	2.85	6.17
m-Bromobenzoic	3.81	6.06
p-Bromobenzoic	3.97	5.86
o-Chlorobenzoic	2.94	6.08
m-Chlorobenzoic	3.83	6.06
p-Chlorobenzoic	3.98	5.82
m-Cyanobenzoic	3.60	6.56
p-Cyanobenzoic	3.55	6.53
m-Dimethylamino-benzoic	5.1 (4.37)	4.89
o-Fluorobenzoic	3.27	5.77
m-Fluorobenzoic	3.86	5.94
p-Fluorobenzoic	4.14	5.61
o-Hydroxybenzoic (salicylic)	3.00	7.45
m-Hydroxybenzoic	4.08	5.35
p-Hydroxybenzoic	4.58	4.94
o-Iodobenzoic	2.86	6.22
m-Iodobenzoic	3.85	6.05
p-Iodobenzoic	3.98	5.85
o-Methoxybenzoic (*o*-anisic)	4.09	3.7?
m-Methoxybenzoic (*m*-anisic)	4.09	5.38
p-Methoxybenzoic (*p*-anisic)	4.47	4.92
o-Methylbenzoic (*o*-toluic)	3.91	4.94
m-Methylbenzoic (*m*-toluic)	4.27	5.13
p-Methylbenzoic (*p*-toluic)	4.37	5.03
o-Nitrobenzoic	2.17	7.44
m-Nitrobenzoic	3.49	6.82
p-Nitrobenzoic	3.42	6.80
2,4-Dichlorobenzoic	2.76	6.55
2,6-Dichlorobenzoic	1.82	7.34
3,4-Dichlorobenzoic	3.64	6.48
2,6-Dimethoxybenzoic	3.44	4.92
2,4-Dimethylbenzoic[e]	4.18	4.72 (4.75*)
2,5-Dimethylbenzoic[e]	3.98	4.86
2,6-Dimethylbenzoic (2,6-xylic)	3.25	5.24
3,5-Dimethylbenzoic (3,5-xylic, mesitylenic)	4.30	5.03
3,5-Dinitrobenzoic	2.82	8.23
2,4,6-Trimethylbenzoic (*β*-isodurylic, mesitoic)	3.44	5.00
Miscellaneous other acids[e]		
Acetic	4.76	4.45*
Isobutyric	4.86	4.44*
Trimethylaeetic (pivalic)	5.05	4.46*
Lauric		4.35*
Stearic		4.37*
trans-Cinnamic	4.44	4.86 (4.91*)
2-Furoic	3.17	6.07
1-Naphthoic	3.69	5.31 (5.34*)
2-Naphthoic	4.16	5.39 (5.41*)

[a] Log K_{BHA} corresponds to $B+HA \rightleftarrows BH^+...A^-$, where the reference base, B, was diphenylguanidine (DPG); bromophthalein magenta E was present as a reference acid (HA′). See accompanying discussion.

[b] *pK_a* values in parentheses are "corrected" values, derived by substituting values of log K_{BHA} in eq 9 of ref. [32].

[c] Log K_{BHA} values marked with an asterisk were derived by applying a correction for the monomer-dimer equilibrium of HA, as explained in the paper cited.

[d] Except as indicated otherwise, all log K_{BHA} and *pK_a* values are taken from Table 1 of M. M. Davis and H. B. Hetzer, J. Res. NBS **60**, 569 (1958). (Ref. No. 32.)

[e] Log K_{BHA} and *pK_a* values are from Tables I to III of M. M. Davis and M. Paabo, J. Org. Chem. **31**, 1804 (1966). (Ref. [254a].)

REFERENCES:

[32] M. M. Davis and H. B. Hetzer, J. Res. NBS **60**, 569 (1958).
[254a] M. M. Davis and M. Paabo, J. Org. Chem. **31**, 1804 (1966).

ortho- and *para*-substituted acids is attributed partly to such factors as chelation and steric hindrance, and partly to solvation of substituents and anomalously enhanced strengths of *ortho*-substituted acids in water. Readers are referred to the original papers for details and further discussion.

Table 73. At the top of this table are values of log K_{BHA}, ΔH, and ΔS for some of the reactions represented in the preceding table, namely, those involving bromophthalein magenta E, benzoic acid, the three toluic acids, and the three monochlorobenzoic acids. At the bottom of the table are corresponding values for association of *triethylamine* with bromophthalein magenta E and with benzoic acid. Points worthy of special comment are:

(1) In benzene, most values of ΔH are in the range -14 to -19 kcal/mole, whereas the corresponding enthalpy changes for ionization of these aromatic

TABLE 73. *Values of log* K_{BHA}, ΔH, *and* ΔS *(molar units, 25°) for some 1:1 associations in benzene*[a]

Acid (pK_a)	Log K_{BHA}	ΔH_c	ΔS_c	$\Delta H/0.298\ \Delta S$	References
Reference Base = 1,3-Diphenylguanidine					
BPM-E[b](4.15[c])	5.34	......	......	......	[14, 5]
	[d] 5.34	[d] −15.9	[d] −28.8	1.85	[594]
	5.41	−15.8	−28.2	1.9	[32, 33]
	5.41	−14.1	−22.6	2.1	[15]
C_6H_5COOH (4.20)	5.30	−16.2	−30.1	1.8	[32, 33]
	5.32	−14.1	−22.9	2.1	[15]
o-$CH_3C_6H_4COOH$ (3.91)	4.97	−16.5	−32.5	1.7	[32, 33]
m-$CH_3C_6H_4COOH$ (4.27)	5.18	−16.5	−31.5	1.8	[32, 33]
p-$CH_3C_6H_4COOH$ (4.37)	5.13	−16.0	−30.1	1.8	[32, 33]
o-ClC_6H_4COOH (2.94)	6.10	−18.8	−35.1	1.8	[32, 33]
m-ClC_6H_4COOH (3.83)	6.08	−19.0	−36.0	1.8	[32, 33]
p-ClC_6H_4COOH (3.98)	5.84	−18.0	−33.7	1.8	[32, 33]
Reference Base = Triethylamine					
BPM-E[b] (4.15[c])	4.36	......	......	......	[14]
	4.44	−15.3	−30.9	1.7	[15]
Benzoic (4.20)	[e] 3.58	−11.0	−20.7	1.8	[15]

[a] ΔH_c and ΔS_c signify that these constants were derived from data expressed in molar units of concentration. As is customary, ΔH_c is in the units kcal/mole and ΔS_c is in entropy units.

[b] BPM—E signifies bromophthalein magenta E (3′,5′,3″,5″-tetrabromophenolphthalein ethyl ester).

[c] An estimated value; see footnote 29 of ref. [32].

[d] Originally expressed in mole fraction units; conversion to molar units was made by this author.

[e] An almost identical value was obtained using 2,5-dinitrophenol (in place of bromophthalein magenta E) as the reference indicator acid.

REFERENCES:

[5] M. M. Davis and H. B. Hetzer, J. Res. NBS **46,** 496 (1951).
[14] M. M. Davis and P. J. Schuhmann, J. Res. NBS **39,** 221 (1947).
[15] M. M. Davis and M. Paabo, J. Am. Chem. Soc. **82,** 5081 (1960).
[32] M. M. Davis and H. B. Hetzer, J. Res. NBS **60,** 569 (1958).
[33] M. M. Davis and H. B. Hetzer, J. Res. NBS **65A,** 209 (1961).
[594] Results of A. R. Anderson and W. F. K. Wynne-Jones, as given in the Ph. D. thesis of A. R. Anderson, The University of Newcastle upon Tyne, 1954, and communicated by Lord Wynne-Jones to M. M. Davis in June, 1964.

acids in water are positive in sign (with one exception) and their magnitude is only about 0.02 to 0.3 kcal/mole (see ref. [33], table 3).

(2) In benzene, ΔG is negative in sign, whereas ΔG for ionization in water is positive.

(3) In benzene, the ratio $\Delta H/T\Delta S$ (where $T = 298$ °K) is substantially constant for the reactions represented. This is not true for the ionic dissociation of the acids in water. Interestingly, the ratio $\Delta H/0.298\Delta S$ for dimerization of the same or closely related aromatic acids in benzene, just as for their association with diphenylguanidine, is close to 1.8. (See further discussion in ref. [33].)

A linear relationship of ΔH and ΔS in a series of association reactions is customarily held to signify that with increasing strength of the bond between a proton donor and acceptor (or between a Lewis acid and an electron donor) there is increased restraint on motions of the component parts (for example, see ref. [102]). These results support our assertion that log K_{BHA} values for an aprotic solvent like benzene are likely to be a better index of intrinsic strengths of acids and bases than aqueous pK_a values. Furthermore, it is evident that the maximum enthalpy change in hydrogen bonding interactions has for a long time been underestimated.

Attention should also be directed to the striking finding [15] that in benzene log K_{BHA} values for the reaction of bromophthalein magenta E with diphenylguanidine (5.41) and the reaction of benzoic acid with diphenylguanidine (5.31) are about the same, paralleling the similarity in the pK_a values (4.15 and 4.20, respectively) of the acids. In contrast, benzoic acid seems much weaker than bromophthalein magenta E when the reference base is triethylamine (log K_{BHA} 3.58 *versus* log K_{BHA} 4.44). To explain this finding, it has been suggested that the diphenylguanidinium ion, $(PhNH)_2C{=}NH_2^+$, can form *two* hydrogen bonds to a carboxylate ion, one to each oxygen (LX), whereas Et_3NH^+ can form only one bond (LIX) [15]. The plausibility of this hypothesis is enhanced by the observation of Streuli and Miron [593] that there is an "enhancement of acidity . . . relative to carboxylic acids" when phenols are transferred from water to the solvent pyridine. Its correctness could be tested by comparing the behavior of 1,3-diphenylguanidine and its 2-methyl-derivative.

Table 74. *Comparative heats of neutralization of different types of organic bases by hydrogen bromide in acetonitrile (24°) and by trichloroacetic acid in benzene (28°)* [a]

Base	pK_{BH^+} [b]	ΔH, MeCN [c]	ΔH_1, C_6H_6 [d]	ΔH_2, C_6H_6 [d]
n-Butylamine	10.60	−25.8	−29.3	−0.7
sec-Butylamine	10.56	−25.8	−29.6	−0.3
i-Butylamine	10.42	−25.5	−29.1	−0.7
Di-*i*-propylamine	11.05	−24.4	−29.4	−1.2
Di-*n*-butylamine	11.3	−26.2	−33.3	−1.9
Di-*sec*-butylamine	11.0	−24.1	−28.5	−1.3
Morpholine	[e] 8.49	−25.5	−25.0	−2.3
Tri-*n*-butylamine	9.93	−23.9	−23.0	−4.9
1,3-Diphenylguanidine	10.0	−20.7	−23.8	−1.9
Aniline	4.60	−14.9	−16.4	—
p-Anisidine	5.29	−17.7	−18.8	0.0
p-Chloroaniline	3.99	−12.3	−9.8	
m-Nitroaniline	2.46	−8.2	−0.3	
N-Methylaniline	4.85	−13.2	−13.8	
N,N-Dimethylaniline	5.06	−14.9	−11.3	
N,N-Diethylaniline	6.56	−15.6	−15.3	
Pyridine	5.19	−14.4	−13.6	

[a] Estimated from initial slopes of thermometric titration curves; ΔH is in kcal/mole and is based on molar concentrations. See accompanying text.

[b] Most pK_{BH^+} values are from ref. [271] or ref. [595].

[c] From results of E. J. Forman and D. N. Hume, J. Phys. Chem. **63**, 1949 (1959).

[d] From results of T. E. Mead, J. Phys. Chem. **66**, 2149 (1962).

[e] See H. B. Hetzer, R. G. Bates, and R. A. Robinson, J. Phys. Chem. **70**, 2869 (1966).

References:

[271] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2d ed. (Academic Press, Inc., New York, N.Y. 1959).
[595] N. F. Hall, J. Am. Chem. Soc. **52**, 5117 (1930).
[596] E. J. Forman and D. N. Hume, J. Phys. Chem. **63**, 1949 (1959).
[597] T. E. Mead, J. Phys. Chem. **66**, 2149 (1962).
[598] H. B. Hetzer, R. G. Bates, and R. A. Robinson, J. Phys. Chem. **70**, 2869 (1966).

Table 74. This table contains values of ΔH obtained by a different procedure. Forman and Hume [596] estimated the isothermal heats of neutralization by hydrogen bromide in acetonitrile (24°) for a large group of aliphatic and aromatic amines from the "initial slopes" of thermometric titration curves, and subsequently, Mead [597] performed analogous experiments (28°) with benzene as the solvent and trichloroacetic acid as the titrant. A representative titration curve obtained in the latter series of experiments is shown in figure 28. It is apparent that in each series the magnitudes of ΔH parallel roughly

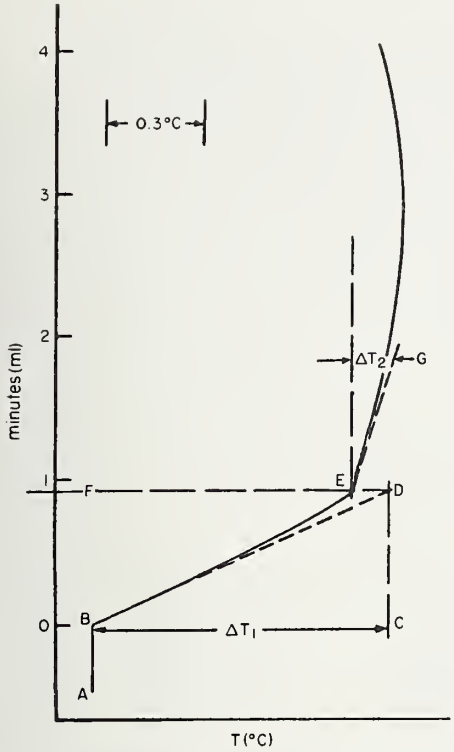


Figure 28. *Representative thermometric titration curve for reaction of tertiary aliphatic amines with trichloroacetic acid in benzene.*

Reproduced from T. E. Mead, J. Phys. Chem. **66**, 2149 (1962), with the permission of the author and the publisher [597].

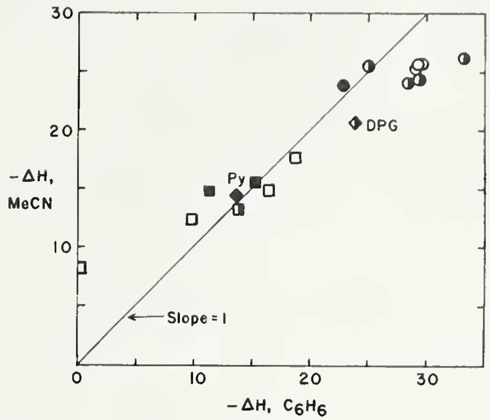


Figure 29. *Heats of neutralization* (−ΔH) *of some bases with hydrogen bromide in acetonitrile* (24°) *plotted against the heats of neutralization of the same bases with trichloroacetic acid in benzene* (28°).

Based on data reported by E. J. Forman and D. N. Hume, J. Phys. Chem. **63**, 1949 (1959) and by T. E. Mead, J. Phys. Chem. **66**, 2149 (1962). (Refs. 596 and 597, respectively.)

the strengths of the bases. The two acids represented are a good deal stronger than the acids represented in table 73, and this explains the greater magnitudes of ΔH.

Because of the large number of bases represented in both series of experiments, ΔH for the series in acetonitrile was plotted against ΔH values for the reactions in benzene, yielding figure 29. It is evident that there is a roughly linear correlation of the two sets of values.

Table 75. This table contains values of $\log_{10} K_N$, ΔH_N°, and ΔS_N° for a large group of acid-base associations in benzene, taken from the Ph. D. thesis (1954) of A. R. Anderson, and made available through the kindness of Lord Wynne-Jones [594]. The last column contains log K_{BHA} values on the molar basis (calculated by this writer). If expressed in molar units of concentration, $-\Delta H$ would have been smaller by 0.5 kcal or less. To illustrate, for triethylamine with 2,4-dinitrophenol (25°) ΔH_c is −13.95 kcal/mole, and for diphenylguanidine with bromophthalein magenta E, ΔH_c is −15.87. The value of $-\Delta S$ on the molar basis is greater by about 3 to 5 entropy units.

A few values from other investigations are included in table 75. It is not feasible to discuss this interesting table in detail. It will suffice to note that the results support the previous general conclusion that log K_{BHA}, ΔH, and ΔS tend to increase in magnitude with the strength of the proton donor or acceptor. Some of the irregularities can be attributed to steric hindrance.

b. Anisole and chlorobenzene.

Table 76. Bell and Bayles [354] compared the strengths of a large group of aromatic amines as well as a few pyridine-type bases in terms of log K for their association with bromophenol blue (first stage, colorless to yellow). Their results are shown in table 76, together with accepted values of pK_a for the bases concerned. They concluded that the indicator constants are about the same in the two solvents. Furthermore, the indicator constants for amines in anisole were found to correlate well with the catalytic constants in the decomposition of nitramide in the same solvent. In previous work of Bell and Trotman-Dickenson [623], where the dissociation constants in water had been the criteria of basic strengths, separate linear relationships with the catalytic coefficients in anisole had been found for primary, secondary, tertiary, and heterocyclic amines.

TABLE 75. *Values of log K_{BHA}, ΔH, and ΔS (mole fraction units, 25°) for some 1:1 associations in benzene* [a]

Base	Log $K_{10}K_N$ [b]	ΔH°_N	ΔS°_N	Log K_c [c]
Reference acid = *p*-Nitrophenol				
n-Propylamine	3.860	−8.214	−9.9	2.81
Diethylamine	3.812	−8.896	−12.4	2.76
Triethylamine	3.464	−8.799	−13.7	2.42 [d]2.46
Reference acid = 2,4-Dinitrophenol				
n-Propylamine	3.017	−11.220	−23.8	1.97
n-Butylamine	3.068	−12.830	−29.0	2.02
n-Butylamine [e]	2.962	−11.86	−26.2	1.91
Diethylamine	4.279	−14.760	−29.9	3.23 [f]3.09
Dipropylamine	4.064	−14.920	−31.5	3.02
Dibutylamine	4.064	−12.830	−24.4	3.02
Dibutylamine [e]	4.098	−13.13	−25.3	3.05
Triethylamine	4.535	−14.450	−27.7	3.49 [f]3.47 [g]3.50
Tripropylamine	3.765	−12.570	−24.9	2.72
Tributylamine	3.831	−11.440	−20.9	2.78 [f]2.79
Tributylamine [e]	3.871	−11.97	−22.4	2.82
Reference acid = 2,4-Dinitro-*o*-cresol				
Diethylamine	3.794	−12.240	−23.7	2.74
Reference acid = Picric acid				
Tribenzylamine	4.248	−10.638	−16.3	3.20 [h,i]3.20
Reference acid = 2,4,6-Trinitro-*m*-cresol				
Tribenzylamine	3.701	−10.058	−16.8	2.65 [i]2.65

[a] Except as indicated otherwise, the values cited are results of A. R. Anderson and W. F. K. Wynne-Jones, as given in the Ph. D. thesis of A. R. Anderson, the University of Newcastle upon Tyne, 1954; they were communicated to M. M. Davis by Lord Wynne-Jones in June, 1964. As usual, ΔH° is in kcal/mole and ΔS° is in entropy units.

[b] Log $K_{10}K_N$ signifies log K_{BHA} in mole fraction units.

[c] Log K_c signifies log K_{BHA} in molar units. Unless otherwise indicated the values in this column were computed by this author from the results given in the second column.

[d] See ref. [17].

[e] See ref. [441].

[f] See ref. [591].

[g] See ref. [16].

[h] See ref. [23].

[i] See ref. [20].

REFERENCES:

[16] M. M. Davis, J. Am. Chem. Soc. **84**, 3623 (1962).

[17] M. M. Davis, unpublished results.

[20] M. M. Davis and E. A. McDonald, J. Res. NBS **42**, 595 (1949).

[23] A. A. Maryott, J. Res. NBS **41**, 7 (1948).

[441] J. W. Bayles and A. F. Taylor, J. Chem. Soc., p. 417 (1961).

