Proton Affinities of Some Oxygenated Compounds[1]

John Long and Burnaby Munson*

Contribution from the Department of Chemistry, University of Delaware, Newark, Delaware 19711. *Received July 8, 1972*

Abstract: Proton affinities, from the bracketing technique of gaseous proton transfer reactions, have been obtained for several oxygenated compounds. For the acids, esters, and alcohols studied, each methyl substituent directly on the functional group increased the proton affinity by about 15 kcal/mol, and each methyl substituent on the α carbon increased the proton affinity by about 5 kcal/mol. Limiting proton affinities for long-chain (greater than C_3) aliphatic alcohols, acids, and esters are given.

The investigations of ion–molecule reactions in the gas phase allow the determination of relative proton affinities (Brønsted base strengths) of molecules without interferences from ionic and molecular solvation, which complicate the interpretation of solution data in terms of molecular properties. A difference in the order of basicity obtained in the solution phase and gas phase has been clearly demonstrated in a study of the proton affinities of ammonia and the methylamines.[2,3] The differences in condensed phase and gas-phase basicities suggest that molecular effects which give the intrinsic gas-phase basicity may be weaker than the solvent effects which control the basicities in solution. The intrinsic order of basicity in the gas phase, then, may offer a basis for a more detailed study of solvation effects.

Studies have been done on the order of basicity and the proton affinities of oxygen-containing molecules.[4–9] The effect of methyl substitution on proton affinity has been noted,[2] and several studies on the order of basicity of amines and the dependence of their proton affinities on molecular structure have recently been reported.[2b,10,11] This study expands the data on proton affinities of oxygenated compounds and presents limits of proton affinities for some functional groups. The series of compounds studied shows the effect of substituting alkyl groups for hydrogens on the basicity of the compounds. Some differences are observed with proton affinities previously assigned by other techniques or other observers, and new proton affinities are given for compounds not previously reported.

The mass spectrometric determination of proton affinities was done by observing the occurrence or nonoccurrence of proton transfer reactions in gaseous mixtures.[2,6] These kinetic experiments on mixtures are used to rank the basicities of compounds, including compounds of known proton affinity. The proton affinities of all of the compounds in the ordered series can then be determined by comparison with the known values.

Experimental Procedure

The majority of the reactions were studied in the Bendix Model 12 TOF mass spectrometer using the pulsed mode. The basic instrument has been modified to operate at higher pressures obtained in an enclosed source with differential pumping on the source housing. The experiments were studies of the time dependence of ionic concentrations at constant pressure.[6,12] The pressures were maintained at a constant value during the course of each experiment; the values were generally 0.03 to 0.06 Torr. The source temperature was also held constant during each experiment and the temperatures varied from 50 to 100° for the different experiments. Several experiments were done on each pair of compounds, and the conditions of pressure, temperature, and composition were varied to minimize the complications of other reactions, particularly solvation to give M_2H^+ ions.

The compounds used in the analyses were research grade compounds and their mass spectra showed no interfering impurities. The studies were done on mixtures of constant composition which had been prepared volumetrically in a gas-handling manifold and allowed to equilibrate overnight. The gas mixture was introduced from the manifold through a heated gold leak and metal tubing into the source of the mass spectrometer. The manifold capacity was sufficient to maintain a constant source pressure throughout an analysis. The electron energy could be varied from 15 to 100 V but was usually set at 100 V for maximum sensitivity. The occurrence of proton transfer reactions in water–formaldehyde mixtures[13] and a few other systems has been shown to be unaffected by electron energy.

Some of the experiments were performed in a Du Pont 110B mass spectrometer which has been modified for high-pressure operation.[14] These experiments were variations of ionic concentration with pressure for a mixture of constant composition.

Results

Table I summarizes the data on proton affinities of all of the compounds studied. The second column lists the compounds used to obtain the upper and lower limits of proton affinity for each compound. The third column lists, in decreasing order of basicity, the proton affinities defined by the limits of column 2. The fourth column lists reference values of proton affinities and other literature data for comparison with our data. The values of proton affinities in column 3 are reported as the averages of the upper and lower limits. The errors for the reference molecules are taken from the quoted works.

---

[1] Taken in part from the Ph.D. thesis of J. Long, University of Delaware, May 1972.

[2] (a) M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 2332 (1965); (b) J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971).

