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# **An Annotated Bibliography on Proton Affinities**

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Prepared for  
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U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, *Secretary*

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## An Annotated Bibliography on Proton Affinities

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### Abstract

This bibliography consists of approximately 150 references about proton affinities which cover the period from 1932 through 1975. Included are experimental determinations of proton affinities in the gas phase (through observation of proton transfer reactions, ion-molecule equilibria, and appearance potential measurements) as well as determinations from crystal lattice energies and other miscellaneous techniques. Also included are reviews concerned with or related to proton affinity determinations.

Key words: Appearance potential; basicity; bibliography; heat of formation; ion-molecule equilibrium; proton affinity; proton transfer

## Introduction

During the past twenty years, major advances have been made in the understanding of the chemical reactions of ions in the gas phase. An important outgrowth of this work is a growing body of information about gas phase acidities and basicities. The scale of gas phase basicities is usually quantified in terms of the proton affinities of the molecules. The proton affinity is defined as the negative of the enthalpy change resulting from the addition of a proton to a base to form the conjugate acid. This definition was originally formulated to express the basicities of molecules in solution.

This field of research has developed to the point that areas of potential scientific usefulness are becoming defined. For example, the scale of gas phase basicities is now being used as a reference scale against which to examine, define, and ultimately understand and control solvent effects on chemical equilibria and reactivity. A practical application of the proton affinity scale is its usefulness for selecting appropriate reagent gases for use in the analytical application of ion-molecule reactions known as "chemical ionization mass spectrometry" which is finding widespread application in biochemical and biomedical studies. Finally, through proton affinity measurements there now exists ion thermochemical information which ultimately must be brought into accord and combined with the much larger body of ion thermochemical information derived from spectroscopic and appearance potential measurements. In fact, this new body of proton affinity measurements imparts for the first time a network character to ion thermochemical information, thus posing opportunities for searching tests of the accuracy of various experimental measurements and their interpretation in terms of thermochemical quantities.

### Scope of Bibliography

This bibliography is intended to cover the literature concerned with gas phase proton affinities of neutral molecules from the earliest papers on the subject until the cut-off date of December 31, 1975.

In principle, there are two ways to define the scope of a bibliography on proton affinities. One could include every paper whose results directly or indirectly give information which can be related to proton affinities, even though the authors did not specifically interpret their results in those terms. Alternatively, one can simply limit the bibliography to work which specifically concerns itself with proton affinities. We have chosen the latter course even though in doing so we may be neglecting to mention certain studies which contribute useful data. The user of this compilation will be able to locate pertinent related data through the references listed in the papers of the bibliography. To include all of these related papers in the bibliography itself would mean including a large fraction of the literature on appearance potential measurements of hydrogen-containing ions. A separate comprehensive compilation of these measurements will appear shortly. Many of these articles would be of only peripheral interest to the subject of proton affinities.

We also include a list of review articles and papers which discuss factors relating to proton affinities. Theoretical calculations are not included.

### Presentation of Bibliography

The main body of the bibliography consists of a numbered list of papers, subdivided into five categories. These are: (X) experimental determinations of proton affinities based on ion-equilibrium measurements, or

limits on proton affinities based on the occurrence (or non-occurrence) of ion-molecule reactions, or on determinations of crystal lattice energies; (Y) experimental determinations of proton affinities based on appearance potential measurements; (Z) experimental determinations of proton affinities through miscellaneous approaches unrelated to those of the first two categories; (Q) derivations of proton affinities through empirical relationships to other quantities such as ionization potentials or core electron binding energies; (R) selected reviews and papers which present related and background information.

For each paper we list the molecules corresponding to the proton affinities determined in that paper. In cases where bracketing techniques or proton transfer equilibria are used to generate proton affinities, we list not only the species whose proton affinity has been determined, but also the reference molecules.

In addition, we present a list sorted according to chemical species. Here again, we give both the molecule whose proton affinity is determined and any reference species used in the determination. The order of presentation of the molecules is that of increasing atomic number and molecular complexity.

An author index is also included.