[594] Results of A. R. Anderson and W. F. K. Wynne-Jones, as given in the Ph. D. thesis of A. R. Anderson, the University of Newcastle upon Tyne, 1954, and communicated by Lord Wynne-Jones to M. M. Davis in June 1964.

[591] R. G. Pearson and D. C. Vogelsong, J. Am. Chem. Soc. **80**, 1038 (1958).

TABLE 76. *Comparative values of log K_{BHA} (molar units, 25°) for some aniline- and pyridine-type bases in anisole and chlorobenzene* [a]

Base	pK_a [b]	Log K_{BHA}	
		Anisole (4.33)	Chlorobenzene (5.62)
Aniline	4.58	1.0	1.0
o-Chloroaniline	2.62	0.1	....
m-Chloroaniline	3.52	0.0	....
p-Chloroaniline	4.0	0.0	....
o-Toluidine	4.39	1.0	1.26
p-Toluidine	5.07	1.75	1.8
N-Methylaniline	4.85	1.74	1.8
N-Methyl-*o*-toluidine	4.59	1.68	1.80
N-Methyl-*p*-toluidine	5.33	2.51	2.66
N-Ethylaniline	5.11	2.43	2.48
N-Ethyl-*p*-toluidine	4.93	3.04	3.26
N,N-Dimethylaniline	5.06	2.87	2.80
N,N-Dimethyl-*o*-toluidine	5.86	3.61	3.51
N,N-Dimethyl-*p*-toluidine	5.5	3.48	3.53
N,N-Diethylaniline	6.56	4.4	4.5
Pyridine	5.37	3.75	[c]3.52
Quinoline	5.0	3.99	4.0
Isoquinoline	5.24	4.15	4.2

[a] Taken with minor changes from Table 6 of R. P. Bell and J. W. Bayles, J. Chem. Soc., p. 1518 (1952). Values shown in parentheses are dielectric constants. Throughout, the reference acid was bromophenol blue.

[b] To obtain these values the pK_b values as given in the paper cited were subtracted from 14.

[c] In a similar measurement Popovych obtained the value 3.40 [85]. Some of his other results were cited earlier (see table 6).

REFERENCES:

[85] O. Popovych, J. Phys. Chem. **66**, 915 (1962).

[354] R. P. Bell and J. W. Bayles, J. Chem. Soc., p. 1518 (1952).

Table 77. Additional values of log K_{BHA} in chlorobenzene are given in this table. It is obvious that in chlorobenzene, as in benzene, the stability of the complex with a given reference acid increases with the strength of the base. We saw earlier (see table 6) that pyridine-type bases listed here associate more extensively with bromophenol blue in chlorobenzene

than in benzene, but less extensively in toluene [85]. A reasonable explanation is that the solvents, as π-electron donors, associate somewhat with the indicator acid. Toluene is the best electron-donor of the three solvents, and chlorobenzene is the most inert.

Reference should be made to an investigation, by Bayles and Evans [634], of the "effect of chain length and freedom of ring rotation" on the tendency of various nitrogen bases to associate with 2,4-dinitrophenol in chlorobenzene.

TABLE 77. *Log* K_{BHA} *(molar units, 25°) for some 1 : 1 associations in chlorobenzene*

Reference acid	Base	Log K_{BHA}	References
2,4-Dinitrophenol	*n*-Hexylamine	1.90	[591]
	Dimethylamine	3.03	[591]
	Diethylamine	3.40	[591]
	Di-*n*-butylamine	3.40	[591]
	Trimethylamine	3.14	[591]
	Triethylamine	3.99	[591]
	Tri-*n*-butylamine	3.58	[591]
Picric acid	Pyridine	[a] 4.30	[592]
Bromophenol blue [b]	Pyridine	3.40	[85]
	3-Picoline	4.16	[85]
	4-Picoline	4.46	[85]
	2,4-Lutidine	5.64	[85]

[a] Ezell and Gilkerson [599] obtained a closely similar value (4.24) using *o-dichlorobenzene* as the solvent instead of chlorobenzene.

[b] First color change (colorless to yellow).

REFERENCES:

[85] O. Popovych, J. Phys. Chem. **66**, 915 (1962).
[591] R. G. Pearson and D. C. Vogelsong, J. Am. Chem. Soc. **80**, 1038 (1958).
[592] T. Jasiński, T. Misiak, and T. Skarżyńska, Roczniki Chem. **39**, 1549 (1965).
[599] J. B. Ezell and W. R. Gilkerson, unpublished results cited in ref. [449].

c. *Miscellaneous aromatic solvents.*

Table 78. This table presents log K_N, ΔH_N, and ΔS_N (and also the corresponding log K_c, calculated by this writer) for 2,4-dinitrophenol with mono-, di-, and tri-*n*-butylamine in six aromatic solvents and also in *n*-butyl ether [441]. As in the work just discussed, log K is greater in chlorobenzene than in benzene, but smaller in toluene. Interested readers will wish to consult the original paper for more details and discussion.

Added in proof: Recently Caldin and Crooks [660], using a microwave temperature-jump technique, determined at room temperature the "forward" and "reverse" rate constants, k_f and k_r, corresponding to eq 44,

$$B + H\text{–}A \underset{k_r}{\overset{k_f}{\rightleftarrows}} B\text{–}H^+ \ldots A^-, \qquad (44)$$

where H–A was 2,4-dinitrophenol, B was mono-, di-, or tri-*n*-butylamine, and the solvent was chlorobenzene. For each of the three systems the experimental value of k_f proved to be much lower than the value calculated on the assumption of a diffusion-controlled reaction. To explain these low values the authors suggest that the forward reactions require an activation energy of the order of 1 kcal/mole (molar units), the activation energy being connected with the necessity of breaking the intramolecular hydrogen bond in 2,4-dinitrophenol. [Compare secs. 4.5.4b and 5.4.1a.]

TABLE 78. *Effect of solvent on log* K_{BHA}, ΔH, *and* ΔS *for mono-, di-, and tri-n-butylamine* (HA=*2,4-dinitrophenol, mole fraction units, 25°*) [a]

Solvent (ϵ)	Log K_N	ΔH_N	ΔS_N	Log K_c
Base = *n*-Butylamine				
Benzene (2.27)	2.96	−11.86	−26.2	1.91
Toluene (2.38)	2.79	−11.81	−26.8	1.83
n-Butyl ether (3.06)	4.00	−15.39	−33.3	3.23
Anisole (4.33)	3.64	−12.11	−24.0	2.68
Bromobenzene (5.40)	2.98	−13.23	−30.8	2.00
Fluorobenzene (5.42)	3.07	−13.23	−30.3	2.05
Chlorobenzene (5.62)	3.21	−11.80	−24.9	2.22
Base = Di-*n*-butylamine				
Benzene (2.27)	4.10	−13.13	−25.3	3.05
Toluene (2.38)	3.92	−13.04	−25.8	2.96
n-Butyl ether (3.06)	4.21	−15.22	−31.8	3.44
Anisole (4.33)	4.62	−13.75	−24.9	3.66
Bromobenzene (5.40)	4.46	−12.91	−22.9	3.48
Fluorobenzene (5.42)	4.37	−12.72	−22.6	3.35
Chlorobenzene (5.62)	4.30	−11.89	−20.2	3.31
Base = Tri-*n*-butylamine				
Benzene (2.27)	3.87	−11.97	−22.4	2.82
Toluene (2.38)	3.66	−11.71	−22.5	2.70
n-Butyl ether (3.06)	3.35	−11.24	−22.4	2.58
Anisole (4.33)	4.42	−12.57	−21.9	3.46
Bromobenzene (5.40)	4.64	−13.49	−24.0	3.66
Fluorobenzene (5.42)	4.64	−13.81	−25.1	3.62
Chlorobenzene (5.62)	4.68	−14.16	−26.1	3.69

[a] Results of J. W. Bayles and A. F. Taylor, J. Chem. Soc., p. 417 (1961). Log K_N signifies log K_{BHA} in mole fraction units whereas log K_c (derived by this author) is log K_{BHA} in molar units. Dielectric constants of solvents are from ref. [35].

REFERENCES:

[441] J. W. Bayles and A. F. Taylor, J. Chem. Soc., p. 417 (1961).
[35] A. A. Maryott and E. R. Smith, Table of dielectric constants of pure liquids, NBS Circ. 514, Aug. 10, 1951.

5.4.2. Aliphatic Hydrocarbons

Table 79. Heptane was used as solvent for determining the log K_{BHA} values in this table, both for its inertness and its transparency in the ultraviolet region. In one case (pyridine with phenol) a dielectrometric procedure was used [589]. Again there is a parallelism between strength of acid and magnitude of log K_{BHA}.

Denyer, Gilchrist, and co-workers have determined log K_{BHA} for trimethylamine with four of the same phenols (phenol, *p*-cresol, and 1- and 2-naphthol) in cyclohexane [603]. All values are of the same order as those given in table 79 for their association with triethylamine in heptane, and in some instances the agreement is very close. Here, the method was partition of one reactant between the vapor phase and the solution [603]. Results of Bellon [604] for triethylamine with these same phenols in cyclohexane, obtained by ultraviolet absorption spectroscopy, are also in good accord; Bellon's values are expressed in mole-fractional units. He pointed out that the log K_{BHA} values in cyclohexane are related linearly to pK_a values of the phenols in water.

TABLE 79. *Log* K_{BHA} (*molar units, 25°*) *for some base-phenol associations in heptane* [a]

Reference acid (pK_a) [b]	Base				
	Py	$BuNH_2$	Bu_2NH	Et_3N	Bu_3N
p-Cresol (10.26)	....	1.83	1.92	1.74	....
m-Cresol (10.09)	....	1.93	1.99	1.82	....
Phenol (10.00)	[c] 1.90	2.06	2.11	1.93 [d] 1.92	....
2-Naphthol (9.57, 19°) [e]	....	2.11	2.14	2.01 [d] 2.01	....
1-Naphthol (9.39) [f]	....	2.16	2.21	2.07 [d] 2.08	....
2,4-Dinitrophenol (4.11)	....	....	[g] 2.56	....	[g] 2.00

[a] With the exceptions noted log K_{BHA} values are from M. Bonnet and A. Julg, J. Chim. Phys. **59**, 723 (1962).

[b] Most pK_a values are for 25° and from ref. [271].

[c] From R. J. Bishop and L. E. Sutton, J. Chem. Soc., p. 6100 (1964); $\Delta H = -6$, $\Delta S = -11$.

[d] See S. Nagakura and M. Gouterman, J. Chem. Phys. **26**, 881 (1957).

[e] See F. Kieffer and P. Rumpf, Compt. Rend. **238**, 360, 700 (1954).

[f] L. K. Creamer, A. Fischer, B. R. Mann, J. Packer, R. B. Richards, and J. Vaughan, J. Org. Chem. **26**, 3148 (1961).

[g] See R. G. Pearson and D. C. Vogelsong, J. Am. Chem. Soc. **80**, 1038 (1958).

REFERENCES:

[600] M. Bonnet and A. Julg, J. Chim. Phys. **59**, 723 (1962).
[271] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2d ed. (Academic Press, Inc., New York, N.Y., 1959).
[589] R. J. Bishop and L. E. Sutton, J. Chem. Soc., p. 6100 (1964).
[353] S. Nagakura and M. Gouterman, J. Chem. Phys. **26**, 881 (1957).
[601] F. Kieffer and P. Rumpf, Compt. Rend. **238**, 360, 700 (1954).
[602] L. K. Creamer, A. Fischer, B. R. Mann, J. Packer, R. B. Richards, and J. Vaughan, J. Org. Chem. **26**, 3148 (1961).
[591] R. G. Pearson and D. C. Vogelsong, J. Am. Chem. Soc. **80**, 1038 (1958).

5.4.3. Carbon Tetrachloride

As would be anticipated, carbon tetrachloride has very often been the solvent for determinations of log K_{BHA} by infrared absorption spectroscopy.

Table 80. This table illustrates how much smaller values of log K_{BHA} are when HA is an alcohol. The enthalpy and entropy changes (see footnotes) are correspondingly small. It will be noted that replacement of hydrogen by phenyl on the primary carbon atom, which increases the acidic character of an alcohol, leads to slightly enhanced association of the alcohol with pyridine. As would be expected, phenol associates more extensively with pyridine than any of the alcohols listed.

TABLE 80. *Log* K_{BHA} (*molar units, 20–27°*) *for association of pyridine with some alcohols in carbon tetrachloride*

Alcohol	20°	22°	25°	27°	References
Methanol	0.78	....	[a] 0.47	....	[135, 606]
Ethanol	0.43	....	[b] 0.38	....	[607, 606]
1-Propanol	....	....	[c] 0.30	....	[609]
Propanol	....	....	....	0.40	[608]
1-Butanol	....	0.32	....	0.35	[605, 608]
2-Butanol	....	−0.03	....	0.04	[605, 608]
t-Butyl alcohol	....	−0.24	[d] 0.16	....	[605, 608]
Pentanol	....	....	....	0.32	[608]
Hexanol	....	....	....	0.42	[608]
Octanol	....	....	....	0.45	[608]
Benzyl alcohol	....	....	....	0.72	[608]
* * * * * *					
Phenol [e]	1.72–1.78	....	1.62, 1.65	1.67	

[a] $\Delta H = -3.88$ (kcal/mole), $\Delta S = -10.8$ (entropy units).

[b] $\Delta H = -3.66$, $\Delta S = -10.5$.

[c] $\Delta H = -4.3$, $\Delta S = -11.9$.

[d] $\Delta H = -3.98$, $\Delta S = -12.6$.

[e] See values of log K_{BHA} listed in tables 82 and 84. See tables 83 and 84 for ΔH and ΔS.

REFERENCES:

[605] T. Zeegers-Huyskens, L. Lamberts, and P. Huyskens, J. Chem. Phys. **59**, 521 (1962).
[135] T. Gramstad, Acta Chem. Scand. **16**, 807 (1962).
[606] E. D. Becker, Spectrochim. Acta **17**, 436 (1961).
[607] I. Prigogine, J. Chim. Phys. **45**, 17 (1948).
[608] A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, J. Chim. Phys. **62**, 336 (1965).
[609] T. J. V. Findlay and A. D. Kidman, Australian J. Chem. **18**, 521 (1965).

Table 81. Once again, it is apparent that log K_{BHA}, ΔH, and ΔS are greater for a phenol than for an alcohol, and, moreover, these constants are greatest for pentachlorophenol. Collidine (trimethylpyridine), being a stronger base than pyridine, associates more extensively with all of the proton donors listed.

TABLE 81. *Log* K_{BHA}, ΔH, *and* ΔS (*molar units, 20°*) *for association of pyridine and collidine with* ROH *or* ArOH *in carbon tetrachloride* [a]

Base	Log K_{BHA}	ΔH	ΔS
ROH = Methanol			
Pyridine	0.78	−3.2	−7.4
Collidine	0.88	−3.6	−8.2
ROH = Ethanol			
Pyridine [b]	0.43	....	....
ArOH = 1-Naphthol ($pK_a = 9.39$)			
Pyridine	1.92	−5.7	−10.5
Collidine	2.30	−6.7	−12.2
ArOH = Pentachlorophenol ($pK_a = 4.82$)			
Pyridine	2.05	−5.8	−10.4
Collidine	2.35	−7.6	−15.1

[a] With the exception noted values are from T. Gramstad, Acta Chem. Scand. **16,** 807 (1962); ΔH in kcal/mole, ΔS in entropy units.

[b] See I. Prigogine, J. Chim. Phys. **45,** 17 (1948).

REFERENCES:

[135] T. Gramstad, Acta Chem. Scand. **16,** 807 (1962).

[607] I. Prigogine, J. Chim. Phys. **45,** 17 (1948).

Table 82. Here, pyridine is the reference base throughout. The increase in stability of the complex with increase in proton-donor ability of the acid, noted in previous tables, is again evident.

Table 83. In this table, phenol is the reference acid throughout and the behavior of pyridine-type bases of varying strength is investigated. The same general trends as before are observable.

Table 84. Comparisons of pyridine-type bases, with phenol as the reference acid, are continued in this table.

Table 85. This table is appropriately compared with table 82. Aniline, being a much weaker base than pyridine, associates much less extensively with phenol and substituted phenols.

TABLE 82. *Log* K_{BHA} (*molar units, 20–27°*) *for association of pyridine with phenol and related acids in carbon tetrachloride*

Acid [a]	20° [b]	21° [c]	25°	27° [d]
p-Cresol (10.26)	....	1.62	....	1.53
p-Methoxyphenol (10.21)	....	1.62	....	1.51
m-Cresol (10.09)	....	1.63	....	1.55
Phenol (10.00)	[e] 1.78	1.77	[f] 1.62	1.67
p-Fluorophenol (9.91)	....	....	....	1.84
p-Chlorophenol (9.42)	....	2.10	....	2.05
1-Naphthol (9.39) [g]	1.92	....	....	....
p-Bromophenol (9.36)	....	....	....	2.04
p-Iodophenol (9.30)	....	2.15	....	1.90
m-Chlorophenol (9.13)	....	2.24	....	2.00
m-Bromophenol (9.03)	....	....	....	2.09
m-Nitrophenol (8.38)	....	....	....	2.34
Pentachlorophenol (4.82) [h]	2.05	....	....	....
Picric acid (0.33) [i]	....	....	[j] 3.73	....

[a] Numbers in parentheses are pK_a values (25°). With exceptions noted they are from A. I. Biggs and R. A. Robinson, J. Chem. Soc., p. 388 (1961).

[b] Results of T. Gramstad, Acta Chem. Scand. **16,** 807 (1962).

[c] Results of J. Rubin, B. Z. Senkowski, and G. S. Panson, J. Phys. Chem. **68,** 1601 (1964).

[d] Obtained by A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, J. Chim. Phys. **62,** 336 (1965).

[e] H. Dunken and H. Fritzsche, Z. Chem. **1,** 249 (1961), obtained 1.72.

[f] R. J. Bishop and L. E. Sutton, J. Chem. Soc., p. 6100 (1964), obtained 1.65 by dielectric polarization measurements.

[g] See L. K. Creamer, A. Fischer, B. R. Mann, J. Packer, R. B. Richards, and J. Vaughan, J. Org. Chem. **26,** 3148 (1961).

[h] See R. A. Robinson and R. G. Bates, J. Res. NBS **70A,** 553 (1966).

[i] M. M. Davis and M. Paabo, J. Res. NBS **67A,** 231 (1963).

[j] T. Jasiński, T. Misiak, and T. Skarżyńska, Roczniki Chem. **39,** 1549 (1965).

REFERENCES:

[535] A. I. Biggs and R. A. Robinson, J. Chem. Soc., p. 388 (1961).

[135] T. Gramstad, Acta Chem. Scand. **16,** 807 (1962).

[610] J. Rubin, B. Z. Senkowski, and G. S. Panson, J. Phys. Chem. **68,** 1601 (1964).

[608] A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, J. Chim. Phys. **62,** 336 (1965).

[611] H. Dunken and H. Fritzsche, Z. Chem. **1,** 249 (1961).

[589] R. J. Bishop and L. E. Sutton, J. Chem. Soc., p. 6100 (1964).

[602] L. K. Creamer, A. Fischer, B. R. Mann, J. Packer, R. B. Richards, and J. Vaughan, J. Org. Chem. **26,** 3148 (1961).

[612] R. A. Robinson and R. G. Bates, J. Res. NBS **70A,** 553 (1966).

[362] M. M. Davis and M. Paabo, J. Res. NBS **67A,** 231 (1963).

[592] T. Jasiński, T. Misiak, and T. Skarżyńska, Roczniki Chem. **39,** 1549 (1965).

Table 86. This table should be compared with tables 83 and 84. The association of aniline-type bases with phenol is far less than that of pyridine-type bases, in accord with expectation.