[3] (a) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972); (b) W. G. Henderson, M. Taagerpera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, **94**, 4727 (1972).

[4] M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3191 (1964).

[5] M. A. Haney and J. L. Franklin, *Trans. Faraday Soc.*, **65**, 1794 (1969).

[6] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).

[7] J. L. Beauchamp and R. C. Dunbar, *J. Amer. Chem. Soc.*, **92**, 1477 (1970).

[8] J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

[9] J. L. Beauchamp and M. C. Caserio, *J. Amer. Chem. Soc.*, **94**, 2638 (1972).

[10] M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *ibid.*, **94**, 1369 (1972).

[11] M. T. Bowers, D. H. Aue, H. W. Webb, and R. T. McIver, Jr., *ibid.*, **93**, 4314 (1971).

[12] V. L. Tal'rose, *J. Pure Appl. Chem.*, **5**, 455 (1962).

[13] J. Long and B. Munson, *J. Chem. Phys.*, **53**, 1356 (1970).

[14] J. Michnowicz, Ph.D. Thesis, University of Delaware.

Table I. Proton Affinities of Oxygenated Compounds

Compd	Limits of proton affinity	PA, kcal/mol	Ref values, kcal/mol	Ref
Ammonia			207 ± 3	6, *a*
n-Propyl acetate	NH_3 ≈ *n*-propyl acetate > ethyl acetate	207 ± 3		
Diethyl ether	$NH_3 > (C_2H_5)_2O > CH_3COCH_3$	205 ± 3		
Methyl propionate	$(C_2H_5)_2O$ ≈ methyl propionate > methyl acetate	205 ± 3		
Ethyl acetate	$(C_2H_5)_2O$ ≈ ethyl acetate > methyl acetate	205 ± 3		
Methyl acetate	CH_3COCH_3 ≈ methyl acetate > CH_2CO	202 ± 2		
Acetone	$(C_2H_5)_2O > CH_3COCH_3 > CH_2CO$	202 ± 2	188 ± 2	6
			196 ± 2	*b*
			202	*c*
Ketene			201 ± 2	*c–e*
n-Propyl formate	$CH_2CO > HCOOC_3H_7 > i\text{-}C_4H_8$	198 ± 3		
Ethyl formate	$CH_2CO > HCOOC_2H_5 > i\text{-}C_4H_8$	198 ± 3		
tert-Butyl alcohol	$CH_2CO > tert\text{-}C_4H_9OH > i\text{-}C_5H_{10}$	198 ± 3	206	9
Isopentene	$i\text{-}C_5H_{10} \approx i\text{-}C_4H_8$	195 ± 3	196 ± 3	*d*, *f*
Isobutene			195 ± 3	*e*
2-Butanol			197	9
Isopropyl alcohol	$i\text{-}C_4H_8 > i\text{-}C_3H_7OH > (CH_3)_2O$	193 ± 5	193 ± 5	7
			195	9
Dimethyl ether	$i\text{-}C_4H_8 > (CH_3)_2O > CH_3CHO$	190 ± 5	191 ± 10	*g*
			187 ± 1	6
			186	7
n-Propyl alcohol	$(CH_3)_2O \gtrsim n\text{-}C_3H_7OH > C_2H_5OH$	189 ± 2		
Methyl formate	$(CH_3)_2O > HCOOCH_3 > CH_3CHO$	188 ± 3		
Propionic acid		~190	185 ± 3	1
Acetic acid	$(CH_3)_2O > CH_3COOH > CH_3CHO$	188 ± 3	184 ± 3	1
			175–178	*h*
Ethyl alcohol	$CH_3COOH > C_2H_5OH > CH_3CHO$	187 ± 2	193	*i*
			186	8
Propionaldehyde			187 ± 2	8, *j*
Acetaldehyde			185 ± 2	*j*
			183 ± 2	7
Methanol	$CH_3CHO > CH_3OH > HCOOH$		182 ± 3	6
			180 ± 3	8, *i*
2-Butene			182 ± 3	*d*, *f*
Propene			182 ± 3	*d*
Formic acid	$CH_3OH > HCOOH > H_2S$	175 ± 5	179 ± 3	6
			166	1
			156	*h*
Hydrogen sulfide			170 ± 3	6
Formaldehyde			168 ± 1	*j*
			166	8
Trifluoroacetic acid	$H_2S > CF_3COOH > H_2O$	167 ± 3		
Water	$HCHO > H_2O > C_2H_4$	165 ± 3	165 ± 3	13
			168 ± 3	*k*
			165 ± 3	6
Methyl chloride	$H_2O > CH_3Cl$	<165	164 ± 3	6
			160	8
Ethylene			159	*d*
Methane			127	*l*

