

Dissociation Constants of Some Substituted Nitrophenols in Aqueous Solution at 25 °C

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The dissociation constants of twelve substituted phenols with a nitro group in the *o*- or *p*-position have been determined by spectrophotometric measurements in aqueous solution at 25 °C.

Key Words: Dissociation constant, nitrophenols, substituted phenols.

1. Introduction

The determination of the dissociation constants of a number of substituted phenols by the spectrophotometric method has been described recently [1, 2, 3, 4, 5, 6, 7].¹ The purpose of this paper is to present data for twelve substituted phenols with an indicator range *pH* 2.1–5.5.

2. Experimental Procedure

2.1. Materials

With the exception of 2,6-diiodo-4-nitrophenol, the materials were commercial products. I am indebted to Dr. Marion M. Davis for the following details of their purification.

2-Chloro-4, 6-dinitrophenol was recrystallized twice from benzene-cyclohexane, mp 111.0–111.5 °C. 4-Chloro-2,6-dinitro-3-methylphenol was recrystallized once from benzene-cyclohexane and then from ligroin, mp 68.0–68.5 °C; 2-chloro-6-nitrophenol first from 95 percent ethanol and then from benzene-cyclohexane, mp 70.0–70.5 °C. 2,4-Dibromo-6-nitrophenol was purified in the same way, mp 117.0–117.5 °C. 2,6-Dibromo-4-nitrophenol was recrystallized three times from benzene-cyclohexane, then from aqueous ethanol and then from benzene-cyclohexane, mp 141.8–142.0 °C, 2,6-dichloro-4-nitrophenol twice from benzene-cyclohexane, mp 125 °C (dec.). 2,6-Diiodo-4-nitrophenol was synthesized by the method of Datta and Prosad [8] by adding *p*-nitrophenol in an excess of ammonia to a solution of iodine in aqueous potassium iodide, recrystallized from aqueous ethanol and then from benzene-cyclohexane, mp 156.5–157.0 °C.

2,4-Dinitro-6-methylphenol was recrystallized twice from benzene-cyclohexane mp 86.0–86.7 °C; 2,6-dinitro-4-methylphenol from benzene-cyclohexane and then from cyclohexane, mp 80.7–81.2 °C; 2,4-dinitro-3-methyl-6-isopropylphenol from aqueous ethanol and then from ligroin, mp 55.0–55.7 °C. 2,4-Dinitro-6-phenylphenol recrystallized from methyl ethyl ketone and then from ethyl acetate, mp 206.6–207.0 °C; 2,4-dinitro-6-isopropylphenol from 95 percent ethanol and then from hexane, mp 54.0–55.0 °C.

Table 1 gives some characteristics of the absorption spectra of these compounds, recording the wavelengths and extinction coefficients at maximum absorption in both acid and alkaline solution, and also those at the isosbestic points. Figure 1 shows the absorption spectrum of one of these phenols, 4-chloro-2,6-dinitro-3-methylphenol, in alkaline solution where the phenol is present in the form of the phenolate anion, in strongly acid solution where it exists as the undissociated molecule, and in a dilute solution of hydrochloric acid where both species are present; the isosbestic point is at 378 $m\mu$ with an extinction coefficient $\epsilon = 2,740$.

TABLE 1. Characteristics of the absorption spectra of substituted phenols in aqueous solution at 25 °C.

	Alkaline solution ϵ_2 $m\mu$	Acid solution ϵ_1 $m\mu$	Isosbestic point ϵ $m\mu$
2-Chloro-4,6-dinitrophenol.....	14,910 370	10,100 268	4,250 326
4-Chloro-2,6-dinitro-3-methylphenol.....	5,660 425	3,950 355	2,740 378
2-Chloro-6-nitrophenol.....	4,580 420	2,620 350	2,200 372
2,4-Dibromo-6-nitrophenol.....	4,180 430	2,370 365	2,110 383
2,6-Dibromo-4-nitrophenol.....	15,720 402	7,650 312	3,900 344
2,6-Dichloro-4-nitrophenol.....	13,850 399	7,020 312	3,500 343
2,6-Diiodo-4-nitrophenol.....	15,620 409	6,550 318	3,570 351
2,4-Dinitro-6-methylphenol.....	14,210 377	13,630 272	5,330 333
2,6-Dinitro-4-methylphenol.....	7,250 450	5,100 365	2,390 393
2,4-Dinitro-3-methyl-6-isopropylphenol.....	14,630 396	5,500 300	3,900 335
2,4-Dinitro-6-phenylphenol.....	14,990 380	8,290 265	4,280 334
2,4-Dinitro-6-isopropylphenol.....	13,400 375	5,680 265	5,220 335

¹ Figures in brackets indicate the literature references at the end of this paper.