Table 87. This table is appropriately compared with table 81; there does not appear to be much

TABLE 83. *Log K_{BHA}, ΔH, and ΔS for association of some pyridine-type bases with phenol in carbon tetrachloride (molar units, 20°)* [a]

Base [b]	Log K_{BHA}	ΔH	ΔS	Log K_{BHA} (25°)
Pyridine (5.17) [c]	1.78	−7.0	−15.6	1.62
Derivatives of pyridine [d]				
3-Methyl (5.68)	1.86	−6.9	−15.0	1.78
2-*t*-Butyl (5.76)	....	....	....	1.28
2,6-Di-*t*-butyl	....	....	....	0.48
2-Methyl (5.97)	1.87	−6.9	−15.0	1.80
4-Methyl (6.02)	1.90	−6.6	−13.9	1.92
3,5-Dimethyl (6.19) [e]	....	....	....	2.03
2,6-Dimethyl (6.74) [f]	1.98	−6.9	−14.4	1.89
2,4-Dimethyl (6.82) [e]	2.02	−6.8	−14.1	....
2,4,6-Trimethyl (7.59) [f]	2.14	−7.5	−15.7	....
Related bases [g]				
Quinoline (4.85)	1.76	−7.2	−16.4	....
Isoquinoline (5.14)	1.79	−6.9	−15.4	....
Quinaldine (5.42) [h]	1.90	−7.1	−15.6	....
Acridine (5.60)	1.83	−6.6	−14.1	....

[a] Values at 20° are from T. Gramstad, Acta Chem. Scand. **16,** 807 (1962); ΔH is in kcal/mole and ΔS is in entropy units. Log K_{BHA} at 25° (see last column) is from A. Halleux, Bull. Soc. Chim. Belg. **68,** 381 (1959). Additional values at 20° for some of the bases, and also values of log K_{BHA} at 27°, are given in table 84.

[b] pK_a values in water (mainly thermodynamic values at 25°) are given in parentheses.

[c] See H. C. Brown and D. H. McDaniel, J. Am. Chem. Soc. **77,** 3752 (1955).

[d] Unless stated otherwise pK_a values for this group are results of H. C. Brown and X. R. Mihm, J. Am. Chem. Soc. **77,** 1723 (1955).

[e] The pK_a value was calculated assuming that effects of alkyl substituents on the pK_a of pyridine are additive.

[f] See H. C. Brown, S. Johnson, and H. Podall, J. Am. Chem. Soc. **76,** 5556 (1954).

[g] pK_a values (at 20° with the exception noted) are from H. C. Brown, D. H. McDaniel, and O. Häfliger, Chapter 14 ("Dissociation Constants") *in* Determination of Organic Structures by Physical Methods (Academic Press, Inc., New York, N.Y., 1955). (E. A. Braude and F. C. Nachod, eds.)

[h] At 25°.

REFERENCES:

[135] T. Gramstad, Acta Chem. Scand. **16,** 807 (1962).
[613] A. Halleux, Bull. Soc. Chim. Belg. **68,** 381 (1959).
[614] H. C. Brown and D. H. McDaniel, J. Am. Chem. Soc. **77,** 3752 (1955).
[615] H. C. Brown and X. R. Mihm, J. Am. Chem. Soc. **77,** 1723 (1955).
[616] H. C. Brown, S. Johnson, and H. Podall, J. Am. Chem. Soc. **76,** 5556 (1954).
[617] H. C. Brown, D. H. McDaniel, and O. Häfliger, Chapter 14 ("Dissociation Constants") *in* Determination of Organic Structures by Physical Methods (Academic Press, Inc., New York, N.Y., 1955). (E.A. Braude and F. C. Nachod, eds.)

difference in the behavior of pyridine and triethylamine as proton acceptors, when the proton donor is an alcohol or 1-naphthol.

Table 88. Four tertiary aliphatic amines, an alcohol, and three phenolic acids are represented in this table. Tribenzylamine, a much weaker base than triethylamine, associates less readily with proton donors of the types represented. The exceptionally low value of log K_{BHA} for tribenzylamine with pentachlorophenol is noteworthy—presumably this is to be attributed to steric hindrance. Values of ΔH and ΔS for associations involving tribenzylamine are all exceptionally low.

Readers should perhaps be reminded that table 43 contains log K_{BHA} values for some amines with acetic acid in carbon tetrachloride and chloroform.

5.4.4. Chloroform

Table 89. As would be predicted, log K_{BHA} for pyridine with phenol in chloroform is less than in carbon tetrachloride (compare table 82). Table 89 may be compared with table 75, which contains log K_{BHA} values for some of the same amine-phenol combinations in benzene. No clear-cut conclusions are possible.

TABLE 84. *Log* K_{BHA}, ΔH, *and* ΔS *for association of some pyridine-type bases with phenol in carbon tetrachloride (molar anits, 20°)*[a]

Substituent in Pyridine[b]	Log K_{BHA}	ΔH	ΔS	Log K_{BHA} (27°)
2–Cl (0.72)[c]				0.95
2–Br (0.90)[c]				0.90
3–CN (1.36)[d]	1.15	−4.9	−11.5	
4–CN (1.90)[d]	1.08	−3.2	−6.0	
3–Br (2.84)[c]	1.18	−4.5	−10.0	1.17
3–Cl (2.84)[c]				1.17
H (5.17)[c]	1.77	−6.5	−14.0	1.67
3–CH_3 (5.68)[e]	1.81	−6.7	−14.5	1.79
2–CH_3 (5.97)[e]				1.80
4–*t*–Bu (5.99)[e]	1.92	−7.1	−12.0	
4–CH_3 (6.02)[e]	1.91	−6.4	−13.0	1.92
4–C_2H_5 (6.02)[e]	1.89	−5.9	−11.5	

[a] Some values of log K_{BHA} at 27° are also given (see last column); these are from A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, J. Chim. Phys. **62,** 336 (1965). The other results are from J. Rubin and G. S. Panson, J. Phys. Chem. **69,** 3089 (1965).

[b] Numbers in parentheses are pK_a values (at 25°, where specified).

[c] Determined by H. C. Brown and D. H. McDaniel, J. Am. Chem. Soc. **77,** 3752 (1955).

[d] See S. F. Mason, J. Chem. Soc., p. 1247 (1959); temperature not specified.

[e] See H. C. Brown and X. R. Mihm, J. Am. Chem. Soc. **77,** 1723 (1955).

REFERENCES:

[624] J. Rubin and G. S. Panson, J. Phys. Chem. **69,** 3089 (1965).
[608] A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, J. Chim. Phys. **62,** 336 (1965).
[614] H. C. Brown and D. H. McDaniel, J. Am. Chem. Soc. **77,** 3752 (1955).
[618] S. F. Mason, J. Chem. Soc., p. 1247 (1959).
[615] H. C. Brown and X. R. Mihm, J. Chem. Soc. **77,** 1723 (1955).

5.4.5. Miscellaneous Aprotic Solvents

Table 90. This is a collection of values, mainly for pyridine, tertiary amines, and their *N*-oxides, with a phenol or iodine as the reference acid. It will be noted that the amine oxides seem to form more stable adducts than the corresponding tertiary amines. Figures 14 and 15 indicated that in amine oxide adducts the proton of the donor is less displaced towards the proton acceptor.

Before leaving the topic of log K_{BHA} values it seems desirable to call attention to some derivatives of phenol that might prove more useful for aprotic media than phenols that form stable chelate rings. A list of phenols covering the pK_a range from about 0.3 to 4.8 is given in table 91. It would be interesting to ascertain log K_{BHA} values for these phenols

TABLE 85. *Log* K_{BHA} *(molar units, 27°) for association of aniline with phenol and some of its monosabstituted derivatives in carbon tetrachloride*[a]

Acid (pK_a[b])	Log K_{BHA}
p-Cresol (10.26)	0.44
p-Methoxyphenol (10.21)	0.42
m-Cresol (10.09)	0.52
Phenol (10.00)	0.60
p-Fluorophenol (9.91)	0.67
p-Chlorophenol (9.42)	0.79
p-Bromophenol (9.36)	0.75
p-Iodophenol (9.30)	0.68
m-Chlorophenol (9.13)	0.75
m-Bromophenol (9.03)	0.80
m-Nitrophenol (5.38)	1.13

[a] Results of A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, J. Chim. Phys. **62,** 336 (1965).

[b] Obtained by A. O. Biggs and R. A. Robinson, J. Chem. Soc., p. 388 (1961).

REFERENCES:

[608] A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, J. Chim. Phys. **62,** 336 (1965).
[535] A. I. Biggs and R. A. Robinson, J. Chem. Soc., p. 388 (1961).

TABLE 86. *Log* K_{BHA} *(molar anits, 27°) for association of some aromatic bases with phenol in carbon tetrachloride*[a]

Aromatic base[b]	Log K_{BHA}
o-Bromoaniline (2.53)	0.32
o-Chloroaniline (2.65)	0.33
o-Fluoroaniline (3.20)	0.29
m-Fluoroaniline (3.59)	0.37
p-Bromoaniline (3.86)	0.51
p-Chloroaniline (3.98)	0.51
o-Toluidine (4.45)	0.56
Aniline (4.60)	[c]0.60
p-Fluoroaniline (4.65)	0.58
m-Toluidine (4.73)	0.66
p-Toluidine (5.08)	0.75
p-Anisidine (5.34)	0.87
N,N-Diethylaniline (6.56[d])	[e]0.42 (20°)

[a] Results of A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, J. Chim. Phys. **62,** 336 (1965).

[b] Values in parentheses are thermodynamic pK_a values (25°). All but the last were determined by A. I. Biggs and R. A. Robinson, J. Chem. Soc., p. 388 (1961).

[c] The same value was obtained at 25° by A. Halleux, Bull. Soc. Chim. Belg. **68,** 381 (1959).

[d] See N. F. Hall and M. R. Sprinkle, J. Am. Chem. Soc. **54,** 3469 (1932).

[e] See T. Gramstad, Acta Chem. Scand. **16,** 807 (1962); combined results for 20° and 50° yielded $\Delta H = -1.3$ and $\Delta S = -2.7$.

REFERENCES:

[608] A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, J. Chim. Phys. **62,** 336 (1965).
[535] A. I. Biggs and R. A. Robinson, J. Chem. Soc., p. 388 (1961).
[613] A. Halleux, Bull. Soc. Chim. Belg. **68,** 381 (1959).
[619] N. F. Hall and M. R. Sprinkle, J. Am. Chem. Soc. **54,** 3469 (1932).
[135] T. Gramstad, Acta Chem. Scand. **16,** 807 (1962).

TABLE 87. *Log* K_{BHA}, ΔH, *and* ΔS *(molar units, 20–25°) for association of triethylamine with some alcohols and phenols in carbon tetrachloride*

Proton donor (pK_a)	Log K_{BHA}[a]	ΔH	ΔS	References
Methanol	0.81 (20)	−3.8	−9.2	[135]
Ethanol	0.65 (22)	[b]−4.83	....	[605, 621]
1-Butanol	0.50 (22)	[b]−4.86	....	[620, 621]
2-Butanol	0.23 (22)	[b]−4.98	....	[605, 621]
Phenol (10.00)	1.87 (20)	−8.35	−20.0	[622]
Phenol	1.96 (20)	−7.8	−17.7	[135]
Phenol	1.95 (25)	−9.2	−21.7	[137]
1-Naphthol (9.39)	2.04 (20)	−6.6	−13.1	[135]

[a] Temperature of measurement (°C) is given in parentheses.

[b] Determined calorimetrically at 20°.

REFERENCES:

[620] T. Zeegers-Huyskens, Bull. Soc. Chim. Belge **69**, 282 (1960).
[621] L. Lamberts and T. Zeegers-Huyskens, J. Chim. Phys. **60**, 435 (1963).
[622] H. Dunken and H. Fritzsche, Z. Chem. **1**, 127 (1961).
[135] T. Gramstad, Acta Chem. Scand. **16**, 807 (1962).
[137] M. D. Joesten and R. S. Drago, J. Am. Chem. Soc. **84**, 3817 (1962).
[605] T. Zeegers-Huyskens, L. Lamberts, and P. Huyskens, J. Chim. Phys. **59**, 521 (1962).

in solvents like benzene and chlorobenzene, using the same reference base or bases, and see how they relate to the aqueous pK_a values.

Several investigators, including Weller [568], have determined aqueous pK_a values for phenolic acids such as 1- and 2-naphthol in the excited state, finding that on excitation the acid strength is much enhanced. Weller has also determined the equilibrium constants (20°) for hydrogen bonding of 3-hydroxypyrene with pyridine and with 2-chloropyridine in some aprotic solvents, making use of both absorption and fluorescence data, and thus deriving both $K°$ and K^*, where $K°$ denotes the equilibrium constant in the ground state, and K^* is the corresponding constant for hydrogen bonding in the excited state. Some of his results, expressed as the logarithms of $K°$ and K^*, are given in table 92. These results support the following conclusions:

(1) In aprotic solvents, as in water, a phenol is a better proton donor in the excited state than when in the ground state.

(2) Pyridine, which is a much stronger base than 2-chloropyridine, associates more extensively with 3-hydroxypyrene in the excited state as well as in the ground state.

(3) The extent of hydrogen bonding is not related to the dielectric constant of the solvent, but rather to its electron-donor properties, since hydrogen

TABLE 88. *Log* K_{BHA}, ΔH, *and* ΔS *(molar units, 20°) for association of some tertiary aliphatic amines with* ROH *or* ArOH *in carbon tetrachloride*[a]

Tertiary amine	Log K_{BHA}	ΔH	ΔS
ROH = Methanol			
Triethyl (10.87)	0.81	−3.8	−9.2
Tripropyl	0.53	−2.7	−6.9
Tributyl	0.61	−3.5	−8.8
Tribenzyl (5.60)	0.53	−1.5	−2.5
ArOH = Phenol (10.00)			
Triethyl (10.87)	1.96	−7.8	−17.7
Tripropyl	1.35	−5.9	−14.1
Tributyl	1.47	−6.9	−16.9
Tribenzyl (5.60)	0.43	−1.6	−3.4
ArOH = 1-Naphthol (9.39)			
Triethyl (10.87)	2.04	−6.6	−13.1
Tripropyl	1.49	−6.1	−14.2
Tributyl	1.65	−5.9	−12.6
Tribenzyl (5.60)	0.28	−1.3	−3.4
ArOH = Pentachlorophenol (4.82)			
Tribenzyl (5.60)	0.11	−3.	−10.0

[a] Results of T. Gramstad, Acta Chem. Scand. **16**, 807 (1962). Numbers in parentheses after the name of a phenol or amine are aqueous pK_a values.

REFERENCE:

[135] T. Gramstad, Acta Chem. Scand. **16**, 807 (1962).

TABLE 89. *Values of log* K_{BHA} *(molar units, 25°) for some acid-base associations in chloroform*[a]

Reference acid	Base	Log K_{BHA}
2,4-Dinitrophenol	$MeNH_2$	1.54
	n-$BuNH_2$	1.65
	n-$HxNH_2$	1.72
	Me_2NH	3.09
	Et_2NH	3.24
	n-Bu_2NH	3.41
	Me_3N	3.43
	Et_3N	4.20
	n-Bu_3N	3.96
Phenol	Py	[b]1.23

[a] All values of log K_{BHA} except the last one are from R. G. Pearson and D. C. Vogelsong, J. Am. Chem. Soc. **80**, 1038 (1958).

[b] A result of J. Rubin and G. S. Panson, J. Phys. Chem. **69**, 3089 (1965); $t = 20°$.

REFERENCES:

[591] R. G. Pearson and D. C. Vogelsong, J. Am. Chem. Soc. **80**, 1038 (1958).
[624] J. Rubin and G. S. Panson, J. Phys. Chem. **69**, 3089 (1965).

TABLE 90. *Log* K_{BHA}, ΔH, *and* ΔS *(molar units) for several tertiary amines and tertiary amine* N-*oxides in some aprotic solvents* [a]

Base	Ref. Acid	Solvent	t °C	Log K_{BHA}	ΔH	ΔS	References
Py	HPi	o-$C_6H_4Cl_2$	25	4.24			[599]
PyO	I_2	CCl_4	23	1.89	−5.85	−11.0	[625]
Me_3NO	I_2	CH_2Cl_2	22	3.75	−10.0	−16.9	[625]
Me_3NO	C_6H_5OH	CH_2Cl_2	20.5	3.57	−7.9	−10.6	[626]
Me_3NO	1-$C_{10}H_7OH$	CH_2Cl_2	20.7	3.80			[626]
Me_3NO	2-$C_{10}H_7OH$	CH_2Cl_2	20.7	3.82			[626]
Et_3N	1-$C_{10}H_7OH$	CH_2Cl_2	20.7	1.74			[626]
Et_3N	2-$C_{10}H_7OH$	CH_2Cl_2	20.7	1.78			[626]
Bu_3N	HPi	o-$C_6H_4Cl_2$	25	7.04			[449]
Bu_3N	HPi	CH_2ClCH_2Cl	25	7.15			[448]
Bu_3NO	HPi	o-$C_6H_4Cl_2$	25	7.89			[449]
$(PhCH_2)_3N$	BPM-E [b]	C_6H_6	25	−0.89			[31]
$(PhCH_2)_3NO$	BPM-E [b]	C_6H_6	25	5.68			[31]
$(PhCH_2)_3NO$	I_2	CH_2Cl_2	20	3.54	−10.5	−19.6	[625]

[a] ΔH in kcal/mole, ΔS in entropy units.

[b] BPM-E symbolizes bromophthalein magenta E (3′,5′,3″,5″-tetrabromophenolphthalein ethyl ester).

REFERENCES:

[31] M. M. Davis and H. B. Hetzer, J. Am. Chem. Soc. **76,** 4247 (1954).
[448] E. K. Ralph, III, and W. R. Gilkerson, J. Am. Chem. Soc. **86,** 4783 (1964).
[449] W. R. Gilkerson and E. K. Ralph, III, J. Am. Chem. Soc. **87,** 175 (1965).
[599] J. B. Ezell and W. R. Gilkerson, unpublished results cited in ref. [449].
[625] T. Kubota, J. Am. Chem. Soc. **87,** 458 (1965).
[626] T. Kubota, J. Am. Chem. Soc. **88,** 211 (1966).

bonding is most extensive in the most inert solvent (methylcyclohexane) and is least in the best electron-donor solvent (benzene).

In section 4.6.2 reference was made to a recent symposium in which Ubbelohde expressed disagreement with the opinion that weak hydrogen bonds may be distinguished from strong hydrogen bonds [554], asserting, instead [555], that "a whole spectrum of hydrogen bonds appears to exist." The tabulated values of log K_{BHA} and ΔH in aprotic solvents, just presented, provide much support for Ubbelohde's view.

TABLE 91. *Values of* pK_a *(water, 25°) for some halogen- and nitro-derivatives of phenol*

Acid	pK_a
Picric acid	[a] 0.33
Trinitro-*m*-cresol	[b] 0.81
Trinitro-3,5-xylenol	[c] 1.38
2-Chloro-4,6-dinitrophenol	[d] 2.10
4-Chloro-2,6-dinitrophenol	[e] 2.97
4-Chloro-2,6-dinitro-*m*-cresol	[d] 3.24
2,6-Diiodo-4-nitrophenol	[d] 3.32
2,6-Dibromo-4-nitrophenol	[d] 3.39
2,6-Dichloro-4-nitrophenol	[d] 3.55
2,6-Dinitrophenol	[f] 3.71
2,4-Dinitro-6-phenylphenol	[d] 3.85
2,4-Dinitro-3-methyl-6-*iso*propylphenol	[d] 3.96
2,4-Dinitrophenol	[g] 4.11
Bromophthalein magenta E	[h] ~ 4.15
2,6-Dinitro-*p*-cresol	[d] 4.23
4,6-Dinitro-*o*-cresol	[d] 4.47
4,6-Dinitro-2-*iso*propylphenol	[d] 4.54
2,4-Dibromo-6-nitrophenol	[d] 4.71
Pentachlorophenol	[i] 4.82

[a] M. M. Davis and M. Paabo, ref. [362].

[b] M. M. Davis and M. Paabo, ref. [627].

[c] M. M. Davis, M. Paabo, and R. A. Robinson, ref. [628].

[d] R. A. Robinson, unpublished result.

[e] E. E. Sager, R. A. Robinson, and R. G. Bates, ref. [636].

