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An INDO Molecular Orbital Approach to the Proton Affinity of Oxygenated Compounds

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The correlation between the gas-phase proton affinities of aliphatic oxygenated compounds (alcohols, acids, and esters and their electronic structures was investigated by means of an INDO-MO theory. There appears to be a satisfactory linear-dependence of the proton affinities with the energy difference between the parent molecule and the energetically most stable protonated species and with the bond energy of the oxygen-proton bond, although the above energies are overestimated in comparison with the proton affinities. The proton affinities are also predicted with a sufficient accuracy using the first ionization potential and the electron density of the oxygen atom (especially, the % p-character in the oxygen lone-pairs) of the parent molecule.

Mass spectroscopic investigations of ion-molecule reactions have recently centered around the determination of the relative proton affinities (Brønsted base strengths) of nitrogenated[1–5] and oxygenated[6–12] compounds, with a particular view to the dependence of the proton affinities on their molecular structures, especially on their substituents and functional groups.[2,5,12] From the trends observed experimentally for a correlation between the proton affinity and the molecular structure, it has already been noted that the proton affinities for similar molecules depend directly on the ionization potentials of the parent molecules.[13]

There have also appeared the extended Hückel[14] and *ab initio*[15–17] MO-theoretical treatments of the proton affinities of small molecules; the former MO-calculations gave energies which are of the correct order of magnitude but are too small, while the latter MO-calculations indicated appreciable percentage errors of estimated proton affinities with respect to the experimental values. Very recently, a potential model based on the Hellmann-Feynman theorem[18] combined with CNDO/2 wave functions has been proposed by Davis and Rabalais[19] for relating the proton affinities to inner-shell electron binding energies.

Recently, the authors began a semi-empirical INDO-MO study on the gas-phase proton affinities of several oxygenated compounds (aliphatic alcohols, acids, and esters) to investigates how the proton affinities depend on the electronic properties of the molecule. In this paper, the calculated results are reported with particular reference to the correlations between the proton affinities and various calculated energies such as theoretical proton affinities, bond energies for the oxygen-proton bond, ionization potentials, *etc.*

Method of Calculation

The gas-phase proton affinities (PA) of the following five series of aliphatic oxygenated compounds were investigated in this work: (a) formates, HCO_2R ($R=H$, CH_3, CH_3CH_2, and $CH_3CH_2CH_2$), (b) methyl esters, RCO_2CH_3 ($R=H$, CH_3, and CH_3CH_2), (c) acetates, CH_3CO_2R ($R=H$, CH_3, CH_3CH_2, and $CH_3CH_2CH_2$), (d) acids, RCO_2H ($R=H$, CF_3, CH_3, and CH_3CH_2), and (e) alcohols, ROH ($R=H$, CH_3, CH_3CH_2, and $CH_3CH_2CH_2$) (see Table 1). All calculations for the above compounds and their protonated species were performed using the INDO-MO method[20] which is relatively reliable for bond angles, although less so for bond lengths.[21] The approximations involved in the INDO are not repeated here, because they have been described in detail in Ref. 20.

The energy, ΔE, for the calculated proton affinity was obtained from the energy difference between the protonated species (BOH^+) and the parent molecule (BO):

$$BO + H^+ \longrightarrow BOH^+ \qquad (1)$$

Since the energy of the proton is zero, the ΔE value can be given by:

$$\Delta E = E(BO) - E(BOH^+) \qquad (2)$$

where the ΔE value is positive because $E(BOH^+)$ is normally a larger negative number than $E(BO)$.

The bond index of E_{OH^+} for the oxygen-proton bond of the protonated species was evaluated by means of a method of energy partitioning:[22]

$$E_{OH^+} = E^R_{OH^+} + E^V_{OH^+} + E^J_{OH^+} + E^K_{OH^+} + E^N_{OH^+} \qquad (3)$$

where each energy term represents, respectively, the resonance, potential, electronic repulsion, electronic exchange interaction, and nuclear repulsion energies, which can be obtained by the usual manner described in detail in Ref. 22.