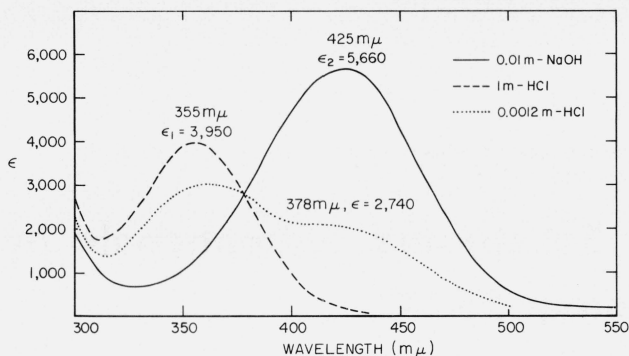


FIGURE 1. Absorption spectra of 4-chloro-2,6-dinitro-3-methylphenol.

2.2. Method

The spectrophotometric method of determining the dissociation constant of a weak acid has been described many times [1, 2, 3, 4, 5, 6, 7]. For the five phenols with pK values less than 3.5, dilute solutions of hydrochloric acid were found to be suitable media in which to make measurements; for the other seven, with pK values greater than 3.8, succinate buffers were used. In some cases a small correction was needed for the effect of the phenol on the acidity of the buffer solution; this correction has already been described [9].

3. Results and Discussion

Details of the spectrophotometric measurements are given in tables 2 to 13. The results are summarized in table 14.

It is known that *ortho* and *para* substitution of a nitro group in phenol have effects which are by no means additive. Thus, if the pK value of phenol itself is 9.99₈ [10], that of *o*-nitrophenol 7.23₀ [11], and that of *p*-nitrophenol 7.15₆ [12], then *o*- and *p*-nitro substitution lowers the pK value of phenol by 2.76₈ and 2.84₂, respectively. We might, therefore, expect $pK = (9.99_8 - 2.76_8 - 2.84_2) = 4.38_8$ for 2,4-dinitrophenol, whereas

TABLE 2. Dissociation constant of 2-chloro-4,6-dinitrophenol in aqueous solution at 25 °C

Concentration of phenol: 1.18×10^{-5} M, cell length 4 cm, wavelength 372 m μ , D_1 0.073, D_2 0.660

$m_{\text{HCl}} \times 10^3$	D	$m_{\text{H}^+} \times 10^3$	$-2 \log \gamma$	pK
2.210	0.542	2.221	0.046	2.100
3.206	.508	3.216	.054	2.090
4.967	.454	4.976	.065	2.101
7.389	.403	7.397	.081	2.103
10.05	.359	10.06	.089	2.108

Average..... 2.10₀

TABLE 3. Dissociation constant of 4-chloro-2,6-dinitro-3-methylphenol in aqueous solution at 25 °C

Concentration of phenol: 2.6×10^{-5} M, cell length 4 cm, wavelength 425 m μ , D_1 0.012, D_2 0.583

$m_{\text{HCl}} \times 10^4$	D	$m_{\text{H}^+} \times 10^4$	$-2 \log \gamma$	pK
2.192	0.420	2.378	0.016	3.241
6.048	.293	6.176	.025	3.248
8.084	.257	8.196	.029	3.239
10.28	.228	10.38	.032	3.232
12.06	.205	12.15	.034	3.241

Average..... 3.24₀

TABLE 4. Dissociation constant of 2-chloro-6-nitrophenol in aqueous solution at 25 °C

Concentration of phenol: 3×10^{-5} M, cell length 4 cm, wavelength 430 m μ , D_1 0.014, D_2 0.538
Buffer solution: Sodium hydrogen succinate and disodium succinate, each at molality m

m	D	$p(a_{\text{H}^+}\gamma_{\text{Cl}})$	pK	pK (corr.)
0.0100	0.294	5.553	5.493	5.491
.0175	.290	5.532	5.485	5.483
.0250	.285	5.511	5.481	5.480
.0375	.281	5.499	5.482	5.481
.0500	.274	5.477	5.483	5.483

Average..... 5.48₃

TABLE 5. Dissociation constant of 2,4-dibromo-6-nitrophenol in aqueous solution at 25 °C