[f] G. Kortüm and H. Wilski, Z. Physik. Chem. **2**, 256 (1954); J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, J. Chem. Soc., p. 2995 (1956).

[g] R. G. Bates and G. Schwarzenbach, ref. [629].

[h] M. M. Davis and H. B. Hetzer, ref. [32], footnote 29.

[i] R. A. Robinson and R. G. Bates, ref. [612].

REFERENCES:

[32] M. M. Davis and H. B. Hetzer, J. Res. NBS **60**, 569 (1958).

[362] M. M. Davis and M. Paabo, J. Res. NBS **67A**, 241 (1963).

[533] R. A. Robinson, unpublished work.

[612] R. A. Robinson and R. G. Bates, J. Res. NBS **70A**, 553 (1966).

[627] M. M. Davis and M. Paabo, J. Res. NBS **64A**, 533 (1960).

[628] M. M. Davis, M. Paabo, and R. A. Robinson, J. Res. NBS **64A**, 531 (1960).

[629] R. G. Bates and G. Schwarzenbach, Helv. Chim. Acta **37**, 1069 (1954).

[630] G. Kortüm and H. Wilski, Z. Physik. Chem. **2**, 256 (1954).

[631] J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, J. Chem. Soc., p. 2995 (1956).

[636] E. E. Sager, R. A. Robinson, and R. G. Bates, J. Res. NBS **69A**, 305 (1964).

TABLE 92. *Log* K_{BHA} *(molar units, 20°) for hydrogen bonding of 3-hydroxypyrene to pyridine and to 2-chloropyridine in the ground and excited states* [a]

Solvent (ε, 20° [c])	Proton acceptor [b]			
	Pyridine (5.17)		2-Chloropyridine (0.72)	
	Log K°	Log K^*	Log K°	Log K^*
Methylcyclohexane (2.02)	2.34	2.99	1.27	1.78
Benzene (2.28)	1.76	2.43	0.8_5	1.26
o-Chlorotoluene (4.45)	1.89	2.63	0.9	1.40

[a] See A. Weller, *in* Progress in Reaction Kinetics, Vol. **1** (G. Porter, Ed.), p. 189 ff. (Pergamon Press, New York, 1961).

[b] pK_a at 25° (see table 84) is given in parentheses.

[c] See ref. [35]

REFERENCES:

[35] A. A. Maryott and E. R. Smith, Table of dielectric constants of pure liquids, NBS Circ. 514, Aug. 10, 1951.

[568] A. Weller, *in* Progress in Reaction Kinetics, Vol. **1** (G. Porter, Ed.), p. 189 ff. (Pergamon Press, New York, 1961).

6. Acid-Base Titrations in Completely Aprotic Solvents

6.1. Introduction

The assigning of an exaggerated importance to water is nowhere better illustrated than in the history of acid-base titrations. The belief still persists that water *must* be present, at least in trace amounts, if acid-base reactions are to occur. However, organic chemists have recognized that water is not needed, and as mentioned earlier, Vorländer discovered more than 60 years ago that aniline is titratable with hydrogen chloride in benzene, using methyl yellow as the indicator [542]. Moreover, about a decade later, Folin and Flanders [637] demonstrated that carboxylic acids can be titrated *more* satisfactorily in mixtures of an alcohol with benzene, carbon tetrachloride, chloroform, or toluene than in alcohol-water mixtures; in their experiments the titrant was sodium ethylate or amylate in the corresponding alcohol, and phenolphthalein was considered the best of the available indicator dyes.

Folin and Flanders' paper was generally overlooked for about 35 years, but eventually alcohol-hydrocarbon mixtures became popular for acid-base titrations—especially mixtures of benzene or toluene with isopropyl alcohol (a medium adopted for ASTM standard methods) [638], ethylene glycol [639], or methanol [50]. A small amount of water is considered necessary when the glass-calomel electrode system is used for locating an end-point, but not in conductance or indicator titrations. As time has passed, analysts have tended to reduce the alcohol content to the point where it is a very minor component of the medium, introduced only as part of the titrant. (For examples, see refs. [476, 484, 485]; several examples are also given in ref. [640]). In titrations requiring a strong base, the presence of a little alcohol and/or water has been unavoidable, since no satisfactory substitute for quaternary ammonium hydroxides (or alkoxides) has yet been found. However, procedures have been devised for reducing their content to a very small percentage of the total solvent.

On the whole, there has been a strong inclination to use *mixed solvents* in nonaqueous titrimetry. Not infrequently, several solvents are present, and it has been comparatively rare for a *single* nonaqueous solvent to be used for titrations—especially an aprotic solvent. However, titrations in completely aprotic solvents are entirely feasible when a proper combination of reactants is selected. Our remaining discussion will consist of a brief survey of such titrations, in which various indicator dyes or physical measurements were used for end-point location. We shall not dwell on modern improvements in instrumentation, since these are widely recognized and taken advantage of. Emphasis will be placed, instead, on the need for further modernization of *chemical* aids, such as reference acids and bases. Comparatively little work has been done in this area, and the aid of organic chemists could well be enlisted—in particular, in developing improved reference bases. Further developmental work with indicator dyes is also needed, since titrations with indicators are still preferred by many because of their speed and simplicity. However, for the most fruitful use of indicator dyes, as much effort should be expended in gaining insight into the structural changes responsible for color changes as is expended in learning about the construction and proper use of instrumental aids.

6.2. Titrations With Indicator Dyes in Completely Aprotic Solvents

Possibilities in this category are indicated in table 93. Bromophthalein magenta E, tamarack green base, and Victoria blue B anhydro-base are examples of indicators intended especially for aprotic solvents. The latter two are bases. *p*-Naphtholbenzein, an acid weaker than bromophthalein magenta E, is sometimes useful in benzene. Diphenyl phosphate was found to be a very satisfactory reference acid in the examples given in the table. It can readily be converted from its dihydrate to the anhydrous state, does not absorb moisture readily, is easily soluble in solvents like benzene, and is colorless in the visible region. In water it appears to be as strong as hydrochloric acid [313]. Some suggestions about reference compounds will be given in section 6.4.

6.3. Instrumental Procedures for Detecting End-points in Completely Aprotic Solvents

6.3.1. Conductance Titrations

Examples from Maryott's work [341] were shown in figures 19 to 21. It will be recalled that he titrated aliphatic amines in benzene with such acids as picric acid, trichloroacetic acid, and *dl*-camphorsulfonic acid. The work was suggested by earlier exploratory titrations of LaMer and Downes [340], who did not continue their investigations after observing anomalies in behavior.

6.3.2. Dielectrometric Titrations

Gur'yanova and Beskina [347] measured changes in the dielectric permeability of a solution of benzoic acid in benzene on the addition of *n*-butylamine, various secondary amines (i-Pr_2NH, Bu_2NH, Et_2NH, piperidine), or a tertiary amine (Et_3N, Am_3N). Their objectives were to determine stoichiometry and relative strengths, rather than to develop titrimetric procedures.

Bryant and Wardrop's conductimetric studies of acid-base interactions in acetone and acetonitrile [474] included dielectrometric titrations of trichloroacetic acid (about 0.001 M) with triethylamine (about 0.2 M) in benzene and also in dioxane. The

TABLE 93. *Some examples of acid-base titrations in completely aprotic solvents, using indicator dyes*

Solvents	Acids	Bases	Indicator dyes	References
Benzene; chloroform [a]	HCl; $ArSO_3H$ [b]	Amines; drugs; alkaloids	[c] MY	[d] [540–543, 641–643]
Chloroform	CH_3COOH; HPi	[e] C_2G	[f] *p*-NB	[360]
Benzene	CCl_3COOH; HPi	[g] *o*-T_2G	[h] BPM–E	[14]
Benzene	[i] RSO_3H	[e] C_2G; [j] Ph_2G	[h] BPM–E	[14]
Benzene	[k] Ph_2HPO_4	[g] *o*-T_2G; [j] Ph_2G	[h] BPM–E; [l, m] TGB	[313]

[a] Also carbon tetrachloride, dichloromethane, tetrachloroethane, ligroin.

[b] Ar = C_6H_5 or *p*-$CH_3C_6H_4$.

[c] *N,N*-Dimethyl-*p*-azoaniline (*p*-dimethylaminoazobenzene); usually called methyl yellow (but occasionally, "dimethyl yellow" or "butter yellow").

[d] This group of papers was reviewed briefly in ref. [14].

[e] 1,3-Dicyclohexylguanidine; see ref. [14].

[f] *p*-Naphtholbenzein.

[g] 1,3-Di-*o*-tolylguanidine.

[h] Bromophthalein magenta E (3′,5′,3″,5″-tetrabromophenolpthalein ethyl ester).

[i] In this table RSO_3H signifies *d*-10-camphorsulfonic acid.

[j] 1,3-Diphenylguanidine.

[k] Diphenyl phosphate (anhydrous).

[l] Tamarack green base (anhydro-*N*,*N*′-diphenyl-*p*,*p*′-diamino-*o*″-chlorotriphenylcarbinol).

[m] Victoria blue B anhydro-base, prepared from the commercial salt, which has Color Index No. (1st ed.) 729, was another satisfactory indicator.

REFERENCES:

[14] M. M. Davis and P. J. Schuhmann, J. Res. NBS **39**, 221 (1947).
[313] M. M. Davis and H. B. Hetzer, J. Res. NBS **54**, 309 (1955).
[360] M. M. Davis and P. J. Schuhmann, unpublished work.
[540] R. Dietzel and W. Paul, Arch. Pharm. **273**, 507 (1935); **276**, 408 (1938).
[541] E. M. Trautner and F. H. Shaw, Australian Chem. Inst. J. & Proc. **12**, 405 (1945).
[542] D. Vorländer, Chem. Ber. **36**, 1485 (1903).
[543] D. Vorländer, J. Fischer, and F. Wildner, Chem. Ber. **66**, 1789 (1933).
[641] D. Vorländer, Chem. Ber. **67**, 145 (1934).
[642] E. M. Trautner and C. E. Neufeld, Australian Chem. Inst. J. & Proc. **13**, 70 (1946).
[643] G. Ya. Khaĭt, Farmatsiya **8**, 26 (1945); see Chem. Abstracts **41**, 2206 (1947).

dielectric constant increased gradually until the equivalence point, then became essentially constant (see their figure 5).

A "simulated" dielectrometric titration curve for picric acid (~ 0.002 *M*) with triethylamine in benzene [644] is shown in figure 30. The points were obtained by measuring the dielectric constant of a series of solutions containing a fixed amount of the acid but varying amounts of the base. In the example shown, the calculated and experimental end-points agreed within 1.7 percent. In this procedure the volume of solvent did not change during the titration. The authors have titrated other acid-base systems in benzene with comparable results. Ishidate and co-workers (for example, see ref. [648]) have recently explored analytical dielectrometric titrations in dioxane.

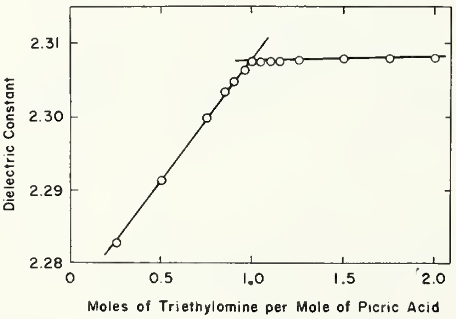


FIGURE 30. *Curve for the simulated dielectrometric titration of picric acid (~ 0.002 M) with triethylamine in benzene.*

Based on unpublished results of R. Megargle, D. Rosenthal, and G. L. Jones, Jr., Clarkson College of Technology, 1966.

6.3.3. Photometric Titrations

What are in effect photometric titrations have been performed frequently in spectrophotometric investigations intended mainly to determine acid-base stoichiometry and relative strengths in solvents like benzene (for examples, see refs. [5, 20, 21, 14] and [482]).

Davis and McDonald [361] titrated picric acid with such bases as diphenyl- and di-*o*-tolylguanidine spectrophotometrically, obtaining curves very similar to figure 30. Here again, the main objectives were to determine stoichiometry and relative strengths. Such work is a necessary stage, of course, in the development of titration methods.

6.3.4. Thermometric Titrations

Here we may refer again to the titrations of bases with hydrogen bromide in acetonitrile, performed by Forman and Hume [596], and to the titrations of similar bases with trichloroacetic acid in benzene by Mead [597]. Mead's principal objective was to determine values of ΔH and correlate them, if possible, with relative strength of the bases. (See fig. 28.)

6.3.5. Titrations by the DVP Method [352]

The reader is referred to figure 12 and related discussion. Here, again, is a method used hitherto for determining stoichiometry and relative strengths, not as an analytical procedure.

6.3.6. Cryoscopic Titrations

Gur'yanova and Beskina [347] performed cryoscopic titrations of benzoic acid in benzene with amines like Am_3N, Et_3N, and piperidine, as an adjunct to dielectrometric titrations, in studying the association of benzoic acid with amines (see sec. 4.3.2).

More recently, Bruckenstein and Vanderborgh [645] have titrated bases in benzene with trifluoroacetic and trichloroacetic acids, using an experimental apparatus for recording continuously the change in the freezing point depression during a titration. They obtained curves which can be interpreted analogously to differential vapor pressure data. The cryoscopic method is useful when the differential vapor pressure method is not applicable (for example, when volatile solutes are involved).

6.3.7. Other Possible Instrumental Procedures

Other physical methods that have been found to indicate changes in composition resulting from acid-base interactions in aprotic solvents are:

a. Refractive index. Giles, McKay, and Good [647] determined changes in the refractive index of carbon tetrachloride solutions containing such mixtures as benzene-phenol, chlorobenzene-phenol, and hexachlorobenzene-phenol. V-shaped curves were obtained for chlorobenzene-phenol on plotting the change in the refractometer reading against the composition (expressed as mole fractions).

b. Density. Changes in density on the addition of tripentylamine to benzoic acid in benzene appear to be very abrupt near the end-point [347]. Changes in density upon varying the proportion of piperidine to propionic acid in benzene have also been measured [646].

c. Optical rotation. Bodforss' studies of the change in optical rotation on adding an acid to brucine in benzene or chloroform were mentioned a little earlier [574].

Although these physical methods may not all be suitable for analytical titrations, this list serves to remind us that there are doubtless many untried types of measurements that could be applied to advantage in determining the composition of acid-base complexes, relative strengths, and possibly also in analytical titrimetry in aprotic media.

6.4. Reference Acids and Bases for Aprotic Organic Solvents

6.4.1. Acids

We shall comment briefly on five chemical types that have been used hitherto.

a. Hydrogen chloride. This was used in the pioneering aminometric titrations of Vörlander and associates [542, 543, 641]. Its proton-donor ability makes it suitable for many titrations, but standard solutions are troublesome to prepare and have to be restandardized frequently. Also, the gas escaping from solutions is likely to contaminate other materials and cause corrosion of metal objects.

b. p-Toluenesulfonic acid. This is a useful solid reference acid, so far supplied commercially only as the monohydrate. Trautner and Shaw [541] described a method for dehydrating it. Maryott used *dl*-10-camphorsulfonic acid for conductance titrations of amines in dioxane [341]. The optically active isomer, *d*-10-camphorsulfonic acid, is somewhat more easily soluble in benzene, and was used for titrations of bases in this solvent in the presence of indicator dyes [14].

c. Picric acid. Although this acid is easily obtained and purified, is conveniently handled, and is a good proton donor, the strong yellow color of its salts is sometimes objectionable. In section 5 a list of possible replacements (for some purposes) was suggested (see table 91).

d. Trichloroacetic acid is a good proton donor and readily soluble. It is somewhat volatile and therefore difficult to dry completely.

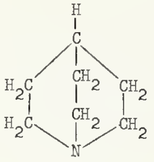
e. Diphenyl phosphate. This acid has been investigated [313] as a reference acid in benzene (as well as in benzene-methanol mixtures). See comments on table 93.

6.4.2. Bases

The discussion will be confined to bases of at least moderate strength.

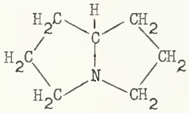
a. Aliphatic amines. We shall only discuss tertiary amines, which are preferable to primary and secondary amines for reasons indicated earlier. Triethylamine is still used extensively, although it seems to be giving place to amines of higher molecular weight—for example, *N,N*-dimethylbenzylamine. Tribenzylamine has admirable physical properties, but is not a very strong base.

It is rather surprising that the cyclic tertiary amine, quinuclidine (XCI) has not been made available commercially. Brown and Eldred [649] described its preparation "in good yield starting with the commercially available 4-pyridineethanol," and later, S. Leonard and Elkin [650] described another procedure for obtaining it from the same starting material. This interesting base is a very close relative of triethylamine, but the ethyl groups are "tied back," thus leaving the nitrogen atom more exposed, and thereby more reactive. As an illustration, Brown and Sujishi [635] found quinuclidine to form the most stable known complex with the Lewis acid, trimethylboron, whereas Brown and Taylor [651] found the association of triethylamine with trimethylboron to be too small to measure. The model of quinuclidine shows it to have a globular structure. Although easily sublimed, it is a solid at ordinary temperatures (m.p. 156° in a sealed tube [650]).



(XCI)

There may also be potentially useful reference bases among derivatives of pyrrolizidine (XCII).



(XCII)

Various bases of this class have been found by Adams and co-workers [652] and by N. J. Leonard and Beck [653] to be more basic than analogous acyclic amines.

b. Amidines. Substituted amidines,

$$R{-}C({=}NR')NR''_2,$$

where the R's are alkyl or aryl, should probably be mentioned as possible reference bases, but they seem less promising for titrimetry than derivatives of guanidine, which will be discussed next.

c. Derivatives of guanidine. We have already referred to 1,3-diphenylguanidine, an easily obtained solid base (much used in the rubber industry), and stated that in benzene it is a stronger base than triethylamine. Its use as a primary standard in acid-base titrations was proposed by Carlton in 1922 [654], and it has been used in such varied nonaqueous solvents as acetic acid, acetonitrile, alcohols, and benzene. Davis and co-workers used both diphenyl- and di-*o*-tolylguanidine successfully for titrations in benzene [14, 313]. The somewhat stronger base, 1,3-dicyclohexylguanidine, whose hydrochloride at one time was available commercially as a research material, was not considered soluble enough in benzene for practical use; it has adequate solubility in chloroform, but reacts with this solvent to some extent [14].

Di- and tri-alkylguanidines have not been obtainable commercially. In fact, 1,3-dialkylguanidines have not been very extensively investigated, perhaps because for almost twenty years they were generally believed to be rather weak bases [655, 190b], and this error has not been universally corrected. However, there is now substantial evidence [656, 657] that partial or complete alkylation of guanidine does not diminish the strength of this very strong base, but, instead, probably increases the strength somewhat.

In the past, derivatives of guanidine have usually been investigated as salts, and comparatively few seem to have been converted into the free bases. However, Joshua [658] has described a preparation of 1,3-diphenyl-2-methylguanidine, and reported the melting point as 107°. On the other hand, Braun and Randall [659] evidently isolated 1,3-dibenzylguanidine and 1,2,3-tribenzylguanidine only as hydrochlorides.

It should be very interesting to compare the behavior of 1,3-diphenyl- and 1,3-diphenyl-2-methylguanidine, as this would test a suggested explanation [15] for the observation that diphenylguanidine combines much more extensively than triethylamine with carboxylic acids in benzene, although it is the weaker base in water. The tendency toward self-association observed for 1,3-diphenylguanidine, and attributed to N–H...N bonding, should be absent in its 2-methyl derivative.

Obviously, whatever the method used for locating the titration end-point in an aprotic solvent, the degree of success will depend on having satisfactory primary standards. The search for improved standards, with aid from organic chemists, should be an interesting and rewarding pursuit for analytical and physical chemists wishing to improve titration procedures.

The author thanks the investigators and publishers who graciously approved the reuse of published figures (see captions to figures 6, 8–12, 19–21, 28), and gives special thanks to the following investigators for contributing previously unpublished results: A. R. Anderson and W. F. K. Wynne-Jones (see table 75), R. A. Robinson (tables 68 and 91), and R. Megargle, D. Rosenthal, and G. L. Jones, Jr. (see figure 30).