Results and Discussion

Geometries of Parent Molecule and Protonated Species. First, the geometries used for the parent molecules are discussed by comparing calculated dipole moments (μ_{calcd}) and first ionization potentials (I_{calcd})[23] with measured experimentally (μ_{obsd} and I_{obsd}). The dipole moments and ionization potentials are summarized in Table 2. Although exact agreements were not found between calculated and experimental dipole moments and ionization potentials, the approximate agreement between the calculated and observed dipole moments suggests that the charge distributions in the parent molecules appear to be plausible, while an almost constant ratio of I_{obsd}/I_{calcd} (around 0.8) indicates a systematic deviation of the calculated results from the experimental results. The deviations found for the dipole moments and ionization potentials may not be due to an inadequacy of the geometries but to the approximations involved in the INDO method, because it is well known that the INDO calculation trends to give an incomplete evaluation of the dipole

TABLE 1. ASSUMED BOND LENGTHS AND ANGLES FOR OXYGENATED COMPOUNDS AND THEIR PROTONATED SPECIES[a)]

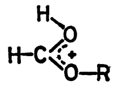
Series	No.	Molecule	$R_{C=O}$	R_{CO}	R_{OH}	∠OCO	∠COC	∠COH
Formates	1	$HCO_2H(H^+)$	1.245	1.312	0.95	124°18′		107°48′
	2	$HCO_2CH_3(H^+)$	1.200	1.334	(0.96)	125°52′	114°47′	(114°47′)
	3	$HCO_2C_2H_5(H^+)$	1.200	1.334	(0.96)	125°52′	114°47′	(114°47′)
	4	$HCO_2C_3H_7(H^+)$	1.200	1.334	(0.96)	125°52′	114°47′	(114°47′)
Acetates	5	$CH_3CO_2H(H^+)$	1.240	1.430	0.95	130°		107°48′
	6	$CH_3CO_2CH_3(H^+)$	1.220	1.360	(0.96)	124°	113°	(116°)
	7	$CH_3CO_2C_2H_5(H^+)$	1.200	1.334	(0.96)	125°52′	114°47′	(114°47′)
	8	$CH_3CO_2C_3H_7(H^+)$	1.200	1.334	(0.96)	125°52′	114°47′	(114°47′)
Methyl esters	1	$HCO_2H(H^+)$	1.245	1.312	0.95	124°18′		107°48′
	2	$HCO_2CH_3(H^+)$	1.200	1.334	(0.96)	125°52′	114°47′	(114°47′)
	6	$CH_3CO_2CH_3(H^+)$	1.220	1.360	(0.96)	124°	113°	(116°)
	9	$C_2H_5CO_2CH_3(H^+)$	1.220	1.360	(0.96)	124°	113°	(114°47′)
Acids	10	$CF_3CO_2H(H^+)$	1.240	1.430	0.95	130°		107°48′
	1	$HCO_2H(H^+)$	1.245	1.312	0.95	124°18′		107°48′
	5	$CH_3CO_2H(H^+)$	1.240	1.430	0.95	130°		107°48′
	11	$C_2H_5CO_2H(H^+)$	1.240	1.430	0.95	130°		107°48′
Alcohols	12	$H_2O(H^+)$			0.9572			
	13	$CH_3OH(H^+)$		1.421	0.958			110°15′
	14	$C_2H_5OH(H^+)$		1.480	0.958			110°15′
	15	$C_3H_7OH(H^+)$		1.480	0.958			110°15′

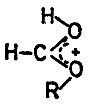
a) All values except those in parentheses were commonly used for the parent and protonated compounds, but the values in the parentheses were given only for the protonated species.

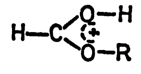
moments and an overestimation of the ionization potentials.