Concentration of phenol: 4.5×10^{-5} M, cell length 4 cm, wavelength 430 m μ , D_1 0.067, D_2 0.757
Buffer solution: sodium hydrogen succinate and sodium chloride, each at molality m

m	D	$p(a_{\text{H}^+}\gamma_{\text{Cl}})$	pK	pK (corr.)
0.02	0.467	4.853	4.713	4.712
.04	.461	4.833	4.709	4.708
.06	.458	4.821	4.704	4.704
.08	.454	4.811	4.705	4.705
.10	.449	4.802	4.709	4.709

Average..... 4.70₈

TABLE 6. Dissociation constant of 2,6-dibromo-4-nitrophenol in aqueous solution at 25 °C

Concentration of phenol: 2.05×10^{-5} M, cell length 4 cm, wavelength 402 m μ , D_1 0.005, D_2 1.274

$m_{\text{HCl}} \times 10^4$	D	$m_{\text{H}^+} \times 10^4$	$-2 \log \gamma$	pK
2.013	0.855	2.150	0.015	3.376
3.106	.726	3.222	.018	3.391
4.018	.649	4.122	.020	3.392
4.980	.584	5.073	.023	3.394
6.057	.527	6.141	.025	3.393
6.999	.482	7.076	.027	3.397
8.015	.447	8.086	.028	3.392
9.003	.415	9.069	.030	3.393
9.996	.385	10.06	.031	3.397
Average.....				3.39 ₂

TABLE 7. Dissociation constant of 2,6-dichloro-4-nitrophenol in aqueous solution at 25 °C

Concentration of phenol: 2.4×10^{-5} M, cell length 4 cm, wavelength 400 m μ , D_1 0.002, D_2 1.340

$m_{\text{HCl}} \times 10^4$	D	$m_{\text{H}^+} \times 10^4$	$-2 \log \gamma$	pK
1.987	0.792	2.129	0.015	3.528
2.989	.655	3.106	.018	3.547
4.033	.562	4.133	.020	3.548
5.008	.497	5.097	.023	3.547
6.314	.426	6.390	.025	3.553
6.583	.415	6.657	.026	3.553
7.786	.370	7.852	.028	3.554
8.773	.340	8.834	.030	3.555
9.973	.308	10.03	.031	3.558
Average.....				3.54 ₉

TABLE 8. Dissociation constant of 2,6-diiodo-4-nitrophenol in aqueous solution at 25 °C

Concentration of phenol: 2.5×10^{-5} M, cell length 4 cm, wavelength 409 m μ , D_1 0.005, D_2 1.540

$m_{\text{HCl}} \times 10^4$	D	$m_{\text{H}^+} \times 10^4$	$-2 \log \gamma$	pK
2.019	1.065	2.192	0.015	3.324
2.975	0.946	3.128	.018	3.323
3.861	.864	4.001	.020	3.314
4.144	.823	4.277	.020	3.332
4.965	.764	5.089	.023	3.326
6.063	.691	6.175	.025	3.327
7.791	.614	7.890	.028	3.313
8.959	.557	9.059	.030	3.324
9.984	.513	10.07	.032	3.335
Average.....				3.32 ₄

TABLE 9. Dissociation constant of 2,4-dinitro-6-methylphenol in aqueous solution at 25 °C

Concentration of phenol: 8.3×10^{-5} M, cell length 1 cm, wavelength 400 m μ , D_1 0.028, D_2 0.969
 Buffer solution: sodium hydrogen succinate and sodium chloride each at molality m

m	D	$p(a_{\text{H}^+}\gamma_{\text{Cl}})$	pK	pK (corr.)
0.02	0.691	4.853	4.476	4.471
.03	.688	4.840	4.469	4.466
.05	.680	4.826	4.473	4.471
.07	.675	4.816	4.474	4.473
.10	.669	4.802	4.472	4.471
Average.....				4.47 ₀

TABLE 10. Dissociation constant of 2,6-dinitro-4-methylphenol in aqueous solution at 25 °C

Concentration of phenol: 2.25×10^{-5} M, cell length 4 cm, wavelength 450 m μ , D_1 0, D_2 0.650
 Buffer solution: mixture of sodium hydrogen succinate (m) and hydrochloric acid (0.6667 m) equivalent to a mixture of sodium hydrogen succinate (0.3333 m), succinic acid (0.6667 m), and sodium chloride (0.6667 m)

m	D	$p(a_{\text{H}^+}\gamma_{\text{Cl}})$	pK^a
0.02	0.206	3.898	4.232
.04	.203	3.887	4.230
.06	.202	3.882	4.228
.08	.199	3.878	4.233
.10	.199	3.875	4.230
Average.....			4.23 ₁

^a The correction to pK is negligible.

the observed value is 4.09 [13]. In the same way, $pK = 4.46_2$ might be predicted for 2,6-dinitrophenol, compared with the observed value of 3.71 [14].