[a] J. Sherman, *Chem Rev.*, **11**, 164 (1932). [b] V. K. Potapov and V. V. Sorokin, *High Energy Chem.* (*USSR*), **4**, 508 (1970). [c] L. Hellner and L. W. Sieck, *J. Res. Nat. Bur. Stand.*, *Sect. A*, **75**, 487 (1971). [d] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Heron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. [e] R. C. Nuttal, A. H. Lauffer, and M. V. Kilday, *J. Chem. Thermodyn.*, **3**, 167 (1971). [f] G. P. Semeluk and F. P. Lossing, *Can. J. Chem.*, **48**, 955 (1970). [g] G. R. Freeman, *Radiat. Res. Rev.*, **1**, 1 (1968). [h] E. W. Godbole and P. Kebarle, *Trans. Faraday Soc.*, **58**, 1897 (1962). [i] V. L. Tal'rose and E. L. Frankevitch, *J. Amer. Chem. Soc.*, **80**, 2344 (1958). [j] K. M. A. Rafaey and W. A. Chupka, *J. Chem. Phys.*, **48**, 5205 (1967). [k] S. L. Chong, R. A. Myers, and J. L. Franklin, *ibid.*, **56**, 2427 (1972). [l] W. A. Chupka and J. Berkowitz, *ibid.*, **54**, 4256 (1971).

The proton transfer reactions were observed clearly in some cases. However, in cases where higher solvated species, M_2H^+, or other known products of reaction of the MH^+ ions were present the relative abundances of these products were added to the relative abundance of MH^+ ions. A brief discussion of the procedure and representative examples of the experimental data are given subsequently.

Acetates

In methyl acetate, the significant reactions are those which involve *m*/*e* 43, the acetyl ion. CH_3CO^+ reacts with methyl acetate by proton transfer and addition.

$$CH_3CO_2CH_3 + CH_3CO^+ \longrightarrow (CH_3CO_2CH_3)H^+ + CH_2CO \quad (1)$$

$$CH_3CO_2CH_3 + CH_3CO^+ \longrightarrow (CH_3CO_2CH_3)H(CH_2CO)^+ \quad (2)$$

Figure 1 shows the continuous increase in relative abundance of *m*/*e* 75 (and the sum of relative concentrations of *m*/*e* 75 and the ester addition product $(CH_3CO_2CH_3)_2H^+$, *m*/*e* 149). The maximum in the relative abundance of the sum (43 + 117) and the continuous increase in relative abundance of the sum (75 + 149) shows that proton transfer occurs from CH_3CO^+

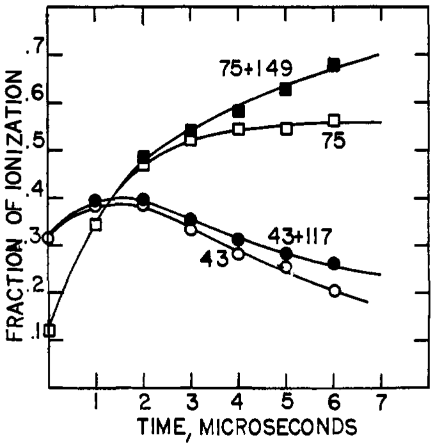

Figure 1. Fraction of ionization *vs.* delay time for methyl acetate.

to methyl acetate; hence, PA($CH_3CO_2CH_3$) > PA(CH_2CO). Similar reactions of CH_3CO^+ are observed with the other acetates.

Mixtures of methyl acetate and acetone show no evidence for proton transfer since the sum of abundances of $H(CH_3COCH_3)^+$ and $H(CH_3COCH_3)_2{}^+$ and the sum of abundances of $H(CH_3CO_2CH_3)^+$ and $H(CH_3CO_2CH_3)_2{}^+$ each increased to essentially constant values of about one-third of the total ionization. We conclude, therefore, that the proton affinities of methyl acetate and acetone are approximately equal.