7. References

[1] J. Stieglitz, The Elements of Qualitative Chemical Analysis, with Special Consideration of the Laws of Equilibrium and of the Modern Theories of Solution, Vol. **1**, p. 73 (The Century Co., New York, 1911).

[2] G. N. Lewis, J. Franklin Inst. **226**, 293 (1938).

[3] J. A. Moede and C. Curran, J. Am. Chem. Soc. **71**, 852 (1949).

[4] J. A. Geddes and C. A. Kraus, Trans. Faraday Soc. **32**, 585 (1936).

[5] M. M. Davis and H. B. Hetzer, J. Res. NBS **46**, 496 (1951).

[6] I. M. Kolthoff, J. Phys. Chem. **48**, 51 (1944).

[7] I. M. Kolthoff, in Treatise on Analytical Chemistry (I. M. Kolthoff, P. M. Elving, and E. B. Sandell, Eds.), Part I–A, Vol. **1**, Ch. 11 (Interscience, New York, 1959).

[8] R. P. Bell, Quart. Rev. London **1**, 113 (1947).

[9] R. P. Bell, Acids and Bases, Their Quantitative Behavior (John Wiley & Sons, Inc., New York, N.Y., 1952).

[10] J. N. Brønsted, Rec. Trav. Chim. **42**, 718 (1923).

[11] J. N. Brønsted, J. Phys. Chem. **30**, 777 (1926).

[12] J. N. Brønsted, Chem. Ber. **61**, 2049 (1928).

[13] J. N. Brønsted, Z. Angew. Chem. **43**, 229 (1930).

[14] M. M. Davis and P. J. Schuhmann, J. Res. NBS **39**, 221 (1947).

[15] M. M. Davis and M. Paabo, J. Am. Chem. Soc. **82**, 5081 (1960).

[16] M. M. Davis, J. Am. Chem. Soc. **84**, 3623 (1962).

[17] M. M. Davis, unpublished results.

[18] A. Hantzsch, Z. Elektrochem. **29**, 221 (1923); **30**, 194 (1924).

[19] A. Hantzsch and W. Voigt, Chem. Ber. **62**, 975 (1929).

[20] M. M. Davis and E. A. McDonald, J. Res. NBS **42**, 595 (1949).

[21] M. M. Davis and H. B. Hetzer, J. Res. NBS **48**, 381 (1952).

[22] A. Weissberger and K. Fasold, Z. Physik. Chem. **A157**, 65 (1931).

[23] A. A. Maryott, J. Res. NBS **41**, 7 (1948).

[24] C. R. Witschonke and C. A. Kraus, J. Am. Chem. Soc. **69**, 2471 (1947).

[25] A. I. Shatenshtein, Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds. Authorized translation from the 1960 Russian edition, by C. N. Turton and T. I. Turton. Consultants Bureau, New York, 1962.

[26] N. A. Izmailov, Theory of the Dissociation of Acids and Bases, as summarized by A. I. Shatenshtein, ref. 25, sect. IV, 5, including references to numerous publications in Russian.

[27] N. D. Sokolov, views on hydrogen bonding, as summarized by A. I. Shatenshtein, ref. 25, including references to articles in Russian.

[28] J. Kendall and J. E. Booge, J. Am. Chem. Soc. **39**, 2323 (1917).

[29] M. M. Davis, P. J. Schuhmann, and M. E. Lovelace, J. Res. NBS **41**, 27 (1948).

[30] M. M. Davis, Sci. Counselor **16**, 88, 110 (1953); NBS Tech. News Bull. **36**, 168 (1952).

[31] M. M. Davis and H. B. Hetzer, J. Am. Chem. Soc. **76**, 4247 (1954).

[32] M. M. Davis and H. B. Hetzer, J. Res. NBS **60**, 569 (1958).

[33] M. M. Davis and H. B. Hetzer, J. Res. NBS **65A**, 209 (1961).

[34] H. L. Clever, J. Chem. Educ. **40**, 637 (1963).

[35] A. A. Maryott and E. R. Smith, Table of Dielectric Constants of Pure Liquids, NBS Circ. 514, Aug. 10, 1951.

[36] C. G. Malmberg, NBS, unpublished data.

[36a] W. Dannhauser and L. W. Bahe, J. Chem. Phys. **40**, 3058 (1964).

[37] F. E. Critchfield, J. A. Gibson, Jr., and J. L. Hall, J. Am. Chem. Soc. **75**, 6044 (1953).

[38] J. T. Denison and J. Ramsey, J. Am. Chem. Soc. **77**, 2615 (1955).

[39] G. R. Leader and J. F. Gormley, J. Am. Chem. Soc. **73**, 5731 (1951).

[39a] T. B. Hoover, J. Phys. Chem. **68**, 876 (1964).

[39b] A. Popov, M. L. Anderson, and R. N. Hammer, Abstrs. Papers 145th Meeting Am. Chem. Soc., New York, N.Y., September, 1963, p. 21N.

[40] J. J. Lindberg and J. Kenttämaa, Suomen Kemistilehti **B33**, 104 (1960).

[41] A. Lüttringhaus and H. W. Dirksen, Angew. Chem. Intern. Ed. Engl. **3**, 260 (1964).

[42] H. Schlundt, Bull. Univ. Wisconsin No. 47; Science Series **2**, No. 5, p. 297–351 (1901).

[43] C. P. Smyth, Dielectric Behavior and Structure (McGraw-Hill Book Co., New York, 1955).

[44] ASTM Standards on Petroleum Products and Lubricants, 38th ed., Vol. **1**, 198–306, Am. Soc. Testing Materials, Philadelphia, Pa., 1961.

[45] S. R. Ames and S. B. Licata, J. Am. Oil Chem. Soc. **25**, 203 (1948).

[46] O. Popovych, Anal. Chem. **36**, 878 (1964).

[47] H. Sadek and R. M. Fuoss, J. Am. Chem. Soc. **72**, 301 (1950).

[48] F. M. Sacks and R. M. Fuoss, J. Am. Chem. Soc. **75**, 5172 (1953).

[49] M. A. Coplan and R. M. Fuoss, J. Phys. Chem. **68**, 1181 (1964).

[50] J. S. Fritz, Acid-Base Titrations in Nonaqueous Solvents, G. Frederick Smith Chemical Co., Columbus, Ohio, 1952.

[51] G. Åkerlöf, J. Am. Chem. Soc. **54**, 4125 (1932).

[52] A. C. Brown and D. J. G. Ives, J. Chem. Soc., p. 1608 (1962).

[53] F. E. Critchfield, J. A. Gibson, Jr., and J. L. Hall, J. Am. Chem. Soc. **75**, 1991 (1953).

[54] J. J. Lindberg, J. Kenttämaa, and A. Nissema, Suomen Kemistilehti **B34**, 156 (1961).

[55] R. J. Campbell and J. L. Hall, Proc. West Va. Acad. Sci. **23**, 64 (1951).

[56] F. Accascina and S. Petrucci, Ricerca Sci. **29**, 1633 (1959).

[57] J. H. LaRochelle and A. A. Vernon, J. Am. Chem. Soc. **72**, 3293 (1950).

[58] J. L. Hall and R. J. Campbell, Proc. West Va. Acad. Sci. **29–30**, 53 (1957–58).

[59] G. L. Starobinets, K. S. Starobinets, and L. A. Ryzhikova, Zhur. Fiz. Khim. **25**, 1186 (1951).

[60] A. A. Vernon, J. Wyman, and R. A. Avery, J. Am. Chem. Soc. **67**, 1422 (1945).

[61] D. S. Berns and R. M. Fuoss, J. Am. Chem. Soc. **82**, 5585 (1960); **83**, 1321 (1961).

[62] H. Sadek and R. M. Fuoss, J. Am. Chem. Soc. **76**, 5905 (1954).

[63] R. M. Fuoss and E. Hirsch, J. Am. Chem. Soc. **82**, 1013 (1960).

[64] H. Sadek and R. M. Fuoss, J. Am. Chem. Soc. **76**, 5897 (1954).

[65] H. Sadek and R. M. Fuoss, J. Am. Chem. Soc. **76**, 5902 (1954).

[66] A. D'Aprano and R. M. Fuoss, J. Phys. Chem. **67**, 1704, 1871 (1963).

[67] J. L. Hall and R. J. Campbell, Proc. West Va. Acad. Sci. **30**, 155 (1958).

[68] J. J. Lindberg, Suomen Kemistilehti **B32**, 12 (1959).

[69] A. A. Antony and C. P. Smyth, J. Am. Chem. Soc. **86**, 152 (1964).

[70] G. Briegleb, Elektronen-Donator-Acceptor-Komplexe (Springer-Verlag, Berlin, 1961).

[71] E. M. Arnett *in* Progress in Physical Organic Chemistry, Vol. **1** (Interscience, 1963).

[72] H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc. **70**, 2832 (1948); **71**, 2703 (1949).

[73] R. S. Mulliken, J. Am. Chem. Soc. **72**, 600 (1950); **74**, 811 (1952).

[74] R. S. Mulliken, J. Phys. Chem. **56**, 801 (1952).

[75] R. S. Mulliken, Rec. Trav. Chim. **75**, 845 (1956).

[76] R. S. Mulliken and W. B. Person, Donor-acceptor complexes, Ann. Rev. Phys. Chem. **13**, 107 (1962).

[77] L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc. **74**, 4500 (1952).

[78] N. Ogimachi, L. J. Andrews, and R. M. Keefer, J. Am. Chem. Soc. **77**, 4202 (1955).

[79] D. A. McCaulay and A. P. Lien, J. Am. Chem. Soc. **73**, 2013 (1951).

[80] H. C. Brown and J. D. Brady, J. Am. Chem. Soc. **74**, 3570 (1952).

[81] C. K. Ingold, Structure and Mechanism in Organic Chemistry (Cornell Univ. Press, Ithaca, N.Y., 1953).

[82] G. A. Olah, S. J. Kuhn, and S. H. Flood, J. Am. Chem. Soc. **83**, 4581 (1961).

[83] M.-L. Josien and G. Sourisseau *in* Hydrogen Bonding (Ljubljana, 1957), p. 129. (D. Hadži and H. W. Thompson, eds.) Pergamon, New York, 1959.

[84] N. Fuson, P. Pineau, and M.-L. Josien *in* Hydrogen Bonding (Ljubljana, 1957), p. 169. (D. Hadži and H. W. Thompson, eds.) Pergamon, New York, 1959.

[85] O. Popovych, J. Phys. Chem. **66**, 915 (1962).

[86] W. G. Schneider, J. Phys. Chem. **66**, 2653 (1962).

[87] J. V. Hatton and R. E. Richards, Mol. Phys. **5**, 139 (1962).

[88] C. J. Creswell and A. L. Allred, J. Phys. Chem. **66**, 1469 (1962).

[89] R. West, J. Am. Chem. Soc. **81**, 1614 (1959).

[90] R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, J. Am. Chem. **84**, 3221 (1962).

[91] P. von R. Schleyer and R. West, J. Am. Chem. Soc. **81**, 3164 (1959).

[92] D. A. K. Jones and J. G. Watkinson, J. Chem. Soc., p. 2366 (1964).

[93] P. J. Krueger and H. D. Mettee, Can. J. Chem. **42**, 288 (1964).

[94] U. Liddel, Ann. N.Y. Acad. Sci. **69**, 70 (1957).

[95] L. J. Bellamy, H. E. Hallam, and R. L. Williams, Trans. Faraday Soc. **54**, 1120 (1958).

[96] S. Glasstone, Trans. Faraday Soc. **33**, 200 (1935).

[97] D. P. Earp and S. Glasstone, J. Chem. Soc., p. 1709 (1935).

[98] J. R. Goates, R. J. Sullivan, and J. B. Ott, J. Phys. Chem. **63**, 589 (1959).

[99] R. Anderson and J. M. Prausnitz, J. Chem. Phys. **39**, 1225 (1963).

[99a] W. B. Person, J. Am. Chem. Soc. **87**, 167 (1965).

[100] A. N. Sharpe and S. Walker, J. Chem. Soc., p. 2974 (1961), p. 157 (1962), p. 2340 (1964).

[100a] I. R. McKinnon and A. G. Williamson, Australian J. Chem. **17**, 1374 (1964).

[101] K. B. Whetsel and R. E. Kagarise, Spectrochim. Acta **18**, 329 (1962).

[102] G. C. Pimentel and A. L. McClellan, The Hydrogen Bond (W. H. Freeman and Co., San Francisco, 1960).

[103] M.-L. Josien, J.-P. Leicknam, and N. Fuson, Bull. Soc. Chim. France, p. 188 (1958).

[104] A. Allerhand and P. von R. Schleyer, J. Am. Chem. Soc. **85**, 1715 (1963).

[105] G. F. Zellhoefer, M. J. Copley, and C. S. Marvel, J. Am. Chem. Soc. **60**, 1337 (1938).

[106] M. J. Copley, G. F. Zellhoefer, and C. S. Marvel, J. Am. Chem. Soc. **60**, 2666, 2714 (1938).

[107] C. S. Marvel, M. J. Copley, and E. Ginsberg, J. Am. Chem. Soc. **62**, 3109 (1940).

[108] W. Gordy, J. Am. Chem. Soc. **60**, 605 (1938).

[109] W. Gordy, J. Chem. Phys. **7**, 163 (1939).

[110] A. M. Buswell, W. H. Rodebush, and M. F. Roy, J. Am. Chem. Soc. **60**, 2528 (1938).

[111] E. Halpern, J. Bouck, H. Finegold, and J. Goldenson, J. Am. Chem. Soc. **77**, 4472 (1955).

[112] K. B. Whetsel and J. H. Lady, J. Phys. Chem. **68**, 1010 (1964).

[113] G. M. Kosolapoff and J. F. McCullough, J. Am. Chem. Soc. **73**, 5392 (1951).

[114] E. R. Kearns, J. Phys. Chem. **65**, 314 (1961).

[115] J. Lascombe, Thesis, Univ. of Bordeaux (1960). Cited in ref. [101].

[116] C. F. Jumper, M. T. Emerson, and B. B. Howard, J. Chem. Phys. **35**, 1911 (1961).

[117] R. E. Kagarise, Spectrochim, Acta **19**, 629 (1963).

[118] G. M. Barrow and E. A. Yerger, J. Am. Chem. Soc. **76**, 5247 (1954).

[119] C. J. Creswell and A. L. Allred, J. Am. Chem. Soc. **85**, 1723 (1963).

[120] C. J. Creswell and A. L. Allred, J. Am. Chem. Soc. **84**, 3966 (1962).

[121] A. Nikuradse and R. Ulbrich, Z. Phys. Chem. (Frankfurt) **2**, 9 (1954).

[122] E. D. Becker, Spectrochim. Acta **15**, 743 (1959).

[123] C. M. Huggins and D. R. Carpenter, J. Phys. Chem. **63**, 238 (1959).

[124] M. J. Copley and C. E. Holley, Jr., J. Am. Chem. Soc. **61**, 1599 (1939).

[125] F. C. Whitmore, Organic Chemistry, p. 66, 2d ed. (Van Nostrand, New York, 1951).

[126] S. C. Stanford and W. Gordy, J. Am. Chem. Soc. **63**, 1094 (1941).

[127] J. C. Brand, G. Eglinton, and J. F. Morman, J. Chem. Soc., p. 2526 (1960).

[128] M. M. Kreevoy, H. B. Charman, and D. R. Vinard, J. Am. Chem. Soc. **83**, 1978 (1961).

[129] M.-L. Josien, P.-V. Huong, and J. Lascombe, Compt. Rend. **251**, 1379 (1960).

[130] R. West and C. S. Kraihanzel, J. Am. Chem. Soc. **83**, 765 (1961).

[131] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., Organic Solvents. Vol. **VII** of Technique of Organic Chemistry (Interscience, New York, 1955).

[132] E. Müller and K. Ehrmann, Chem. Ber. **69B**, 2207 (1936).

[133] R. F. Collins, Chem. and Ind. (London), p. 704 (1957).

[134] R. W. Foster, Chem. and Ind. (London), p. 1354 (1960).

[135] T. Gramstad, Acta Chem. Scand. **16**, 807 (1962).

[136] D. P. Stevenson and G. M. Coppinger, J. Am. Chem. Soc. **84**, 149 (1962).

[137] M. D. Joesten and R. S. Drago, J. Am. Chem. Soc. **84**, 3817 (1962).

[138] N. H. Cromwell, P. W. Foster, and M. W. Wheeler, Chem. and Ind. (London), p. 228 (1959).

[139] G. J. Beichl, J. E. Colwell, and J. G. Miller, Chem. and Ind. (London), p. 203 (1960).

[140] H. Williams, Chem. and Ind. (London), p. 900 (1960).

[141] A. J. Parker, Quart. Rev. (London) **16**, 263 (1962).

[142] L. G. Wesson, Tables of Electric Dipole Moments, Technical Report No. II, Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Mass., April, 1947.

[143] C. D. Ritchie and A. L. Pratt, J. Am. Chem. Soc. **86**, 1571 (1964).

[144] C. D. Ritchie, verbal discussion following Symposium on Linear Free Energy Correlations, U.S. Army Research Office – Durham, Durham, North Carolina, 19–21 October 1964.

[145] R. W. Taft, G. B. Klingensmith, E. Price, and I. R. Fox, Preprints, p. 265, Symposium on Linear Free Energy Correlations, U.S. Army Research Office – Durham, Durham, North Carolina, 19–21 October 1964; also verbal discussion by R. W. Taft.

[146] K. Højendahl, Studies of Dipole Moment, Thesis, Copenhagen, 1928, cited in C. P. Smyth, Dielectric Constant and Molecular Structure (The Chemical Catalog Co., New York, 1931, p. 173).

[147] F. Buckley and A. A. Maryott, J. Res. NBS **53**, 229 (1954).

[148] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

[149] J. G. Kirkwood, J. Chem. Phys. **7**, 911 (1939).

[150] P. A. D. deMaine, M. M. deMaine, A. A. Briggs, and G. E. McAlonie, J. Mol. Spectry. **4**, 398 (1960).

[151] R. L. Williams, in Ann. Rept. Progr. Chem., Chem. Soc. London, LVIII, 34 (1961).

[152] H. E. Hallam, *in* Infrared Spectroscopy and Molecular Structure. An Outline of the Principles (M. M. Davies, ed.), Ch. XII (Elsevier, New York, 1963).

[153] W. Gordy, J. Chem. Phys. **9**, 215 (1941).

[153a] M. M. Davies, *in* Hydrogen Bonding (Ljubljana, 1957), p. 560 (D. Hadži and H. W. Thompson, Eds.) (Pergamon, New York, 1959).

[154] J. D. Lambert and E. D. T. Strong, Proc. Roy. Soc. (London) **A200**, 566 (1950).

[155] J. C. Evans and J.C. Wahr, J. Chem. Phys. **31**, 655 (1959).

[156] R. H. Linnell, M. Aldo, and F. Raab, J. Chem. Phys. **36,** 1401 (1962).

[157] J. Feeney and L. H. Sutcliffe, Proc. Chem. Soc., p. 118 (1961); J. Chem. Soc., p. 1123 (1962).

[158] V. F. Bystrov and V. P. Lezina, Opt. Spectry. (USSR) (English Transl.) **16,** 430 (1964).

[159] H. Wolff and D. Staschewski, Z. Elektrochem. **65,** 840 (1961); **66,** 140 (1962).

[160] H. Wolff and A. Höpfner, Z. Elektrochem. **66,** 149 (1962).

[161] H. Wolff, A. Höpfner, and H.-M. Höpfner, Ber. Bunsenges. Physik. Chem. (formerly Z. Elektrochem.) **68,** 410 (1964).

[162] H. Wolff, Z. Elektrochem. **66,** 529 (1962).

[163] H. Wolff and U. Schmidt, Ber. Bunsenges. Physik. Chem. **68,** 579 (1964).

[164] W. Gordy, J. Chem. Phys. **7,** 167 (1939).

[165] W. Gordy and S. C. Stanford, J. Am. Chem. Soc. **62,** 497 (1940).

[166] N. Fuson, M.-L. Josien, R. L. Powell, and E. Utterback, J. Chem. Phys. **20,** 145 (1952).