#### Literature Search

Literature references were obtained initially both by a computer search for Chemical Abstracts entries on proton affinities going back to 1970, and also by an issue-by-issue search of the following major journals, going back to 1960:

- Journal of Chemical Physics
- Journal of Physical Chemistry
- Journal of the American Chemical Society
- Journal of Research of the National Bureau of Standards
- The International Journal of Mass Spectrometry and Ion Physics
- International Journal of Chemical Kinetics
- Canadian Journal of Chemistry
- Chemical Physics Letters
- Transactions of the Faraday Society

Additional entries were found by cross-referencing articles referred to in reviews and papers of interest.

#### Acknowledgements

We are grateful to Mrs. Candyce L. Schmidt for her skillful assistance in all phases of the preparation of this document, to Mr. K. Draxl and Mr. J. G. Koch who provided helpful information on searching and document preparation, to Dr. L. W. Sieck for his assistance in the literature search, and to Dr. G. W. A. Milne of the National Institutes of Health for his help and encouragement.



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- X2 - 73 Cotter, R. J., and Koski, W. S., Reaction of D<sub>3</sub>O<sup>+</sup> with  
D<sub>2</sub>: Proton Affinity of Water, J. Chem. Phys. 59,  
784 (1973).  
  
D<sub>2</sub>O, H<sub>2</sub>O
- X3 - 70 Long, J., and Munson, B., On the Proton Affinity of Water,  
J. Chem. Phys. 53, 1356 (1970).  
  
H<sub>2</sub>O, C<sub>3</sub>H<sub>6</sub>, cis-2-C<sub>4</sub>H<sub>8</sub>, (CH<sub>3</sub>)<sub>2</sub>CO, HCHO, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>OH
- X4 - 69 DePaz, M., Leventhal, J. J., and Friedman, L., Tandem  
Mass-Spectrometer Study of D<sub>3</sub>O<sup>+</sup> and Solvated Derivatives  
J. Chem. Phys. 51, 3748 (1969).  
  
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- X5 - 69 Holtz, D., and Beauchamp, J. L., Relative Basicity of Phosphine  
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Determination of Proton Affinity from the Kinetics of  
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J. Chem. Phys. 55, 5480 (1971).  
  
CO, N<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub>, CF<sub>4</sub>, NO, N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, Ar
- X7 - 73 Hemsworth, R. S., Rundle, H. W., Bohme, D. K., Schiff, H. I.,  
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- X9 - 65 Munson, M. S. B., and Field, F. H., Reactions of Gaseous Ions. XV. Methane + 1% Ethane and Methane + 1% Propane, J. Am. Chem. Soc. 87, 3294 (1965).

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- X10 - 57 Lampe, F. W., and Field, F. H., Reactions of Gaseous Ions. III. Formation of Protonated Methane, J. Am. Chem. Soc. 79, 4244 (1957).

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$\text{H}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$

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- X15 - 68 Leventhal, J. J., and Friedman, L., Experimental Determination of  $D_3^+$  Dissociation Energy, J. Chem. Phys. 49, 1974 (1968).
- $D_2$
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CH<sub>3</sub>CθθH, NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N

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CH<sub>3</sub>Br, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>Cl, C<sub>2</sub>H<sub>2</sub>, CH<sub>3</sub>F, Cθ, HCl

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C<sub>4</sub>H<sub>4</sub>N<sub>3</sub>θC<sub>5</sub>H<sub>9</sub>θ<sub>4</sub> (Cytidine), C<sub>5</sub>H<sub>3</sub>N<sub>4</sub>C<sub>5</sub>H<sub>9</sub>θ<sub>4</sub> (9-β-D-Ribo-