An additivity principle works much better with meta substitution; $pK = 8.35_5$ has been found [15] for m -nitrophenol and hence one would predict pK 6.71 for 3,5-dinitrophenol, compared with the observed value of 6.69 [1].

The substitution of a methyl group in the para position to give p -cresol raises the pK value of phenol by 0.26₄ [16]; $pK = 7.49_4$ might be predicted for 4-methyl-2-nitrophenol compared with the observed value of 7.59₇ [6]. The difference between the observed and calculated value is not large, but the

observed value is higher than the calculated, whereas for the dinitrophenols mentioned above the observed value was lower than the calculated. A quantitative explanation of this anomaly, the difference between the observed and calculated pK values, is not yet possible, but the change in sign of the difference in going from 4-methyl-2-nitrophenol to 2,4- or 2,6-dinitrophenol suggests that the anomaly increases with a decrease in the pK value of the phenol into which an *o*- or *p*-nitro group is introduced.

TABLE 11. Dissociation constant of 2,4-dinitro-3-methyl-6-isopropylphenol in aqueous solution at 25 °C

Concentration of phenol: 1.09×10^{-4} M, cell length 1 cm, wavelength 396 m μ , D_1 0.032, D_2 1.594
 Buffer solution: mixture of sodium hydrogen succinate (m) and hydrochloric acid (0.6667*m*) equivalent to a mixture of sodium hydrogen succinate (0.3333*m*), succinic acid (0.6667*m*), and sodium chloride (0.6667*m*)

m	D	$p(a_H\gamma_{Cl})$	pK	pK (corr.)
0.02	0.758	3.898	3.959	3.954
.03	.752	3.892	3.960	3.957
.04	.749	3.887	3.958	3.955
.05	.746	3.884	3.959	3.957
.06	.743	3.882	3.961	3.959
.08	.738	3.878	3.961	3.960
.10	.735	3.875	3.962	3.961

Average.....3.95₈

TABLE 12. Dissociation constant of 2,4-dinitro-6-phenylphenol in aqueous solution at 25 °C

Concentration of phenol: 1.79×10^{-5} M, cell length 4 cm, wavelength 380 m μ , D_1 0.142, D_2 1.070
 Buffer solution: mixture of sodium hydrogen succinate (m) and hydrochloric acid (0.6667*m*) equivalent to a mixture of sodium hydrogen succinate (0.3333*m*), succinic acid (0.6667*m*), and sodium chloride (0.6667*m*).

m	D	$p(a_H\gamma_{Cl})$	pK	pK (corr.)
0.01	0.634	3.906	3.854	3.852
.02	.629	3.898	3.855	3.851
.03	.627	3.892	3.853	3.852
.04	.626	3.887	3.850	3.849
.05	.628	3.884	3.843	3.843
.06	.627	3.882	3.843	3.843
.07	.627	3.880	3.841	3.841
.08	.620	3.878	3.852	3.852
.09	.620	3.877	3.851	3.851

Average.....3.84₈

TABLE 13. Dissociation constant of 2,4-dinitro-6-isopropylphenol in aqueous solution at 25 °C

Concentration of phenol: 9.6×10^{-5} M, cell length 1 cm, wavelength 400 m μ , D_1 0.029, D_2 0.791
 Buffer solution: sodium hydrogen succinate and sodium chloride each at molality m .

m	D	$p(a_H\gamma_{Cl})$	pK	pK (corr.)
0.02	0.541	4.853	4.542	4.536
.03	.539	4.840	4.534	4.530
.05	.529	4.826	4.545	4.543
.07	.528	4.816	4.538	4.536
.10	.524	4.802	4.534	4.533

Average.....4.53₆

TABLE 14. Summary of the pK values of substituted phenols in aqueous solution at 25 °C

	pK
2-Chloro-4,6-dinitrophenol.....	2.10 ₀
4-Chloro-2,6-dinitro-3-methylphenol.....	3.24 ₀
2-Chloro-6-nitrophenol.....	5.48 ₃
2,4-Dibromo-6-nitrophenol.....	4.70 ₃
2,6-Dibromo-4-nitrophenol.....	3.39 ₂
2,6-Dichloro-4-nitrophenol.....	3.54 ₉
2,6-Diiodo-4-nitrophenol.....	3.32 ₄
2,4-Dinitro-6-methylphenol.....	4.47 ₀
2,6-Dinitro-4-methylphenol.....	4.23 ₁
2,4-Dinitro-3-methyl-6-isopropylphenol.....	3.95 ₃
2,4-Dinitro-6-phenylphenol.....	3.84 ₃
2,4-Dinitro-6-isopropylphenol.....	4.53 ₆