[167] K. B. Whetsel, W. E. Roberson, and M. W. Krell, Anal. Chem. **32,** 1281 (1960).

[168] J. H. Lady and K. B. Whetsel, J. Phys. Chem. **68,** 1001 (1964).

[169] F. J. C. Rossotti and H. Rossotti, J. Phys. Chem. **65,** 926, 930, 1376 (1961).

[170] F. J. C. Rossotti and H. Rossotti, The Determination of Stability Constants, Ch. 16 (McGraw-Hill Book Co., New York, 1961).

[171] D. M. W. Anderson, J. L. Duncan, and F. J. C. Rossotti, J. Chem. Soc., p. 140, 4201, 2165 (1961).

[172] J. C. Dearden, Can. J. Chem. **41,** 2683 (1963).

[173] A. V. Few and J. W. Smith, J. Chem. Soc., p. 753 (1949).

[174] R. E. Dodd and G. W. Stephenson *in* Hydrogen Bonding (Ljubljana, 1957), p. 177. (D. Hadži and H. W. Thompson, Eds.) (Pergamon, New York, 1959).

[175] N. Fuson and M.-L. Josien, J. Chem. Phys. **20,** 1043 (1952).

[176] S. N. Vinogradov and R. H. Linnell J. Chem. Phys. **23,** 93 (1955).

[177] N. Fuson, P. Pineau, and M.-L. Josien, J. Chim. Phys. **55,** 454 (1958).

[178] J. A. Happe, J. Phys. Chem. **65,** 72 (1961).

[179] H. J. Wimette and R. H. Linnell, J. Phys. Chem. **66,** 546 (1962).

[180] H. Lumbroso, J. Chim. Phys. **61,** 132 (1964).

[181] N. E. White and M. Kilpatrick, J. Phys. Chem. **59,** 1044 (1955).

[182] S. N. Vinogradov and M. Kilpatrick, J. Phys. Chem. **68,** 181 (1964).

[183] V. F. Bystrov, I. I. Grandberg, and G. I. Sharova, Opt. Spectry. (USSR) (English Transl.) **17,** 31 (1964).

[184] L. Hunter and J. A. Marriott, J. Chem. Soc., p. 777 (1941).

[185] R. M. Roberts, J. Am. Chem. Soc. **72,** 3608 (1950).

[186] D. G. O'Sullivan, J. Chem. Soc., p. 3278 (1960).

[187] H. Zimmermann, Z. Elektrochem. **65,** 821 (1961).

[188] N. Joop and H. Zimmermann, Z. Elektrochem. **66,** 440, 541 (1962).

[189] E. N. Lassettre, Chem. Rev. **20,** 259 (1937).

[190] L. Pauling, (a) J. Am. Chem. Soc. **58,** 94 (1936); (b) The Nature of the Chemical Bond, 3d ed. (Cornell Univ. Press, Ithaca, N.Y., 1960).

[191] G. W. Wheland, (a) Resonance in Organic Chemistry, p. 341; 1955; (b) The Theory of Resonance, p. 167; 1944, (John Wiley & Sons, New York, N.Y.).

[192] F. A. Philbrick, J. Am. Chem. Soc. **56,** 2581 (1934).

[193] E. N. Lassettre and R. G. Dickinson, J. Am. Chem. Soc. **61,** 54 (1939).

[193a] H. Kempter and R. Mecke, Z. Physik. Chem. **B46,** 229 (1940).

[194] N. D. Coggeshall and E. L. Saier, J. Am. Chem. Soc. **73,** 5414 (1951).

[195] C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, J. Phys. Chem. **60,** 1311 (1956).

[196] M. Saunders and J. B. Hyne, J. Chem. Phys. **29,** 1319 (1958); **31,** 270 (1959).

[197] M. Ito, J. Mol. Spectry. **4,** 125 (1960).

[198] M. M. Maguire and R. West, Spectrochim. Acta **17,** 369 (1961).

[199] E. D. Becker, J. Chem. Phys. **31,** 269 (1959).

[200] J. A. Davison, J. Am. Chem. Soc. **67,** 228 (1945).

[201] G. H. Stillson, D. W. Sawyer, and C. K. Hunt, J. Am. Chem. Soc. **67,** 303 (1945).

[202] N. D. Coggeshall, J. Am. Chem. Soc. **69,** 1620 (1947).

[203] N. D. Coggeshall and E. M. Lang, J. Am. Chem. Soc. **70,** 3283 (1948).

[204] W. C. Sears and L. J. Kitchen, J. Am. Chem. Soc. **71,** 4110 (1949).

[205] R. A. Friedel, J. Am. Chem. Soc. **73,** 2881 (1951).

[206] L. Hunter *in* Progress in Stereochemistry, Vol. **I,** ch. 6 (W. Klyne, ed.) (Academic Press, New York, 1954).

[207] R. F. Goddu, Anal. Chem. **30,** 2009 (1958).

[208] R. F. Goddu, J. Am. Chem. Soc. **82,** 4533 (1960).

[209] N. A. Puttnam, J. Chem. Soc., p. 486, 5100 (1960).

[210] L. J. Bellamy and R. L. Williams, Proc. Roy. Soc. (London) **A254,** 119 (1960).

[211] K. U. Ingold, Can. J. Chem. **40,** 111 (1962).

[212] B. G. Somers and H. S. Gutowsky, J. Am. Chem. Soc. **85,** 3065 (1963).

[213] V. F. Bystrov, K. M. Dyumaev, V. P. Lezina, and G. A. Nikiforov, Dokl. Chem. Sci. Sect. (English Transl.) **148,** 139 (1963).

[214] M. Rieger and F. H. Westheimer, J. Am. Chem. Soc. **72,** 19 (1950).

[215] A. I. Biggs, Trans. Faraday Soc. **52,** 35 (1956).

[216] O. R. Wulf, U. Liddel, and S. B. Hendricks, J. Am. Chem. Soc. **58,** 2287 (1936).

[217] J. A. Leermakers and A. Weissberger *in* Organic Chemistry. An advanced treatise (H. Gilman, Ed.), 2d ed., Vol. **II,** ch. 23 (John Wiley & Sons, New York, N.Y., 1943).

[218] J. R. Johnson *in* Organic Chemistry. An advanced treatise (H. Gilman, Ed.), 2d ed., Vol. **II,** ch. 25 (John Wiley & Sons, New York, N.Y., 1943).

[219] W. Lüttke and R. Mecke, Z. Physik. Chem. **196,** 56 (1950).

[220] G. M. Badger, Rev. Pure Appl. Chem. **7,** 55 (1957).

[221] A. W. Baker, J. Am. Chem. Soc. **80,** 3598 (1958).

[222] A. W. Baker and W. W. Kaeding, J. Am. Chem. Soc. **81,** 5904 (1959).

[223] A. W. Baker and A. T. Shulgin, J. Am. Chem. Soc. **80,** 5358 (1958).

[223a] K. Bradley, result cited by A. W. Baker and A. T. Shulgin (see ref. [223]).

[224] C. N. R. Rao, Chemical Applications of Infrared Spectroscopy, chs. III, VIII (Academic Press, New York, N.Y., 1963).

[225] H. H. Jaffé, J. Am. Chem. Soc. **79,** 2373 (1957).

[226] L. L. Ingraham, J. Corse, G. F. Bailey, and F. Stitt, J. Am. Chem. Soc. **74,** 2297 (1952).

[227] L. P. Hammett, (a) J. Am. Chem. Soc. **59,** 96 (1937); (b) Physical Organic Chemistry (McGraw-Hill Book Co., New York, N.Y., 1940).

[228] S. B. Hendricks, O. R. Wulf, G. E. Hilbert, and U. Liddel, J. Am. Chem. Soc. **58,** 1991 (1936).

[229] E. A. Allan and L. W. Reeves, J. Phys. Chem. **66,** 613 (1962).

[230] J. N. Finch and E. R. Lippincott, J. Phys. Chem. **61,** 894 (1957).

[231] I. Brown, G. Eglinton, and M. Martin-Smith, Spectrochim. Acta **18,** 1593 (1962); **19,** 463, 1089 (1963).

[232] H. Bourassa-Bataille, P. Sauvageau, and C. Sandorfy, Can. J. Chem. **41,** 2240 (1963).

[233] D. A. K. Jones and J. G. Watkinson, J. Chem. Soc., p. 2371 (1964).

[234] V. von Keussler and G. Rossmy, Z. Elektrochem. **60,** 136 (1956).

[235] J. Dearden and W. F. Forbes, Can. J. Chem. **38,** 1837 (1960).

[236] R. Cardinaud, Bull. Soc. Chim. France, p. 634 (1960).

[237] R. A. Nyquist, Spectrochim. Acta **19,** 1655 (1963).

[238] S. H. Bauer and R. M. Badger, J. Chem. Phys. **5,** 852 (1937).

[239] Y. Morino and S. Mizushima, Sci. Papers Inst. Phys. Chem. Res. Tokyo **32,** 33 (1937).

[240] M. M. Davies and G. B. B. M. Sutherland, J. Chem. Phys. **6**, 765 (1938).

[241] S. Mizushima, Structure of Molecules and Internal Rotation, p. 88 (Academic Press, New York, N.Y., 1954).

[242] M. Davies *in* Hydrogen Bonding (Ljubljana, 1957), p. 393. (D. Hadži and H. W. Thompson, Eds.) (Pergamon, New York, N.Y., 1959).

[243] W. G. Schneider, J. Chem. Phys. **23**, 26 (1955).

[244] C. J. W. Brooks, G. Eglinton, and J. F. Morman, J. Chem. Soc., p. 106 (1961).

[245] (a) G. E. K. Branch and D. L. Yabroff, J. Am. Chem. Soc. **56**, 2568 (1934); (b) G. E. K. Branch and M. Calvin, The Theory of Organic Chemistry (Prentice-Hall, New York, N.Y., 1941).

[246] W. Baker, Nature **137**, 236 (1936).

[247] R. P. Bell and M. H. M. Arnold, J. Chem. Soc., p. 1432 (1935).

[248] B. C. Barton and C. A. Kraus, J. Am. Chem. Soc. **73**, 4561 (1951).

[249] H. Dunken and G. Rudakoff, Z. Chem. **1**, 26, 54 (1961).

[250] G. Allen and E. F. Caldin, (a) Trans. Faraday Soc. **49**, 895 (1953); (b) Quart. Rev. (London) **7**, 255 (1953).

[251] (a) F. T. Wall and F. W. Banes, J. Am. Chem. Soc. **67**, 898 (1945); (b) F. T. Wall and P. E. Rouse, J. Am. Chem. Soc. **63**, 3002 (1941).

[252] H. Dunken and G. Jäger, Z. Chem. **3**, 432 (1963).

[253] A. Weissberger, J. Am. Chem. Soc. **65**, 102 (1943).

[254] M. M. Davis and M. Paabo; see tables 3 and 4 of ref. [32].

[254a] M. M. Davis and M. Paabo, J. Org. Chem. **31**, 1804 (1966).

[255] R. J. W. LeFèvre and H. Vine, J. Chem. Soc., p. 1795 (1938).

[256] H. A. Pohl, M. E. Hobbs, and P. M. Gross, (a) Ann. N.Y. Acad. Sci. **40**, 389 (1940); (b) J. Chem. Phys. **9**, 408 (1941).

[257] A. A. Maryott, M. E. Hobbs, and P. M. Gross, (a) J. Chem. Phys. **9**, 415 (1941); (b) J. Am. Chem. Soc. **71**, 1671 (1949).

[258] K. Palm and H. Dunken, Z. Physikal. Chem. (Leipzig) **217**, 248 (1961).

[259] M. Davies, P. Jones, D. Patnaik, and E. A. Moelwyn-Hughes, J. Chem. Soc., p. 1249 (1951).

[260] (a) J. Wenograd and R. A. Spurr, J. Am. Chem. Soc. **79**, 5844 (1957); (b) J. Wenograd, Dissertation Abstr. **16**, 38 (1956).

[261] E. Calvet and C. Paoli, Compt. Rend. **257**, 3376 (1963).

[262] W. Maier, L. Borucki, B. Dischler, P. Manogg, and H. Rieseberg, Z. Physikal. Chem. (Frankfurt) **26**, 27 (1960).

[263] W. Maier, J. Chim. Phys. **61**, 239 (1964).

[264] J. T. Harris, Jr. and M. E. Hobbs, J. Am. Chem. Soc. **76**, 1419 (1954).

[265] G. M. Barrow and E. A. Yerger, J. Am. Chem. Soc. **76**, 5248 (1954).

[266] J. J. Lindberg and C. Majani, Suomen Kemistilehti **B37**, 21 (1964).

[267] H. E. Affsprung, S. D. Christian, and A. M. Melnick, Spectrochim. Acta **20**, 285 (1964).

[267a] Y. I'Haya and T. Shibuya, Bull. Chem. Soc. Japan **38**, 1144 (1965).

[267b] F. Thyrion and D. Decroocq, Compt. Rend. **260**, 2797 (1965).

[267c] A. L. Henne and C. J. Fox, J. Am. Chem. Soc. **73**, 2323 (1951).

[268] M. Ito, J. Mol. Spectry. **4**, 144 (1960).

[269] W. F. Forbes, A. R. Knight, and D. L. Coffen, Can. J. Chem. **38**, 728 (1960).

[270] L. W. Reeves, Trans. Faraday Soc. **55**, 1684 (1959).

[271] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2d ed. (Academic Press, New York, 1959).

[272] K. Fredenhagen, Physikal. Z. **36**, 321 (1935).

[273] S. D. Christian, H. E. Affsprung, and S. A. Taylor, J. Phys. Chem. **67**, 187 (1963).

[274] F. E. Murray and S. Sundaram, Can. J. Chem. **39**, 1625 (1961).

[275] J. Lascombe, M. Haurie, and M.-L. Josien, J. Chim. Phys. **59**, 1233 (1962).

[276] A. J. Collings and K. J. Morgan, J. Chem. Soc., p. 3437 (1963).

[277] H. E. Ungnade and R. W. Lamb, J. Am. Chem. Soc. **74**, 3789 (1952).

[278] W. F. Forbes and A. R. Knight, Can. J. Chem. **37**, 334 (1959).

[279] F. H. MacDougall and D. R. Blumer, J. Am. Chem. Soc. **55**, 2236 (1933).

[280] A. Katchalsky, H. Eisenberg, and S. Lifson, J. Am. Chem. Soc. **73**, 5889 (1951).

[281] M. Davies and D. M. L. Griffiths, Z. Physik. Chem. (Frankfurt) **2**, 353 (1954).

[282] J. J. Fox and A. E. Martin, Trans. Faraday Soc. **36**, 897 (1940); *Nature* **143**, 199 (1939).

[283] M. Davies and D. M. L. Griffiths, J. Chem. Soc., p. 132 (1955).

[284] A. E. Lutskii, L. A. Kochergina, and B. A. Zadorozhnyi, Russ. J. Phys. Chem. English Transl. Zh. Fiz. Khim. **37** 347 (1963).

[285] M. Kilpatrick and W. H. Mears, J. Am. Chem. Soc. **62**, 3051 (1940).

[286] L. J. Bellamy, R. F. Lake, and R. J. Pace, Spectrochim. Acta **19**, 443 (1963).

[287] S. Fénéant, Compt. Rend. **235**, 240 (1952).

[288] A. S. N. Murthy, C. N. R. Rao, B. D. Nageswara Rao, and P. Venkateswarlu, Trans. Faraday Soc. **58**, 855 (1962).

[289] C. J. Hardy, B. F. Greenfield, and D. Scargill, J. Chem. Soc., p. 90 (1961).

[290] J. M. P. J. Verstegen, J. Inorg. Nucl. Chem. **26**, 1085 (1964).

[291] U. Bertocci and G. Rolandi, J. Inorg. Nucl. Chem. **23**, 323 (1961).

[292] E. Högfeldt, J. Inorg. Nucl. Chem. **27**, 271 (1965).

[293] E. Högfeldt and B. Bolander, Arkiv Kemi **21**, 161 (1963).

[294] L. W. Daasch and D. C. Smith, Anal. Chem. **23**, 853 (1951).

[295] L. J. Bellamy and L. Beecher, J. Chem. Soc., (a) p. 1701 (1952); (b) p. 728 (1953).

[296] D. Dyrssen, Acta Chem. Scand. **11**, 1771 (1957).

[297] D. Dyrssen and L. D. Hay (sic), Acta Chem. Scand. **14**, 1091 (1960).

[298] D. Dyrssen, S. Ekberg, and D. H. Liem, Acta Chem. Scand. **18**, 135 (1964).

[299] D. F. Peppard, J. R. Ferraro, and G. W. Mason, J. Inorg. Nucl. Chem. (a) **7**, 231 (1958); (b) **12**, 60 (1959); (c) **16**, 246 (1961).

[300] J. R. Ferraro, G. W. Mason, and D. F. Peppard, J. Inorg. Nucl. Chem. **22**, 285 (1961).

[301] J. R. Ferraro and D. F. Peppard, Nucl. Sci. Eng. **16**, 389 (1963).

[302] J. R. Ferraro and D. F. Peppard, J. Phys. Chem. **67**, 2639 (1963).

[303] C. J. Hardy and D. Scargill, J. Inorg. Nucl. Chem. **11**, 128 (1959).

[304] B. F. Greenfield and C. J. Hardy, J. Inorg. Nucl. Chem. **21**, 359 (1961).

[305] C. F. Baes, Jr., J. Inorg. Nucl. Chem. **24**, 707 (1962).

[306] H. T. Baker and C. F. Baes, Jr., J. Inorg. Nucl. Chem. **24**, 1277 (1962).

[307] F. Krašovec and J. Jan, Croat. Chem. Acta **35**, 183 (1963).

[308] H. W. Stone and E. R. Skavinski, Ind. Eng. Chem., Anal. Ed. **17**, 495 (1945).

[309] G. M. Kosolapoff and J. S. Powell, (a) J. Am. Chem. Soc. **72**, 4291 (1950); (b) J. Chem. Soc., p. 3535 (1950).

[310] E. C. Ashby and G. M. Kosolapoff, J. Am. Chem. Soc. **75**, 4903 (1953).

[311] L. C. Thomas, R. A. Chittenden, and H. E. R. Hartley, Nature **192**, 1283 (1961).

[313] M. M. Davis and H. B. Hetzer, J. Res. NBS **54**, 309 (1955).

[314] W. G. Wright, J. Chem. Soc., p. 683 (1949).

[315] S. Detoni and D. Hadži, J. Chem. Soc., p. 3163 (1955).

[316] H. V. Kehiaian and C. D. Nenitzescu, Chem. Ber. **90**, 685 (1957).

[317] H. V. Kehiaian, Acad. Rep. Pop. Romine Studii Cercetari Chim. **7**, 603 (1959).

[318] C. Walling and L. Heaton, J. Am. Chem. Soc. **87**, 48 (1965).

[319] G. R. Plourde, Dissertation Abstr. **22**, 1400 (1962).

[320] M. D. Taylor and M. B. Templeman, J. Am. Chem. Soc. **78**, 2950 (1956).