Figure 2 shows the relative ionic abundances of major ions in a 21% mixture of ethyl acetate in methyl acetate. The sum of abundances of protonated methyl acetate, *m/e* 75, and its association product, *m/e* 149, passed through a maximum, and the sum of relative abundances of protonated ethyl acetate, *m/e* 89, and its association product, *m/e* 177, increased continuously over this time interval. The mixed product at *m/e* 163, $H(CH_3CO_2CH_3)(CH_3CO_2C_2H_5)^+$ which cannot be assigned unequivocally to either series, is only 5% of the total ionization at the highest pressure. From Figure 2, therefore, we conclude that PA($CH_3CO_2CH_3$) < PA($CH_3CO_2C_2H_5$).

Mixtures of ethyl acetate and diethyl ether show no evidence for proton transfer, an observation which suggests that their proton affinities are approximately equal. However, mixtures of ethyl acetate and ammonia show evidence for the proton transfer reaction

$$H(CH_3CO_2C_2H_5)^+ + NH_3 \longrightarrow NH_4{}^+ + CH_3CO_2C_2H_5 \quad (3)$$

The relative abundance of $NH_4{}^+$ increased continuously (to ~50% of the ionization), and the sum of relative abundances of protonated ethyl acetate and its association product (89 + 117) passed through a maximum for times up to 5 μsec in a mixture of ethyl acetate and ammonia (CH_3COOEt)/(NH_3) $\cong$ 2, at a pressure of 0.06 Torr. The ion at *m/e* 106, $H(NH_3)(CH_3COOC_2H_5)^+$, was less than 10% of the total ionization.

Analogous systems and observations as noted in Table I were used to obtain the approximate values for proton affinities of methyl propionate, diethyl ether, and *n*-propyl acetate.

Ketene and CH_3CO^+

The proton affinity of ketene was calculated from

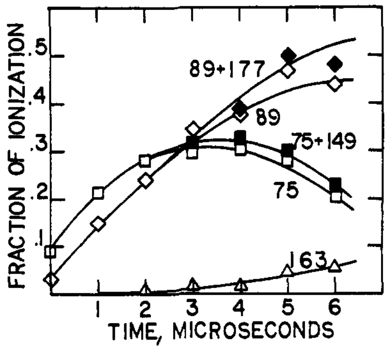

Figure 2. Fraction of ionization *vs.* delay time for 21% ethyl acetate in methyl acetate.

thermochemical data:[15–17] $\Delta H_f(CH_3CO^+)$ = 152 kcal/mol[16] and $\Delta H_f(CH_2CO)$ = −13 kcal/mol (the average of recent,[17] $\Delta H_f(CH_2CO)$ = −11 kcal, and earlier values,[16] $\Delta H_f(CH_2O)$ = −15 kcal). This value conveniently fills the gap in reference values between isobutene and ammonia. Since CH_3CO^+ occurs as a major fragment ion in the electron impact spectra of many compounds, it is a convenient reference ion. In particular, proton transfer is not observed from CH_3CO^+ to either acetic acid or acetaldehyde, and these gases provide convenient sources of CH_3CO^+. Since the ion and this value for the proton affinity of ketene are obtained from the heat of formation of CH_3CO^+ (or what should be CH_3CO^+ rather than CH_2COH^+) formed by electron impact, it probably refers to the C-protonated species.

Acetone

Two of the literature values for acetone, given in Table I, appear to be low since the acetyl ion formed in acetone reacts by proton transfer with acetone.[15,18] In a mixture of ketene and acetone, the sum of relative ionic abundances of the ions from protonated acetone, $H(CH_3COCH_3)^+$ and $H(CH_3COCH_3)_2{}^+$, was a continuously increasing function of time, and the sum of abundances of ions produced from CH_3CO^+, excluding proton transfer, passed through a maximum. In a mixture of ketene and hexadeuterioacetone, the relative intensity of CH_3CO^+ passed through a maximum, essentially no CH_2DCO^+ at *m/e* 44 was observed, and the major product ions observed in the mixture were the protonated hexadeuterioacetone and its addition product.

$$CH_3CO^+ + CD_3COCD_3 \longrightarrow CH_2CO + CD_3COHCD_3{}^+ \quad (4)$$

If ketene is all or partially O protonated by reactions in ketene (about which we can say nothing), then the O-protonated species also transfers a proton to acetone. Proton transfer was also observed from $t\text{-}C_4H_9{}^+$ (from neopentane) to acetone; therefore, PA(CH_3COCH_3) > PA($i\text{-}C_4H_8$) = 195 kcal/mol.[19]

Ethyl and Propyl Formates

In a mixture of ethyl formate and acetic acid or of propyl formate and acetic acid, the CH_3CO^+ ion

---

(15) L. Hellner and L. W. Sieck, *Res. Nat. Bur. Stand. Sect. A*, **75**, 487 (1971).