The available literature values have been used to study this possibility. Data are available for *p*-nitro substitution in the following compounds, pK values being known for the phenols before and after substitution:

Parent phenols	pK Parent phenols	pK Nitro derivatives		Differences
		Pre-dicted	Observed	
<i>o</i> -Chlorophenol.....	8.53 ₄ [10]	5.69 ₂	5.45 [17]	0.24
<i>o</i> -Nitrophenol.....	7.23 ₀ [11]	4.38 ₃	4.09 [13]	0.30
2,6-Dichlorophenol.....	6.79 ₁ [4]	3.94 ₉	3.54 ₉	0.40
2,6-Dibromophenol.....	6.67 ₄ [7]	3.83 ₂	3.39 ₂	0.44
2-Chloro-6-nitrophenol...	5.48 ₃	2.64 ₁	2.10 ₀	0.54
2,6-Dinitrophenol.....	3.71 [14]	0.87	0.33 [18]	0.54

Thus, *o*-chlorophenol, with a pK value of 8.53₄, can be converted to 2-chloro-4-nitrophenol, whose predicted pK value (pK 5.69₂) is 2.84₂ lower, the observed value being 5.45 and the anomaly 0.24. The absence of a literature reference in the above table means that the datum was taken from the present paper.

For *o*-nitro substitution the following data have been found, assuming 2.76₈ for the effect of the nitro group:

Parent phenols	<i>pK</i> parent phenols	<i>pK</i> nitro derivatives		Differences
		Predicted	Observed	
<i>p</i> -Cresol.....	10.26 ₂ [16]	7.49 ₄	7.59 ₇ [6]	-0.10
<i>p</i> -Chlorophenol....	9.41 ₈ [10]	4.38 ₈	4.09 [13]	0.30
<i>o</i> -Chlorophenol....	8.53 ₄ [11]	5.77 ₆	5.48 ₃	0.29
2,4-Dibromophenol.	7.79 ₀ [7]	5.02 ₂	4.70 ₈	0.31
<i>o</i> -Nitrophenol.....	7.23 ₀ [11]	4.46 ₂	3.71 [14]	0.75
<i>p</i> -Nitrophenol.....	7.15 ₆ [12]	4.38 ₈	4.09 [13]	0.30
4-Chloro-2-nitrophenol.	6.46 [17]	3.69	2.96 ₉ [5]	0.72
2-Chloro-4-nitrophenol.	5.45 [17]	2.68	2.10 ₀	0.58
2,4-Dinitrophenol.	4.09 [13]	1.32	0.33 [18]	0.99

These anomalies, ($\Delta pK = pK_{\text{calcd.}} - pK_{\text{obsd.}}$), are plotted in figure 2 against the *pK* value of the phenol