[322] P. Walden, Salts, Acids, and Bases: Electrolytes: Stereo-Chemistry, Chapters VIII–XII (McGraw-Hill Book Co., New York, N.Y., 1929).
[323] P. Walden and E. J. Birr, Z. Phys. Chem. **A163,** 263 (1933).
[324] P. Walden and E. J. Birr, Z. Phys. Chem. **A160,** 327 (1932).
[325] W. F. K. Wynne-Jones, J. Chem. Soc., p. 795 (1931).
[326] R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. **55,** 3614 (1933).
[327] C. A. Kraus, J. Phys. Chem. **43,** 231 (1939).
[328] C. A. Kraus, Science **90,** 281 (1939).
[329] C. A. Kraus, J. Chem. Educ. **35,** 324 (1958).
[330] R. L. McIntosh, D. J. Mead. and R. M. Fuoss, J. Am. Chem. Soc. **62,** 506 (1940).
[331] D. J. Mead, C. A. Kraus, and R. M. Fuoss, J. Am. Chem. Soc. **61,** 3257 (1939).
[332] D. S. Burgess and C. A. Kraus, J. Am. Chem. Soc. **70,** 706 (1948).
[333] M. J. McDowell and C. A. Kraus, J. Am. Chem. Soc. **73,** 3293 (1951).
[334] M. B. Reynolds and C. A. Kraus, J. Am. Chem. Soc. **70,** 1709 (1948).
[335] E. G. Taylor and C. A. Kraus, J. Am. Chem. Soc. **69,** 1731 (1947).
[336] V. Deitz and R. M. Fuoss, J. Am. Chem. Soc. **60,** 2394 (1938).
[337] C. M. French and D. F. Muggleton, J. Chem. Soc., p. 2131 (1957).
[338] I. Kablukoff, Z. physikal. Chem. **4,** 428 (1889).
[339] G. J. Janz and S. S. Danyluk, Chem. Revs. **60,** 209 (1960).
[340] V. K. La Mer and H. C. Downes, J. Am. Chem. Soc. **53,** 888 (1931).
[341] A. A. Maryott, J. Res. NBS **38,** 527 (1947).
[342] C. A. Kraus, J. Franklin Inst. **225,** 687 (1938).
[343] A. A. Maryott, J. Res. NBS **41,** 1 (1948).
[344] M. Davies and G. Williams, Trans. Faraday Soc. **56,** 1619 (1960).
[345] L. Sobczyk and J. K. Syrkin, Roczniki Chem. **30,** 881, 893 (1956); **31,** 197 (1957); **CA 51,** 7786, 14347 (1957).
[346] L. Sobczyk, *in* Hydrogen Bonding (Ljubljana, 1957) (D. Hadži and H. W. Thompson, Eds.), p. 323 (Pergamon Press, New York, 1959).
[347] E. N. Gur'yanova and I. G. Beskina, J. Gen. Chem. USSR Eng. Transl. **33,** 914 (1963).
[348] F. M. Batson and C. A. Kraus, J. Am. Chem. Soc. **56,** 2017 (1934).
[349] D. A. Rothrock, Jr. and C. A. Kraus, J. Am. Chem. Soc. **59,** 1699 (1937).
[350] D. T. Copenhafer and C. A. Kraus, J. Am. Chem. Soc. **73,** 4557 (1951).
[351] H. S. Young and C. A. Kraus, J. Am. Chem. Soc. **73,** 4732 (1951).
[352] S. Bruckenstein and A. Saito, J. Am. Chem. Soc. **87,** 698 (1965).
[353] S. Nagakura and M. Gouterman, J. Chem. Phys. **26,** 881 (1957).
[354] R. P. Bell and J. W. Bayles, J. Chem. Soc., p. 1518 (1952).
[355] D. C. Griffiths, J. Chem. Soc., p. 818 (1938).
[356] M. M. Davis, J. Am. Chem. Soc. **71,** 3544 (1949).
[357] V. K. LaMer and H. C. Downes, J. Am. Chem. Soc. **55,** 1840 (1933).
[358] I. M. Kolthoff, Acid-Base Indicators, 4th German ed. (1932), translated by C. Rosenblum, p. 122 (The Macmillan Company, New York, 1937).
[359] M. M. Davis, Abstrs. Papers 145th Meeting Am. Chem. Soc., New York, N.Y., September 1963, p. 18T.
[360] M. M. Davis and P. J. Schuhmann, unpublished results.
[361] M. M. Davis and E. A. McDonald, unpublished results.
[362] M. M. Davis and M. Paabo, J. Res. NBS **67A,** 241 (1963).
[363] H. von Halban and B. Szigeti, Helv. Chim. Acta **20,** 746 (1937),
[364] J. W. Bayles and A. Chetwyn, J. Chem. Soc., p. 2328 (1958).
[365] S. F. Mason, Quart. Rev. (London) **15,** 287 (1961).
[366] G. N. Lewis and M. Calvin, Chem. Rev. **25,** 273 (1939).
[367] L. N. Ferguson, Chem. Rev. **43,** 385 (1948).
[368] G. W. Wheland, Resonance in Organic Chemistry, section 6.5 (John Wiley & Sons, New York, 1955).
[369] L. Doub and J. M. Vandenbelt, (a) J. Am. Chem. Soc. **69,** 2714 (1947); (b) ibid., **71,** 2414 (1949); (c) ibid., **77,** 4535 (1955).
[370] C. N. R. Rao, Ultra-Violet and Visible Spectroscopy (Butterworth, London, 1961).
[371] H. H. Jaffé and M. Orchin, Theory and Applications of Ultraviolet Spectroscopy (John Wiley & Sons, Inc., New York, N.Y., 1962).
[372] J. M. Vandenbelt and C. Henrich, Appl. Spectroscopy **7,** 171 (1953).
[373] M. J. Kamlet, H. G. Adolph, and J. C. Hoffsommer, J. Am. Chem. Soc. **86,** 4018 (1964). Also see M. J. Kamlet, J. C. Hoffsommer, and H. G. Adolph, J. Am. Chem. Soc. **84,** 3925 (1962); H. G. Adolph, B. Johnson, and M. J. Kamlet, J. Org. Chem. **30,** 2864 (1965).
[374] R. C. Lord and R. E. Merrifield, J. Chem. Phys. **21,** 166 (1953).
[375] B. Chenon and C. Sandorfy, Can. J. Chem. **36,** 1181 (1958).
[376] C. Brissette and C. Sandorfy, Can. J. Chem. **38,** 34 (1960).
[377] J. Donohue, J. Phys. Chem. **56,** 502 (1952).
[378] W. Fuller, J. Phys. Chem. **63,** 1705 (1959).
[379] R. D. Waldron, J. Chem. Phys. **21,** 734 (1953).
[380] M. P. Marzocchi, C. W. Fryer, and M. Bambagiotti, Spectrochim. Acta **21,** 155 (1965).
[381] A. A. Lipovskii and S. A. Nikitina, Russ. J. Inorg. Chem. (English Transl.) **10,** 93 (1965).
[382] R. C. Plumb and D. F. Hornig, J. Chem. Phys. **23,** 947 (1955).
[383] H. A. Levy and S. W. Peterson, J. Am. Chem. Soc. **75,** 1536 (1953).
[384] G. L. Coté and H. W. Thompson, Proc. Roy. Soc. (London) Ser. **A210,** 217 (1951).
[385] B. Cox and A. G. Sharpe, J. Chem. Soc., p. 1798 (1954).
[386] T. C. Waddington, J. Chem. Soc., p. 4340 (1958).
[387] J. P. Mathieu and H. Poulet, Spectrochim. Acta **16,** 696 (1960).
[388] R. H. Nuttall, D. W. A. Sharp, and T. C. Waddington, J. Chem. Soc., p. 4965 (1960).
[389] A. A. Lipovskii and M. G. Kuzina, Russ. J. Inorg. Chem. (English Transl.) **10,** 740 (1965).
[390] D. Hadži, J. Chem. Soc., p. 5128 (1962).
[391] D. Hadži, A. Novak, and J. E. Gordon, J. Phys. Chem. **67,** 1118 (1963).
[392] G. M. Barrow and E. A. Yerger, J. Am. Chem. Soc. **76,** 5211 (1954).
[393] E. A. Yerger and G. M. Barrow, J. Am. Chem. Soc. **77,** 4474 (1955).
[394] E. A. Yerger and G. M. Barrow, J. Am. Chem. Soc. **77,** 6206 (1955).
[395] G. M. Barrow, J. Am. Chem. Soc. **78,** 5802 (1956).
[396] C. L. Bell and G. M. Barrow, J. Chem. Phys. **31,** 1158 (1959).
[397] G. M. Barrow, J. Am. Chem. Soc. **80,** 86 (1958).
[398] D. B. Cook, Interactions of Amino Acids in Non-Aqueous Solvents, Dissertation, Univ. of Calif., Davis, 1965. (Univ. Microfilms, Inc., Ann Arbor, Mich.) Dissertation Abstr. **26** (8), 4260 (1966).
[399] S. L. Johnson and K. A. Rumon, J. Phys. Chem. **69,** 74 (1965).
[400] M. Davies and L. Sobczyk, J. Chem. Soc., p. 3000 (1962).
[401] H. Baba, A. Matsuyama, and H. Kokubun, J. Chem. Phys. **41,** 895 (1964).
[402] R. M. Fuoss, D. Edelson, and B. L. Spinrad, J. Am. Chem. Soc. **72,** 327 (1950).
[403] J. J. Zwolenik and R. M. Fuoss, J. Phys. Chem. **68,** 434 (1964).
[404] R. P. Bell and J. E. Crooks, J. Chem. Soc., p. 3513 (1962).
[405] T. L. Smith and J. H. Elliott, J. Am. Chem. Soc. **75,** 3566 (1953).
[406] I. M. Kolthoff and S. Bruckenstein, J. Am. Chem. Soc. **78,** 1 (1956).
[407] J. F. Coetzee and G. P. Cunningham, J. Am. Chem. Soc. **87,** 2534 (1965).
[408] J. M. P. Verstegen, Trans. Faraday Soc. **58,** 1878 (1962).
[409] J. I. Bullock, S. S. Choi, D. A. Goodrick, D. G. Tuck, and E. J. Woodhouse, J. Phys. Chem. **68,** 2687 (1964).
[410] T. Sato, J. Appl. Chem. **15,** 10 (1965).

[411] T. Sato, J. Appl. Chem. **15,** 92 (1965).

[412] W. E. Keder and L. L. Burger, J. Phys. Chem. **69,** 3075 (1965).

[413] J. L. Ryan, Inorg. Chem. **2,** 348 (1963).

[414] J. L. Ryan, Inorg. Chem. **3,** 211 (1964).

[415] W. Madelung, J. Prakt. Chem. **219,** 100 (1925); **222,** 1 (1926).

[416] G. Schwarzenbach, M. Brandenberger, G. H. Ott, and O. Hagger, Helv. Chim. Acta **20,** 490 (1937).

[417] L. E. Drain, Dis. Faraday Soc. **19,** 200 (1955).

[418] D. Pendred and R. E. Richards, Trans. Faraday Soc. **51,** 468 (1955).

[419] G. Kotowycz, T. Schaefer, and E. Bock, Can. J. Chem. **42,** 2541 (1964).

[420] W. E. Keder and A. S. Wilson, Nucl. Sci. Eng. **17,** 287 (1963).

[421] M. Cocivera and E. Grunwald, J. Am. Chem. Soc. **87,** 2070 (1965).

[422] M. Cocivera, J. Am. Chem. Soc. **88,** 672 (1966).

[423] D. Cook, Can. J. Chem. **39,** 2009 (1961).

[424] M. Kilpatrick, J. Phys. Chem. **43,** 288 (1939).

[425] A. Hantzsch and W. Langbein, Z. Anorg. Allgem. Chem. **204,** 193 (1932).

[426] A. Hantzsch, Chem. Ber. **60,** 1933 (1927).

[427] K. Fajans, J. Phys. Chem. **43,** 289 (1939).

[428] See M. M. Davis and P. J. Schuhmann, ref. [14], section IV, 8.

[429] I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc. **85,** 2195 (1963).

[430] R. M. Diamond, J. Phys. Chem. **63,** 659 (1959).

[431] D. G. Tuck and R. M. Diamond, J. Phys. Chem. **65,** 193 (1961).

[432] D. C. Whitney and R. M. Diamond, J. Phys. Chem. **67,** 209 (1963).

[433] D. C. Whitney and R. M. Diamond, J. Phys. Chem. **67,** 2583 (1963).

[434] M. I. Tocher, D. C. Whitney, and R. M. Diamond, J. Phys. Chem. **68,** 368 (1964).

[435] T. J. Conocchioli, M. I. Tocher, and R. M. Diamond, J. Phys. Chem. **69,** 1106 (1965).

[436] R. M. Diamond, J. Phys. Chem. **67,** 2513 (1963).

[437] B. E. Douglas and D. H. McDaniel, Concepts and Models of Inorganic Chemistry, ch. V (Blaisdell Publishing Company, New York, N.Y., 1965).

[438] J. F. Coetzee and I. M. Kolthoff, J. Am. Chem. Soc. **79,** 6110 (1957).

[439] A. F. Trotman-Dickenson, J. Chem. Soc., p. 1293 (1949).

[440] R. P. Bell, The Proton in Chemistry, p. 176 (Cornell Univ. Press, Ithaca, N.Y., 1959).

[441] J. W. Bayles and A. F. Taylor, J. Chem. Soc., p. 417 (1961).

[442] J. J. Bucher and R. M. Diamond, J. Phys. Chem. **69,** 1565 (1965).

[443] I. M. Kolthoff, D. Stŏcesocá, and T. S. Lee, J. Am. Chem. Soc. **75,** 1834 (1953).

[444] W. S. Muney and J. F. Coetzee, J. Phys. Chem. **66,** 89 (1962).

[445] J. F. Coetzee, G. R. Padmanabhan, and G. P. Cunningham, Talanta **11,** 93 (1964).

[446] J. F. Coetzee and G. R. Padmanabhan, J. Am. Chem. Soc. **87,** 5005 (1964).

[447] D. Feakins, W. A. Last, and R. A. Shaw, J. Chem. Soc., p. 2387 (1964).

[448] E. K. Ralph, III, and W. R. Gilkerson, J. Am. Chem. Soc. **86,** 4783 (1964).

[449] W. R. Gilkerson and E. K. Ralph, III, J. Am. Chem. Soc. **87,** 175 (1965).

[450] D. Hadži, Boll. Sci. Fac. Chim. Ind. Bologna **21,** 23 (1963).

[451] D. Cook, Chem. Ind. (London), p. 607 (1963).

[452] H. H. Mills and J. C. Speakman, Proc. Chem. Soc., p. 216 (1963).

[453] M. Szafran, Bull. Acad. Polon. Sci. Ser. Sci. Chim. **11,** 111, 169, 497, 503 (1963).

[454] M. Szafran, Bull. Acad. Polon. Sci. Ser. Sci. Chim. **12,** 289, 383 (1964).

[455] M. Szafran, Spectrochim. Acta **19,** 2132 (1963).

[456] B. R. Agarwal and R. M. Diamond, J. Phys. Chem. **67,** 2785 (1963).

[457] N. Smith and J. C. Speakman, Trans. Faraday Soc. **44,** 1031 (1948).

[458] P. Pfeiffer, Chem. Ber. **47,** 1580 (1914).

[459] J. C. Speakman, J. Chem. Soc., p. 3357 (1949).

[460] M. Davies and W. J. Orville Thomas, J. Chem. Soc., p. 2858 (1951).

[461] J. M. Skinner, G. M. D. Stewart, and J. C. Speakman, J. Chem. Soc., p. 180 (1954).

[462] J. C. Speakman, Proc. Chem. Soc., p. 316 (1959).

[463] R. Blinc and D. Hadži, Spectrochim. Acta **16,** 853 (1960).

[464] G. E. Bacon and N. A. Curry, Acta Cryst. **13,** 717 (1960).

[465] H. N. Shrivastava and J. C. Speakman, J. Chem. Soc., p. 1151 (1961).

[466] J. C. Speakman and H. H. Mills, J. Chem. Soc., p. 1164 (1961).

[467] R. F. Bryan, H. H. Mills, and J. C. Speakman, J. Chem. Soc., p. 4350 (1963).

[468] H. H. Mills and J. C. Speakman, J. Chem. Soc., p. 4355 (1963).

[469] L. Golič and J. C. Speakman, J. Chem. Soc., p. 2521 (1965).

[470] L. Golič and J. C. Speakman, J. Chem. Soc., p. 2530 (1965).

[471] E. Larsson, Z. Physik. Chem. Leipzig **153,** 466 (1931).

[472] I. M. Kolthoff and W. Bosch, J. Phys. Chem. **36,** 1685 (1932).

[472a] A. Brändström, Acta Chem. Scand. **20,** 1335 (1966).

[473] S. Kaufman and C. R. Singleterry, J. Phys. Chem. **56,** 604 (1952).

[474] P. J. R. Bryant and A. W. H. Wardrop, J. Chem. Soc., p. 895 (1957).

[475] H. B. van der Heijde, Anal. Chim. Acta **16,** 392 (1957).

[476] G. A. Harlow and D. B. Bruss, Anal. Chem. **30,** 1833 (1958).

[477] D. Hadži and A. Novak, Spectrochim. Acta **18,** 1059 (1962).

[478] J. E. Gordon, J. Phys. Chem. **67,** 19 (1963).

[479] I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc. **85,** 426 (1963).

[480] I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc. **87,** 1004 (1965).

[481] I. M. Kolthoff and M. K. Chantooni, Jr., J. Phys. Chem. **70,** 856 (1966).

[482] M. M. Davis and H. B. Hetzer, Anal. Chem. **38,** 451 (1966).

[483] M. L. Crossley, R. J. Turner, C. M. Hofmann, P. F. Dreisbach, and R. P. Parker, J. Am. Chem. Soc. **74,** 578 (1952).

[484] D. B. Bruss and G. A. Harlow, Anal. Chem. **30,** 1836 (1958).

[485] L. E. I. Hummelstedt and D. N. Hume, Anal. Chem. **32,** 1792 (1960).

[486] S. Bruckenstein and L. M. Mukherjee, J. Phys. Chem. **66,** 2228 (1962).

[487] J. F. Coetzee and G. R. Padmanabhan, J. Phys. Chem. **69,** 3193 (1965).

[488] I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc. **87,** 4428 (1965).

[489] R. A. Spurr and H. F. Byers, J. Phys. Chem. **62,** 425 (1958).

[490] S. H. Marcus and S. I. Miller, J. Am. Chem. Soc. **88,** 3719 (1966).

[491] J. N. Brønsted and R. P. Bell, J. Am. Chem. Soc. **53,** 2478 (1931).

[492] R. P. Bell, Proc. Roy. Soc. (London) Ser. **A143,** 377 (1934).

[493] R. P. Bell and E. F. Caldin, J. Chem. Soc., p. 382 (1938).

[494] G. R. Sprengling, J. Am. Chem. Soc. **76,** 1190 (1954).

[495] H. Meerwein, Ann. Chem. **455,** 227 (1927).

[496] H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, J. Am. Chem. Soc. **76,** 4046 (1954).

[497] E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker, J. Chem. Soc., p. 1206 (1957).

[498] S. F. Mok, cited in ref. [497], p. 1216.

[499] Y. Pocker, J. Chem. Soc., p. 240 (1958).

[500] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., J. Am. Chem. Soc. **83,** 3927 (1961).

[501] I. R. Beattie and G. J. Leigh, J. Chem. Soc., p. 4726 (1962).

[502] D. G. Tuck and E. J. Woodhouse, Proc. Chem. Soc., p. 53 (1963).

[503] J. C. Evans and G. Y-S. Lo, J. Phys. Chem. **69,** 3223 (1965).

[504] J. C. Evans and G. Y-S. Lo, J. Phys. Chem. **70,** 11 (1966).

[505] H. Hart and F. A. Cassis, J. Am. Chem. Soc. **76,** 1634 (1954).

[506] E. F. Westrum, Jr. and K. S. Pitzer, J. Am. Chem. Soc. **71,** 1940 (1949).

[507] J. A. Salthouse and T. C. Waddington, J. Chem. Soc. **(A),** p. 28 (1966).

[508] D. H. McDaniel and R. E. Valleé, Inorg. Chem. **2,** 996 (1963).

[509] T. C. Waddington, J. Chem. Soc., p. 1708 (1958).

[510] T. C. Waddington, Trans. Faraday Soc. **54,** 25 (1958).

[511] S. A. Harrell and D. H. McDaniel, J. Am. Chem. Soc. **86,** 4497 (1964).

[512] H. C. Brown and R. R. Holmes, J. Am. Chem. Soc. **77,** 1727 (1955).

[513] D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoll, J. Inorg. Nucl. Chem. **4,** 334 (1957).

[514] D. F. Peppard, J. R. Ferraro, and G. W. Mason, J. Inorg. Nucl. Chem. **4,** 371 (1957).

[515] H. Van Looy and L. P. Hammett, J. Am. Chem. Soc. **81,** 3872 (1959).