furanosylpurine),  $C_5H_4N_5C_5H_9O_4$  (Adenosine),  
 $C_5H_4N_5OC_8H_{13}O_4$  (2',3'-O-Isopropylidene-guanosine),  
 $C_4H_3N_2O_2C_5H_9O_4$  (Uridine),  $C_5H_5N_2O_2C_5H_9O_3$  (Thymidine),  
 $C_4H_5N_2O_2C_5H_9O_4$  (5,6-Dihydrouridine),  $C_4H_3N_2O_2C_8H_{13}O_4$   
(2',3'-O-Isopropylideneuridine),  $C_{10}H_{13}N_5$  (6-Amino-  
9-cyclopentylpurine),  $C_6H_7N_5O$  (8-Methylguanine),  
 $C_4H_5N_3O$  (Cytosine),  $C_6H_6N_4$  (6-Methylpurine),  
 $C_5H_5N_5$  (6-Aminopurine),  $C_5H_5N_5O$  (Guanine),  $C_4H_4N_2S_2$   
(Dithiouracil),  $C_5H_4N_4$  (Purine),  $C_5H_4N_4O$  (Hypoxanthine)  
 $C_4H_3N_2OH$  (2-Hydroxy-1,3-diazine),  $C_5H_6N_2O_2$  (Thymine),  
 $C_4H_4N_2O_2$  (Uracil),  $C_5H_3N_4Cl$  (6-Chloropurine),  
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 $(CH_3)_2CO$ ,  $CH_2=CO$ ,  $HCCH_2CH_2CH_3$ , *iso*- $C_4H_8$ ,  $HCCH_2C_2H_5$ ,  
*tert*- $C_4H_9OH$ , *iso*- $C_5H_{10}$ , *iso*- $C_3H_7OH$ ,  $(CH_3)_2O$ , *n*- $C_3H_7OH$ ,  
 $HCCH_2CH_3$ ,  $CH_3CHO$ ,  $CH_3COH$ ,  $C_2H_5OH$ ,  $CH_3OH$ ,  $HCCH_3$ ,  $H_2S$ ,  
 $CF_3COH$ ,  $HCHO$ ,  $H_2O$ ,  $C_2H_4$ ,  $CH_3Cl$ ,  $(C_2H_5)_2O$

X35 - 68 Gray, G. A., Study of Ion-Molecule Reactions and  
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X36 - 69 Searles, S. K., Džidić, I., and Kebarle, P., Proton  
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X39 - 72

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X40 - 72

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X41 - 72

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X42 - 71

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X43 - 71

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X44 - 75

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 $\text{CH}_3\text{C}\theta\theta\text{CH}_3$ ,  $\text{CH}_3\text{C}\theta\theta\text{C}_2\text{H}_5$ ,  $(\text{CH}_3)_2\text{C}\theta$ ,  $\text{C}_2\text{H}_5\text{C}\theta\text{CH}_3$ ,  $(\text{C}_2\text{H}_5)_2\text{C}\theta$ ,  
 $\text{CH}_3\text{C}\theta\text{SC}_2\text{H}_5$ ,  $\text{CH}_3\text{C}\theta\theta\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $\text{CH}_3\text{C}\theta\text{SCH}_2\text{CH}_2\text{CH}_3$ ,  $(\text{n-C}_4\text{H}_9)_2\theta$ ,  
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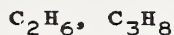
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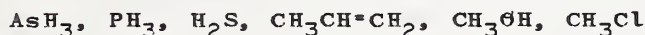




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C<sub>5</sub>H<sub>5</sub>N (Pyridine), (CH<sub>2</sub>)<sub>5</sub>NH (Piperidine), (CH<sub>2</sub>)<sub>2</sub>NH (Ethylenimine), (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>CH=NC<sub>2</sub>H<sub>5</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N, (CH<sub>2</sub>)<sub>3</sub>NH (Trimethylenimine), (CH<sub>2</sub>)<sub>2</sub>NCH<sub>3</sub> (N-Methylethylenimine), C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, CH<sub>3</sub>NH<sub>2</sub>, C<sub>3</sub>H<sub>5</sub>N (1-Azabicyclo[1.1.0]butane), CH<sub>3</sub>CN, C<sub>2</sub>H<sub>5</sub>CN, CH<sub>3</sub>OH, (CH<sub>2</sub>)<sub>2</sub><sup>⊖</sup> (1,2-Epoxyethane), (CH<sub>3</sub>)<sub>2</sub><sup>⊖</sup>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub><sup>⊖</sup>, (CF<sub>2</sub>)<sub>3</sub><sup>⊖</sup> (1,3-Epoxypropane), (CH<sub>3</sub>)<sub>2</sub>C<sup>⊖</sup>, H<sub>2</sub><sup>⊖</sup>

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$\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$

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(CH<sub>2</sub>)<sub>2</sub>O (1,2-Epoxyethane)

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$\text{PH}_3$

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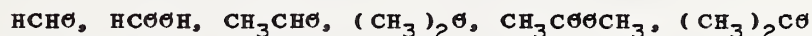
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