(16) Table I, footnote *d*.

(17) R. C. Nuttal, A. H. Lauffer, and M. V. Kilday, *J. Chem. Thermodyn.*, 3, 167 (1971).

(18) M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 5313 (1965).

(19) G. P. Semeluk and F. P. Lossing, *Can. J. Chem.*, **48**, 955 (1970).

formed as a fragment ion from CH_3COOH undergoes no rapid reactions, an observation which sets an upper limit for the proton affinities of these compounds. In mixtures of each of these two formates with neopentane, the *tert*-butyl ion reacted by proton transfer to the formates because the sum of abundances of the *tert*-butyl ion and its formate adducts decreased in abundance with increasing time, and the protonated formates and their adducts increased in abundance with increasing time. A mixture of these two formates gave no obvious indication of proton transfer in either direction.

tert-Butyl Alcohol

For times up to 4 μsec in the TOF mass spectrometer for *tert*-butyl alcohol at 70° and 0.08 Torr, the fragment ion at *m/e* 59 (protonated acetone) remained substantially constant at 30% of the total ionization. Only a very small amount (~2%) of addition ions of $t\text{-}C_4H_9^+$ with *tert*-butyl alcohol are observed. The nonoccurrence of this proton transfer reaction in the absence of any competing process indicates that $PA(t\text{-}C_4H_9OH) < PA(CH_3COCH_3)$.

CH_3CO^+ ions from either CH_3COOH or CH_3CHO (with which the acetyl ions are nonreactive) showed no marked decrease with time in mixtures with *tert*-butyl alcohol. The only reaction was indicated by a small amount of addition ion at *m/e* 117. Since the relative abundance of CH_3CO^+ and its adduct did not decrease with time, proton transfer to *tert*-butyl alcohol does not occur; therefore, $PA(t\text{-}C_4H_9OH) < PA(CH_2CO)$.

Since protonated *tert*-butyl alcohol exists, we can reasonably assume that the dissociation to $t\text{-}C_4H_9^+$ and H_2O is endothermic. With the recent value of $\Delta H_f(t\text{-}C_4H_9^+) = 167$ kcal/mol[19] and the standard value of $\Delta H_f(H_2O) = -58$ kcal/mol,[16] we estimate that $\Delta H_f(t\text{-}C_4H_9OH_2^+) < 109$ kcal. With this estimate and $\Delta H_f(t\text{-}C_4H_9OH) = -75$ kcal/mol,[20] we estimate a lower limit for the proton affinity of *tert*-butyl alcohol: $PA(t\text{-}C_4H_9OH) > 182$ kcal/mol.

Several mixtures with $t\text{-}C_4H_9OH$ were studied, but mixtures with $i\text{-}C_5H_{12}$ gave the lower limit of Table I. The pentyl ions formed by ion–molecule reactions in $i\text{-}C_5H_{12}$ are predominantly $t\text{-}C_5H_{11}^+$,[21] and these ions react with *tert*-butyl alcohol by both association and proton transfer. However, in a pressure study made with a modified Du Pont 110B mass spectrometer, the sum of the relative abundances of the pentyl ions and their association products passed through a maximum (32% of the total ionization), and the sum of the relative abundances of protonated *tert*-butyl alcohol and its reaction products was a continuously increasing function of pressure up to 0.5 Torr (20% of the total ionization at the highest pressure). The time and pressure curves for *tert*-butyl ions in *tert*-butyl alcohol are complicated but are consistent with proton transfer from $t\text{-}C_4H_9^+$ to $t\text{-}C_4H_9OH$.

2-Propanol and Dimethyl Ether

Our values for isopropyl alcohol and dimethyl ether agree with the previously reported values reasonably well. The present values were established by the absence of proton transfer from $t\text{-}C_4H_9^+$ ions (from neopentane), proton transfer from protonated dimethyl ether to isopropyl alcohol, and proton transfer from protonated acetaldehyde to dimethyl ether.