[516] I. M. Kolthoff and M. K. Chantooni, Jr., J. Phys. Chem. **66,** 1675 (1962).

[517] M. Calleri and J. C. Speakman, Acta Cryst. **17,** 1097 (1964).

[518] P. D. Bartlett and H. J. Dauben, Jr., J. Am. Chem. Soc. **62,** 1339 (1940).

[519] R. C. Miller and R. M. Fuoss, J. Am. Chem. Soc. **75** 3076 (1953).

[520] H. Lund, Acta Chem. Scand. **12,** 298 (1958).

[521] J. Bufalini and K. H. Stern, Science **130,** 1249 (1959).

[522] J. Bufalini and K. H. Stern, J. Am. Chem. Soc. **83,** 4362 (1961).

[523] E. A. Richardson and K. H. Stern, J. Am. Chem. Soc. **82,** 1296 (1960).

[524] J. B. Hyne and R. M. Levy, Can. J. Chem. **40,** 692 (1962).

[525] A. Allerhand and P. von R. Schleyer, J. Am. Chem. Soc. **85,** 1233 (1963).

[526] M. J. Blandamer, T. E. Gough, and M. C. R. Symons, Trans. Faraday Soc. **60,** 488 (1964).

[527] M. J. Blandamer, T. E. Gough, and M. C. R. Symons, Trans. Faraday Soc. **62,** 296 (1966).

[528] S. C. Mohr, W. D. Wilk, and G. M. Barrow, J. Am. Chem. Soc. **87,** 3048 (1965).

[529] J. C. Evans and G. Y-S. Lo, J. Phys. Chem. **70,** 20 (1966).

[530] K. Fajans and O. Johnson, J. Am. Chem. Soc. **64,** 668 (1942).

[531] F. A. Long and P. Balinger, *in* Electrolytes (Trieste Symposium, 1959, B. Pesce, Ed.), p. 152 (Pergamon Press, New York, 1962).

[532] H. C. Ko, W. F. O'Hara, T. Hu, and L. G. Hepler, J. Am. Chem. Soc. **86,** 1003 (1964).

[533] R. A. Robinson, unpublished work.

[534] A. G. Ogston, J. Chem. Soc., p. 1713 (1936).

[535] A. I. Biggs and R. A. Robinson, J. Chem. Soc., p. 388 (1961).

[536] G. T. Tiessens, Rec. Trav. Chim. **50,** 112 (1931).

[537] C. G. Swain, J. Am. Chem. Soc. **70,** 1119 (1948).

[538] E. Gelles, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., p. 2918 (1954).

[539] Y. Pocker, J. Chem. Soc., p. 1179 (1959).

[540] R. Dietzel and W. Paul, Arch. Pharm. **273,** 507 (1935); **276,** 408 (1938).

[541] E. M. Trautner and F. H. Shaw, Australian Chem. Inst. J. & Proc. **12,** 405 (1945).

[542] D. Vorländer, Chem. Ber. **36,** 1485 (1903).

[543] D. Vorländer, J. Fischer, and F. Wildner, Chem. Ber. **66,** 1789 (1933).

[544] M. M. Davis and P. J. Schuhmann, ref. [14], Section IV–12.

[545] J. Steigman and P. M. Lorenz, J. Am. Chem. Soc. **88,** 2083, 2093 (1966).

[546] M. M. Davis and P. J. Schuhmann, ref. [14], Sections IV–4 to IV–8, inclusive.

[547] G. C. Pimentel and others *in* Hydrogen Bonding (Ljubljana, 1957), p. 555. (D. Hadži and H. W. Thompson, Eds.) (Pergamon, New York, 1959).

[548] J. E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, p. 120 ff. (John Wiley & Sons, Inc., New York, N.Y., 1963).

[549] W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc. **42,** 1419 (1920).

[550] W. Gordy and S. C. Stanford, J. Chem. Phys. **9,** 204 (1941).

[551] C. A. Coulson, Research (London) **10,** 149 (1957).

[552] C. G. Cannon, Spectrochim. Acta **10,** 341 (1958).

[553] R. S. Mulliken, J. Chim. Phys. **61,** 20 (1964).

[554] H. C. Longuet-Higgins, J. Chim. Phys. **61,** 18 (1964).

[555] A. R. Ubbelohde, J. Chim. Phys. **61,** 19 (1964).

[556] P. C. McKinney and G. M. Barrow, J. Chem. Phys. **31,** 294 (1959).

[557] C. L. Bell and G. M. Barrow, J. Chem. Phys. **31,** 300 (1959).

[558] G. M. Barrow, Spectrochim. Acta **16,** 799 (1960).

[559] R. P. Bell, The Proton in Chemistry, ch. 10 (Cornell Univ. Press, Ithaca, N.Y., 1959).

[560] E. A. Pshenichnov and N. D. Sokolov, Opt. Spectry. (USSR) (English Transl. **11,** 8 (1961).

[561] P.-O. Löwdin, Rev. Mod. Phys. **35,** 724 (1963).

[562] H. Zimmermann, Angew. Chem. Intern. Ed. Engl. **3,** 157 (1964).

[563] H. Zimmermann, Angew. Chem. Intern. Ed. Engl. **4,** 40 (1965).

[564] R. Schroeder and E. R. Lippincott, J. Phys. Chem. **61,** 921 (1957).

[565] G. Biczo, J. Ladik, and J. Gergely, Magy. Kem. Folyoirat **71** (7), 292 (1965), through Chem. Abstracts **63,** 14055 (1965).

[566] J. W. Smith, J. Chim. Phys. **61,** 125 (1964).

[567] M. Eigen, R. P. Bell, E. F. Caldin, and others *in* The Kinetics of Proton Transfer Processes (Discussions of the Faraday Society No. 39, 1965). The Faraday Society, London.

[568] A. Weller, *in* Progress in Reaction Kinetics, Vol. **1** (G. Porter, Ed.), p. 189 ff. (Pergamon Press, New York, 1961).

[569] N. Mataga, Y. Kawasaki, and Y. Torihashi, Bull. Chem. Soc. Japan **36,** 358 (1963).

[570] N. Mataga, Y. Kawasaki, and Y. Torihashi, Theoret. Chim. Acta **2,** 168 (1964).

[571] H. Beens, K. H. Grellmann, M. Gurr, and A. H. Weller, *in* The Kinetics of Proton Transfer Processes (Discussions of the Faraday Society No. 39, 1965), p. 183. The Faraday Society, London.

[572] L. P. Hammett, J. Am. Chem. Soc. **50,** 2666 (1928).

[573] V. K. LaMer and H. C. Downes, Chem. Rev. **13,** 47 (1933).

[574] S. Bodforss, Kungl. Fysiografiska Sällskapets i Lund Förhandlingar **19,** 55 (1949).

[575] M. Rumeau and B. Trémillon, Bull. Soc. Chim. France, p. 1049 (1964).

[576] A. Rieux, M. Rumeau, and B. Trémillon, Bull. Soc. Chim. France, p. 1053 (1964).

[577] B. Trémillon, Bull. Soc. Chim. France, p. 1057 (1964).

[578] G. Charlot and B. Trémillon, Les Reactions Chimiques dans les Solvents et Sels Fondus (Gauthier-Villars, Paris, 1963).

[579] N. A. Izmailov and L. L. Spivak, Russ. J. Phys. Chem. English Transl. Zh. Fiz. Khim. **36,** 395, 615 (1962).

[580] N. J. Rose and R. S. Drago, J. Am. Chem. Soc. **81,** 6138 (1959).

[581] P. J. Trotter and N. W. Hanna, J. Am. Chem. Soc. **88,** 3724 (1966).

[582] W. R. Brode, J. H. Gould, and G. M. Wyman, J. Am. Chem. Soc. **74,** 4641 (1952).

[583] W. R. Brode, J. H. Gould, and G. M. Wyman, J. Am. Chem. Soc. **75,** 1856 (1953).

[584] A. Hantzsch and A. Burawoy, Chem. Ber. **63,** 1760 (1930).

[585] G. E. Lewis, Tetrahedron **10,** 129 (1960).

[586] H. Zollinger, Azo and Diazo Chemistry. Aliphatic and Aromatic Compounds, Ch. 13 (Interscience, New York, 1961).

[587] R. A. Robinson, M. M. Davis, M. Paabo, and V. E. Bower, J. Res. NBS **64A,** 347 (1960).

[588] C. G. Swain and J. F. Brown, Jr., J. Am. Chem. Soc. **74,** 2691 (1952).

[589] R. J. Bishop and L. E. Sutton, J. Chem. Soc., p. 6100 (1964).

[590] M. M. Davis, M. Paabo, and N. Matheny, unpublished results.

[591] R. G. Pearson and D. C. Vogelsong, J. Am. Chem. Soc. **80,** 1038 (1958).

[592] T. Jasiński, T. Misiak, and T. Skarżyńska, Roczniki Chem. **39,** 1549 (1965).

[593] C. A. Streuli and R. R. Miron, Anal. Chem. **30,** 1978 (1958).

[594] Results of A. R. Anderson and W. F. K. Wynne-Jones, as given in the Ph. D. thesis of A. R. Anderson, The University of Newcastle upon Tyne, 1954, and communicated by Lord Wynne-Jones to M. M. Davis in June, 1964.

[595] N. F. Hall, J. Am. Chem. Soc. **52,** 5117 (1930).

[596] E. J. Forman and D. N. Hume, J. Phys. Chem. **63,** 1949 (1959).

[597] T. E. Mead, J. Phys. Chem. **66,** 2149 (1962).

[598] H. B. Hetzer, R. G. Bates, and R. A. Robinson, J. Phys. Chem. **70,** 2869 (1966).

[599] J. B. Ezell and W. R. Gilkerson, unpublished results cited in ref. [449].

[600] M. Bonnet and A. Julg, J. Chim. Phys. **59,** 723 (1962).

[601] F. Kieffer and P. Rumpf, Compt. Rend. **238,** 360, 700 (1954).

[602] L. K. Creamer, A. Fischer, B. R. Mann, J. Packer, R. B. Richards, and J. Vaughan, J. Org. Chem. **26,** 3148 (1961).

[603] R. L. Denyer, A. Gilchrist, J. A. Pegg, J. Smith, T. E. Tomlinson, and L. E. Sutton, J. Chem. Soc., p. 3889 (1955).

[604] L. Bellon, Trav. Inst. Sci. Chérifien Ser. Sci. Phys., No. 6 (1960).

[605] T. Zeegers-Huyskens, L. Lamberts, and P. Huyskens, J. Chim. Phys. **59,** 521 (1962).

[606] E. D. Becker, Spectrochim. Acta **17,** 436 (1961).

[607] I. Prigogine, J. Chim. Phys. **45,** 17 (1948).

[608] A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, J. Chim. Phys. **62,** 336 (1965).

[609] T. J. V. Findlay and A. D. Kidman, Australian J. Chem. **18,** 521 (1965).

[610] J. Rubin, B. Z. Senkowski, and G. S. Panson, J. Phys. Chem. **68,** 1601 (1964).

[611] H. Dunken and H. Fritzsche, Z. Chem. **1,** 249 (1961).

[612] R. A. Robinson and R. G. Bates, J. Res. NBS **70A,** 553 (1966).

[613] A. Halleux, Bull. Soc. Chim. Belg. **68,** 381 (1959).

[614] H. C. Brown and D. H. McDaniel, J. Am. Chem. Soc. **77,** 3752 (1955).

[615] H. C. Brown and X. R. Mihm, J. Am. Chem. Soc. **77,** 1723 (1955).

[616] H. C. Brown, S. Johnson, and H. Podall, J. Am. Chem. Soc. **76,** 5556 (1954).

[617] H. C. Brown, D. H. McDaniel, and O. Häfliger, Ch. 14 ("Dissociation Constants") *in* Determination of Organic Structures by Physical Methods (E. A. Braude and F. C. Nachod, Eds.) (Academic Press, New York, 1955).

[618] S. F. Mason, J. Chem. Soc., p. 1247 (1959).

[619] N. F. Hall and M. R. Sprinkle, J. Am. Chem. Soc. **54,** 3469 (1932).

[620] T. Zeegers-Huyskens, Bull. Soc. Chim. Belg. **69,** 282 (1960).

[621] L. Lamberts and T. Zeegers-Huyskens, J. Chim. Phys. **60,** 435 (1963).

[622] H. Dunken and H. Fritzsche, Z. Chem. **1,** 127 (1961).

[623] R. P. Bell and A. F. Trotman-Dickenson, J. Chem. Soc., p. 1288 (1949).

[624] J. Rubin and G. S. Panson, J. Phys. Chem. **69,** 3089 (1965).

[625] T. Kubota, J. Am. Chem. Soc. **87,** 458 (1965).

[626] T. Kubota, J. Am. Chem. Soc. **88,** 211 (1966).

[627] M. M. Davis and M. Paabo, J. Res. NBS **64A,** 533 (1960).

[628] M. M. Davis, M. Paabo, and R. A. Robinson, J. Res. NBS **64A,** 531 (1960).

[629] R. G. Bates and G. Schwarzenbach, Helv. Chim. Acta **37,** 1069 (1954).

[630] G. Kortüm and H. Wilski, Z. Physik. Chem. **2,** 256 (1954).

[631] J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, J. Chem. Soc., p. 2995 (1956).

[632] M. M. Davis and H. B. Hetzer, unpublished results.

[634] J. W. Bayles and B. Evans, J. Chem. Soc., p. 6984 (1966).

[635] H. C. Brown and S. Sujishi, J. Am. Chem. Soc. **70,** 2878 (1948).

[636] E. E. Sager, R. A. Robinson, and R. G. Bates, J. Res. NBS **69A,** 305 (1964).

[637] O. Folin and F. F. Flanders, J. Am. Chem. Soc. **34,** 774 (1912).

[638] L. Lykken, P. Porter, H. D. Ruliffson, and F. D. Tuemler, Ind. Eng. Chem., Anal. Ed., **16,** 219 (1944).

[639] S. R. Palit, Anal. Chem. **18,** 246 (1946).

[640] J. Kucharský and L. Šafařík, Titrations in Non-Aqueous Solvents, 2d ed. (Elsevier, New York, 1965).

[641] D. Vorländer, Chem. Ber. **67,** 145 (1934).

[642] E. M. Trautner and C. E. Neufeld, Australian Chem. Inst. J. & Proc. **13,** 70 (1946).

[643] G. Ya. Khaĭt, Farmatsiya **8,** 26 (1945); see Chem. Abstracts **41,** 2206 (1947).

[644] R. Megargle, D. Rosenthal, and G. L. Jones, Jr., Clarkson College of Technology, unpublished results (1966).

[645] S. Bruckenstein and N. E. Vanderborgh, Anal. Chem. **38,** 687 (1966).

[646] E. B. R. Prideaux and R. N. Coleman, J. Chem. Soc., p. 462 (1937).

[647] C. H. Giles, R. B. McKay, and W. Good, J. Chem. Soc., p. 5434 (1961).

[648] M. Ishidate, H. Nishizawa, H. Sano, and I. Horikoshi, Yakugaku Zasshi **81,** 1303 (1961), translated by I. Oiwa.

[649] H. C. Brown and N. R. Eldred, J. Am. Chem. Soc. **71,** 445 (1949).

[650] S. Leonard and S. Elkin, J. Org. Chem. **27,** 4635 (1962).

[651] H. C. Brown and M. D. Taylor, J. Am. Chem. Soc. **69,** 1332 (1947).

[652] R. Adams, M. Carmack, and J. E. Mahan, J. Am. Chem. Soc. **64,** 2593 (1942).

[653] N. J. Leonard and K. M. Beck, J. Am. Chem. Soc. **70,** 2504 (1948).

[654] C. A. Carlton, J. Am. Chem. Soc. **44,** 1469 (1922).

[655] T. L. Davis and R. C. Elderfield, J. Am. Chem. Soc. **54,** 1499 (1932).

[656] B. Neivelt, E. C. Mayo, J. H. Tiers, D. H. Smith, and G. W. Wheland, J. Am. Chem. Soc. **73,** 3475 (1951).

[657] S. J. Angyal and W. K. Warburton, J. Chem. Soc., p. 2492 (1951).

[658] C. P. Joshua, J. Sci. Indust. Res. (Delhi) **B21,** 588 (1962).

[659] C. E. Braun and W. M. Randall, J. Am. Chem. Soc. **56,** 2134 (1934).

[660] E. F. Caldin and J. E. Crooks, J. Chem. Soc. [B], p. 959 (1967).

8. Author Index

Reference numbers (see preceding bibliography) are given in brackets after the name of each author. Other numbers designate figures, tables, and pages in which references are cited or discussed.

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in three broad program areas and provides central national services in a fourth. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, and the Center for Radiation Research.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Standard Reference Data and a group of divisions organized by the following areas of science and engineering:

Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Cryogenics[2]—Radio Physics[2]—Radio Engineering[2]—Astrophysics[2]—Time and Frequency.[2]

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to methods, standards of measurement, and data needed by industry, commerce, educational institutions, and government. The Institute also provides advisory and research services to other government agencies. The Institute consists of an Office of Standard Reference Materials and a group of divisions organized by the following areas of materials research:

Analytical Chemistry—Polymers—Metallurgy — Inorganic Materials — Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides for the creation of appropriate opportunities for the use and application of technology within the Federal Government and within the civilian sector of American industry. The primary functions of the Institute may be broadly classified as programs relating to technological measurements and standards and techniques for the transfer of technology. The Institute consists of a Clearinghouse for Scientific and Technical Information,[3] a Center for Computer Sciences and Technology, and a group of technical divisions and offices organized by the following fields of technology:

Building Research—Electronic Instrumentation — Technical Analysis — Product Evaluation—Invention and Innovation— Weights and Measures — Engineering Standards—Vehicle Systems Research.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center for Radiation Research consists of the following divisions:

Reactor Radiation—Linac Radiation—Applied Radiation—Nuclear Radiation.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C. 20234.

[2] Located at Boulder, Colorado 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, chemistry, and engineering. Comprehensive scientific papers give complete details of the work, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Illustrated with photographs, drawings, and charts.

Published in three sections, available separately:

- **Physics and Chemistry**

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, $5.00; foreign, $6.00*.

- **Mathematical Sciences**

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, $2.25; foreign, $2.75*.

- **Engineering and Instrumentation**

Reporting results of interest chiefly to the engineer and the applied scientist. This section includes many of the new developments in instrumentation resulting from the Bureau's work in physical measurement, data processing, and development of test methods. It will also cover some of the work in acoustics, applied mechanics, building research, and cryogenic engineering. Issued quarterly. Annual subscription: Domestic, $2.75; foreign, $3.50*.

TECHNICAL NEWS BULLETIN

The best single source of information concerning the Bureau's research, developmental, cooperative and publication activities, this monthly publication is designed for the industry-oriented individual whose daily work involves intimate contact with science and technology—*for engineers, chemists, physicists, research managers, product-development managers, and company executives.* Annual subscription: Domestic, $1.50; foreign, $2.25*.

NONPERIODICALS

Applied Mathematics Series. Mathematical tables, manuals, and studies.

Building Science Series. Research results, test methods, and performance criteria of building materials, components, systems, and structures.

Handbooks. Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications. Proceedings of NBS conferences, bibliographies, annual reports, wall charts, pamphlets, etc.

Monographs. Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

National Standard Reference Data Series. NSRDS provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated.

Product Standards. Provide requirements for sizes, types, quality and methods for testing various industrial products. These standards are developed cooperatively with interested Government and industry groups and provide the basis for common understanding of product characteristics for both buyers and sellers. Their use is voluntary.

Technical Notes. This series consists of communications and reports (covering both other agency and NBS-sponsored work) of limited or transitory interest.

CLEARINGHOUSE

The Clearinghouse for Federal Scientific and Technical Information, operated by NBS, supplies unclassified information related to Government-generated science and technology in defense, space, atomic energy, and other national programs. For further information on Clearinghouse Services, write:

Clearinghouse
U.S. Department of Commerce
Springfield, Virginia 22151

Order NBS publications from:
Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

---

*Difference in price is due to extra cost of foreign mailing.

U.S. GOVERNMENT PRINTING OFFICE : 1968 OL—280-613