With regard to the geometries of the protonated compounds, it is noteworthy that the C=O bond length of the parent molecule is lengthened by the protonation so that it is nearly equal to the single C–O bond length,[16,17,24)] while the O–C–O bond angle is not so different for the parent molecule and the protonated species. For protonated formic acid, $R_{CO}=1.31$ Å ($R_{OH}=R_{OH^+}=0.979$ Å) and ∠OCO=124 ° have been given by Ros,[24)] and $R_{CO}=1.279$ Å ($R_{OH}=R_{OH^+}=0.96$ Å) have been assumed by Csizmadia *et al.*[16)] The INDO optimization of the geometry for the above compound gave $R_{CO}=1.30$ Å and ∠OCO=118 °, together with ∠COH=∠COH⁺=120 °, $R_{CH}=1.12$ Å, and $R_{OH}=R_{OH^+}=1.04$ Å. For simplicity of computation in the present work, the bond lengths and angles for the protonated compounds were taken to be the same as those (supplied by a standard compendium[25)]) for the parent molecules, as shown in Table 1. Regarding the values of R_{CO}, R_{OH^+}, and ∠COH⁺, for the protonated species, they were taken to be as follows on the basis of the R_{CO}, R_{OH}, and ∠COH (or ∠COR) values of the parent molecules: R_{CO} of C–OH⁺=R_{CO} of C–OH or C–OR, $R_{OH^+}=R_{OH}$, and ∠COH⁺=∠COH or ∠COR. If we assume the geometries listed in Table 1 to be equilibrium geometries, the force constants (K_{AB})[26)] for the protonated compounds are evaluated to be $K_{CO}=4.04-6.65$ mdyn/Å and $K_{OH}=7.62$ mdyn/Å; the former value is somewhat small in comparison with $K_{CO}=8.11$ mdyn/Å given by Ros[24)] for protonated formaldehyde. Furthermore, the INDO calculations gave the following relative stabilities of the protonated conformers in the case of R=H, although the difference in the total energies of the isomers is very small: I(−43.834 a.u.)>II (−43.830 a.u.)>III(−43.827 a.u.) in the protonated formates; IV(−52.238 a.u.)>V(−52.225 a.u.) in the protonated acetates; VI(−52.285 a.u.)>VII(−52.284 a.u.)>VIII(−52.283 a.u.)>IX(−52.278 a.u.) in the protonated methyl esters. The INDO calculation tends to underestimate the electron-electron repulsions,[20,27)] so that the *trans-trans* isomer, VII, was calculated to be more stable than the *cis-cis* isomers such as IX. As a matter of fact, alkoxy-protonated isomers such as X and XI are less stable than such keto-protonated isomers as I, II, and III. For example,

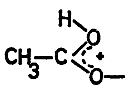
Protonated formates

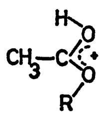

cis-trans
I


cis-cis
II

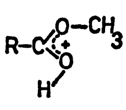

trans-trans
III

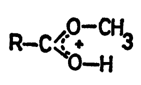
Protonated acetates

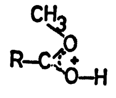

IV


V

Protonated methyl esters


VI


VII


VIII

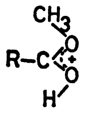
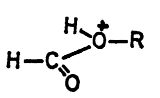