1-Propanol, Acetic Acid, and Ethanol

In a mixture of ethanol and 1-propanol, the sum of the relative abundances of $H(C_3H_7OH)^+$ and $H(C_3H_7OH)_2^+$ increased continuously over the experimental time interval reaching a value of approximately 50% of the total ionization, and the sum of the relative abundances of $H(C_2H_5OH)^+$ and $H(C_2H_5OH)_2^+$ passed through a maximum under the same conditions. The ion at *m/e* 107, $H(C_2H_5OH)(C_3H_7OH)^+$, contributed only about 5% of the total ionization. Proton transfer was observed from CH_3CHOH^+ (from acetaldehyde) to both ethanol and 1-propanol; hence, $PA[1\text{-}C_3H_7OH) > PA(C_2H_5OH) > PA(CH_3CHO)$.

No obvious proton transfer was detected in either direction in mixtures of 1-propanol and dimethyl ether, and proton transfer was not observed from $t\text{-}C_4H_9^+$ to 1-propanol. Hence, $PA(i\text{-}C_4H_8) > PA(1\text{-}C_3H_7OH) \cong PA(CH_3OCH_3)$.

One of the reactions resulting from proton transfer to acetic acid in either pure acetic acid or in mixtures containing acetic acid is the dehydration of the protonated molecule to give the acetyl ion. CH_3CO^+ will add to some extent to the other oxygenated compounds of low proton affinity. Consequently, in mixtures containing acetic acid, one is concerned with the increase in abundance of CH_3CO^+ and its addition products as well as the formation of $CH_3CO_2H_2^+$.

Proton transfer was observed from CH_3CHOH^+ to CH_3COOH and from $CH_3CO_2H_2^+$ to CH_3OCH_3. In mixtures of 25% CH_3COOH and 75% C_2H_5OH the dominant ions at long reaction times were the following: $H(CH_3COOH)^+$ and $H(CH_3COOH)_2^+$ (20% of the total ionization), $H(C_2H_5OH)^+$ and $H(C_2H_5OH)_2^+$ (15% of the total ionization), and CH_3CO^+ and $CH_3CO(C_2H_5OH)^+$ (45% of the total ionization). The sum of the relative abundances of protonated ethanol and its products (except for proton transfer) passed through a maximum with increasing time, and the sum of the relative abundances of protonated acetic acid and its reaction products increased continuously. Consequently, proton transfer occurs from $C_2H_5OH_2^+$ to CH_3COOH and $PA(C_2H_5OH) < PA(CH_3COOH)$.

Propionic Acid

Protonated propionic acid formed from ion–molecule reactions in the pure acid readily dehydrates to form $C_3H_5O^+$, a result which complicates the analyses of mixtures of propionic acid. In a mixture of acetic acid and propionic acid, the sum of the relative abundances of $CH_3CO_2H_2^+$ and its products (excluding proton transfer) passed through a maximum with increasing time, and there is a continuous increase in the sum of relative abundances of $C_2H_5CO^+$ and $C_2H_5CO_2H_2^+$ and their adducts. These observations suggest that $PA(C_2H_5COOH) > PA(CH_3COOH)$. However, because of the extensive decomposition of protonated propionic acid, an upper limit for the proton affinity could not be obtained from proton transfer reactions.

Discussion

The general trends in basicity with molecular structure seen in Table I can be discussed in terms of two

---

(20) K. Pihlaja and J. Kankare, *Acta Chem. Scand.*, 23, 1745 (1969).
(21) J. Long and B. Munson, *J. Amer. Chem. Soc.*, 94, 3339 (1972).

types of variations in molecular structure: functional group substitution and methyl or alkyl substitution. It has been shown that there is a general correlation between ionization potentials and proton affinities for similar molecules; an increase in ionization potential parallels a decrease in the proton affinity.[16,22] A similar trend can be observed if one plots ionization potentials *vs.* proton affinities for the oxygenated compounds in Table I. The correlation is not satisfactory for accurate predictions, however, because the $PA(HCOOH_3) \cong PA(CH_3COOH)$ but $IP(HCOOCH_3) - IP(CH_3COOH) = 11$ kcal/mol[16] and $PA(HCOOH) - PA(HCHO) \cong 8$ kcal/mol and $IP(HCOOH) - IP(HCHO) = +4$ kcal/mol.[16]

The change in proton affinity, δPA (substituted − unsubstituted compound), can be used also as a semiquantitative measure of the change in basicity with alteration in molecular structure, although the uncertainty in δPA is probably ±5 kcal/mol. Table II shows the variation of δPA for substitution of different functional groups for hydrogen on the same molecule. The increase in base strength caused by substitution of a functional group can be ranked relative to hydrogen as $CH_3O > CH_3 > OH > H > CF_3$. The methoxy, methyl, and hydroxy groups are electron donating substituents, while the trifluoro group is an electron withdrawing group. We do not have a sufficiently large series of compounds to attempt a correlation with substituent parameters.