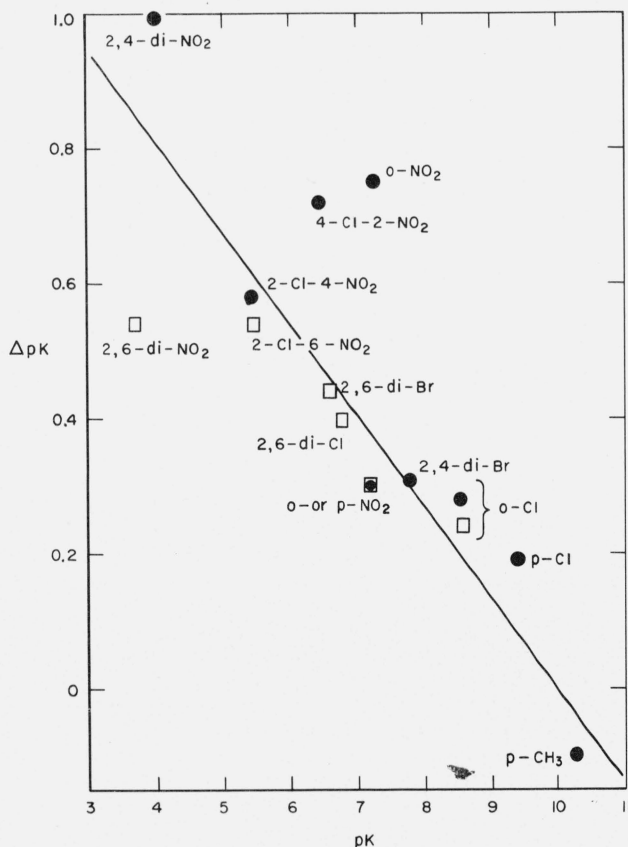


FIGURE 2. $\Delta pK = pK(\text{calcd.}) - pK(\text{obsd.})$, where *pK* (*calcd.*) is derived on the assumption that (1) *o*-nitration of a substituted phenol lowers the *pK* value by 2.76₈, identical with the lowering of *pK* found for the *o*-nitration of phenol itself; (2) *p*-nitration of a substituted phenol lowers the *pK* value by 2.84₂, identical with the lowering of *pK* found for the *p*-nitration of phenol itself.

The lettering within the figure indicates the structure of the parent substituted phenol which undergoes *o*-nitration (●) or *p*-nitration (□). The abscissa gives the *pK* value of the parent phenol.

into which the nitro group is introduced. It can be seen that, in general, the anomaly increases in magnitude as the acid strength of the phenol increases (*pK* decreases). For *p*-nitro substitution, the value for the formation of picric acid from 2,6-dinitrophenol seems somewhat small.

For *o*-nitro substitution, the anomaly seems to be uniformly greater as the *pK* value of the phenol decreases but there are three peculiar cases, the formation of 2,6-dinitrophenol from *o*-nitrophenol, that of 4-chloro-2,6-dinitrophenol from 4-chloro-2-nitrophenol, and that of picric acid from 2,4-dinitrophenol. In each case the anomaly seems to be somewhat large. It should be noted that in each case the synthetic process is one in which an *o*-nitrophenol is converted into a 2,6-dinitrophenol, each of which has adjacent $\text{NO}_2\text{-OH-NO}_2$ groups. In such cases marked steric inhibition of resonance would be expected.

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4. References

- [1] R. A. Robinson, M. M. Davis, M. Paabo, and V. E. Bower, *J. Res. NBS* **64A**, (Phys. and Chem.) No. 4, 347 (1960).
- [2] M. M. Davis, M. Paabo, and R. A. Robinson, *J. Res. NBS* **64A**, (Phys. and Chem.) No. 6, 531 (1960).
- [3] M. M. Davis and M. Paabo, *J. Res. NBS* **64A**, (Phys. and Chem.) No. 6, 533 (1960).
- [4] R. A. Robinson, *J. Res. NBS* **68A** (Phys. and Chem.) No. 2, 159 (1964).
- [5] E. E. Sager, R. A. Robinson, and R. G. Bates, *J. Res. NBS* **68A** (Phys. and Chem.) No. 3, 305 (1964).
- [6] R. A. Robinson and R. G. Bates, *J. Res. NBS* **70A** (Phys. and Chem.) No. 6, 553 (1966).
- [7] R. A. Robinson, *J. Res. NBS* **71A** (Phys. and Chem.) No. 3, 217-222 (1967).
- [8] R. L. Datta and N. Prosd, *J. Am. Chem. Soc.* **39**, 441 (1917).
- [9] R. A. Robinson and A. K. Kiang, *Trans. Faraday Soc.* **51**, 1398 (1955).
- [10] A. I. Biggs and R. A. Robinson, *J. Chem. Soc. (London)* 388 (1961).
- [11] R. A. Robinson and A. Peiperl, *J. Phys. Chem.* **67**, 1723 (1963).
- [12] G. F. Allen, R. A. Robinson, and V. E. Bower, *J. Phys. Chem.* **66**, 171 (1962).
- [13] H. von Halban and G. Kortüm, *Z. physik. Chem.* **A170**, 351 (1934).
- [14] G. Kortüm and H. Wiłski, *Z. physik. Chem.* **2**, 256 (1954).
- [15] R. A. Robinson and A. Peiperl, *J. Phys. Chem.* **67**, 2860 (1963).
- [16] A. I. Biggs, *Trans. Faraday Soc.* **52**, 35 (1956).
- [17] V. E. Bower and R. A. Robinson, *J. Phys. Chem.* **64**, 1078 (1960).
- [18] M. M. Davis and M. Paabo, *J. Res. NBS* **67A** (Phys. and Chem.) No. 3, 241 (1963).