Table II. Group Substituent Effects on Molecules

Substituent	Molecule	δPA, kcal/mol
CH_3	H_2O	15
CH_3O	HCHO	20
CH_3	HCHO	17
OH	HCHO	7
CH_3	HCOOH	13
CF_3	HCOOH	−8

Table III. Order of Basicity and Proton Affinities (kcal/mol) in the Polar Series Studied

Formates			
HCOOH <	$HCOOCH_3$ <	$HCOOC_2H_5$ ≈	$HCOOC_3H_7$
175	188	198	198
Acetates			
CH_3COOH <	CH_3COOCH_3 <	$CH_3COOC_2H_5$ <	$CH_3COOC_3H_7$
188	202	205	207
Methyl Esters			
HCOOH <	$HCOOCH_3$ <	CH_3COOCH_3 <	$CH_3CH_2COOCH_3$
175	188	202	205
Acids			
CF_3COOH <	HCOOH <	CH_3COOH <	CH_3CH_2COOH
167	175	188	~190
Alcohols			
H_2O <	CH_3OH <	C_2H_5OH <	n-C_3H_7OH ≈
165	180	187	189
	n-C_4H_9OH <	i-C_3H_7OH <	t-C_4H_9OH
	189	193	198

Table III summarizes the series of oxygenated compounds which were investigated to study the effect of substituting a methyl or other alkyl group for hydrogen. Addition of a methyl group on the carbon α to the functional group causes an approximately constant increase in basicity: $PA(CH_3CH_2OH) - PA(CH_3OH) = 7$ kcal/mol; $PA(CH_3CHOHCH_3) - PA(CH_3CH_2OH) = 6$ kcal/mol; $PA[(CH_3)_3COH] - PA(CH_3CHOHCH_3) = 5$ kcal/mol; $PA(HCOOCH_2CH_3) - PA(HCOOCH_3) = 10$ kcal/mol; $PA(CH_3COOCH_2CH_3) - PA(CH_3COOCH_3) = 3$ kcal/mol.

These values of 3–10 kcal/mol per methyl substitution for hydrogen on a carbon α to the functional group are less than the values of 13–17 kcal/mol caused by methyl substitution for hydrogen directly on the functional group given in Table II for –O–, =CO, and –COO–. With respect to the effect of a second methyl substitution for hydrogen directly on a functional group, our data on oxygenated compounds yield the following: $PA(CH_3OCH_3) - PA(CH_3OH) = 9$ kcal/mol; $PA(CH_3COCH_3) - PA(CH_3CHO) = 17$ kcal/mol; $PA(CH_3COOCH_3) - PA(HCOOCH_3) = 14$ kcal/mol; $PA(CH_3COOCH_3) = 14$ kcal/mol; and $PA(CH_3COOCH_3) - PA(CH_3COOH) = 14$ kcal/mol. That is, the second methyl group has only a slightly smaller effect than the first on the proton affinities. It has been observed, however, for ammonia and the methylamines, that there is a decrease in δPA with increasing methyl substitution.[3]

The order of basicity for the alcohols is very similar to that observed for the aliphatic amines.[2b]

An X-ray photoelectron study on the 1s orbital electrons of nitrogen in the amines gave the order of binding energies: $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$. The decrease in energy with each methyl addition was nearly constant, showing an equal contribution to the electron density on the nitrogen for each substitution in the series.[23]

The insulating effect of methylene groups is shown for the 1-alkanols in Table III: $PA(CH_3CH_2CH_2CH_2OH) \cong PA(CH_3CH_2CH_2OH)$; $PA(CH_3CH_2CH_2OH) - PA(CH_3CH_2OH) = 2$ kcal/mol; $PA(CH_3CH_2OH) - PA(CH_3OH) = 7$ kcal/mol. Replacement of a hydrogen on a carbon atom β to the functional group has a smaller effect on the proton affinity than replacement of a hydrogen on the α carbon. Substitution on the γ position had essentially no effect on the proton affinity. This trend is expected if one considers the insulating effect of methylene groups on the transmission of electronic effects through a chain.[24,25] A similar insulating (or saturation) effect is observed for ionization potentials:[16] $IP(C_2H_5OH) = 10.48 \pm 0.05$ eV; $IP(n\text{-}C_3H_7OH) = 10.20$ eV; $IP(n\text{-}C_4H_9OH) = 10.04$ eV; $IP(CH_3COOH) = 10.35 \pm 0.03$ eV; $IP(C_2H_5COOH) = 10.24 \pm 0.03$ eV; and $IP(n\text{-}C_3H_7COOH) = 10.16 \pm 0.05$ eV.

The approach to a constant base strength with increasing chain length was observed for all the series investigated. From the observed proton affinities in Table II, the limits of proton affinity for these groups are estimated and shown on Table IV. Any compound with a chain length greater than C_3 should have

---

[22] J. Long and B. Munson, paper presented at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970.

[23] P. Finn, R. Pearson, J. Hollander, and W, L, Jolly, *Inorg. Chem.*, 10, 578 (1971).

[24] R. T. Morrison and Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Boston, Mass., 1967, p 600.

[25] P. D. Bolton and L. G. Hepler, *Quart. Rev. Chem. Soc.*, 25, 521 (1971).

Table IV. Estimated Proton Affinity Limits for Oxygenated Species of Chain Length > C_3

Compound	General formula $R > C_3$	PA, kcal/mol
Primary alcohols	RCH_2OH	189
Secondary alcohols	R_2CHOH	197
Tertiary alcohols	R_3COH	204
Formates	$HCOOR$	198
Acetates	CH_3COOR	207
Methyl esters	$RCOOCH_3$	205
Ethyl esters	$RCOOC_2H_5$	208
Long-chain esters	$RCOOR$	210

a proton affinity approximately equal to the limits given. The error limits for values in Table IV are the same magnitude as the error limits for the compounds from which they are estimated, that is, a few kilocalories per mole.

Conclusions

The general trends in basicity found for the oxygenated series are useful for further work in obtaining more accurate proton affinities. These data help fill in the gaps in lists of basicities. Along with the amine data,[3] the list on Table I provides basicity data from diatomic molecules[26] through the most basic amines. Using the trends observed for the substituent and functional groups studied, one can estimate proton affinities for many molecules not already studied.

It is not possible to decide from our data whether the acids and esters are keto protonated or alkoxy protonated in the gas phase. Solution data in strong acids indicate that the stable protonated species are keto protonated.[27]

More accurate values are now being obtained for proton affinities by studying the equilibrium between gas mixtures using both high pressure[28,29] and ion cyclotron resonance techniques.[3,8,11] The equilibrium technique will work well if the difference in the basicities of the two gases is small, that is, if the proton affinities are approximately equal. Table I suggests several compounds which can be studied by this method to generate very accurate relative proton affinity values. The thermochemical data which can be obtained from accurate values are valuable in predicting the heats of reaction and probability of occurrence of other ion–molecule reactions.

Proton affinities for commonly available organic gases are particularly useful for the analytical application of chemical ionization mass spectrometry.[30] Selective ionization of the additives and differentiation of functional groups can be achieved if limiting proton affinities are available for complex molecules. Applications of dual reagent gas mixtures to structure elucidation by CIMS[31] clearly indicate that an extended list of proton affinity values will be most useful in applying this technique extensively.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(26) A. E. Roche, M. M. Sulton, D. K. Bohme, and H. I. Schiff, *J. Chem. Phys.*, **55**, 5480 (1971).

(27) (a) G. Fraenkel, *ibid.*, **34**, 1466 (1961); (b) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 3591 (1967); (c) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967).

(28) S. L. Chong, R. A. Myers, and J. L. Franklin, *J. Chem. Phys.*, **56**, 2427 (1972).

(29) J. P. Briggs, R. Yamdagni, and P. Kebarle, 20th ASMS Meeting, Dallas, Tex., 1972.

(30) B. Munson, *Anal. Chem.*, **43**, 28A (1971).

(31) D. F. Hunt and J. F. Ryan, III, *Tetrahedron Lett.*, **47**, 4335 (1971).