IX

TABLE 2. DIPOLE MOMENTS AND FIRST IONIZATION POTENTIALS FOR OXYGENATED COMPOUNDS

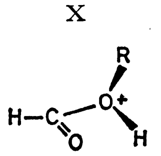
Compound No.	μ_{calcd}/D	μ_{obsd}/D	I_{calcd}/eV	I_{obsd}/eV
1	1.441	1.415[a]	13.74	11.05[j]
2	1.333	1.52[b]	13.52	10.92[k]
3	1.436	1.81[c]	13.33	10.5[l]
4	1.487		13.28	
5	1.053	1.50[d]	13.25	10.35[j]
6	1.343	1.67[e]	12.95	10.92[k]
7	1.353	1.82[f]	12.62	10.09[j]
8	1.365		12.60	
9	1.362		12.60	10.5[l]
10	2.283	2.28[g]	14.12	
11	1.089	1.74[g]	12.84	10.47[m]
12	2.182	1.846[h]	16.30	12.69[n]
13	1.979	1.83[i]	14.42	10.85[j]
14	1.919	1.80[i]	14.26	10.50[j]
15	1.906	1.79[i]	14.20	10.15[o]

a) H. Kim, R. Keller, and W. D. Gwinn, *J. Chem. Phys.*, **37**, 2748 (1962). b) E. Bock, *Can. J. Chem.*, **45**, 2761 (1967). c) J. M. Rineros and F. B. Wilson, *J. Chem. Phys.*, **46**, 4605 (1967). d) J. O. Jenkins and J. W. Smith, *J. Chem. Soc., B*, **1970**, 1538. e) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York (1955). f) Y. Koga, H. Takahashi, and K. Higasi, This Bulletin, **47**, 84 (1974). g) S. S. Krishnamurthy and S. S. Soundarajan, *Tetrahedron*, **24**, 167 (1968). h) G. Birnbaum and S. K. Chatterijie, *J. Appl. Phys.*, **23**, 220 (1952). i) D. A. Ibbitson and L. F. Moore, *J. Chem. Soc., B*, **1967**, 80. j) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). k) C. J. Varsel, F. A. Morrell, F. E. Resnik, and W. A. Powell, *Anal. Chem.*, **32**, 182 (1960). l) A. B. King and F. A. Long, *J. Chem. Phys.*, **29**, 374 (1958). m) J. D. Morrison and A. J. C. Nicholson, *ibid.*, **20**, 1021 (1952). n) L. P. Lindeman and J. G. Guffy, *ibid.*, **29**, 247 (1958). o) A. J. Harrison, B. J. Cedesholm, and M. A. Terwillger, *ibid.*, **30**, 355 (1959).

in the case of R=H (the bond lengths and angles of X and XI were taken to be the same to those of I, II, or III), the planar species, X, is less stable than I by 8.79 kcal/mol, and the nonplanar species, XI, is 12.55 kcal/mol higher than I. Although the relative stabilities of the protonated isomers on the basis of the INDO calculation results produce some discrepancies in connection with those determined by NMR observations,[28] the energetically most stable *cis-trans* conformers, I, IV, and VI which were predominantly detected by NMR spectroscopy[28] will be used in the discussions developed below.


planar

X


nonplanar

(H-OH plane perpendicular to O-C=O plane)

XI

Ionization Potential vs. *Proton Affinity*. The calculated first ionization potentials (I_{calcd}) for the protonated compounds in Table 1 were evaluated to be higher by 0.25—0.43 a.u. than those for their parent molecules. This trend can be well explained by the decrease in the electron densities of the oxygen lone-pair orbitals due to the protonation, which causes a lowering of the HOMO (the highest-occupied MO) localized by the so-called lone-pairs. If the nonbonding lone-pair orbitals play a predominant role in the protonation, the I_{calcd} values for the parent molecules may directly correlated with the proton affinities (*PA*). This consideration is related to the fact that the proton affinity corresponds to the Brønsted base strength which is inversely proportional to the ionization potential. As shown in Fig. 1, the *PA* values are satisfactorily linearly dependent on the reciprocal values of I_{calcd} ($1/I_{calcd}$) throughout the series investigated:

$$PA = a_1/I_{calcd} + b_1 \tag{4}$$

where a_1 and b_1 are constants specified by a least squares error analysis, and are listed in Fig. 1.

Equation (4) is particularly useful, because it predicts the proton affinities within a relative error of 2% of the experimental values.

We should here mention the limit of the linear cor-

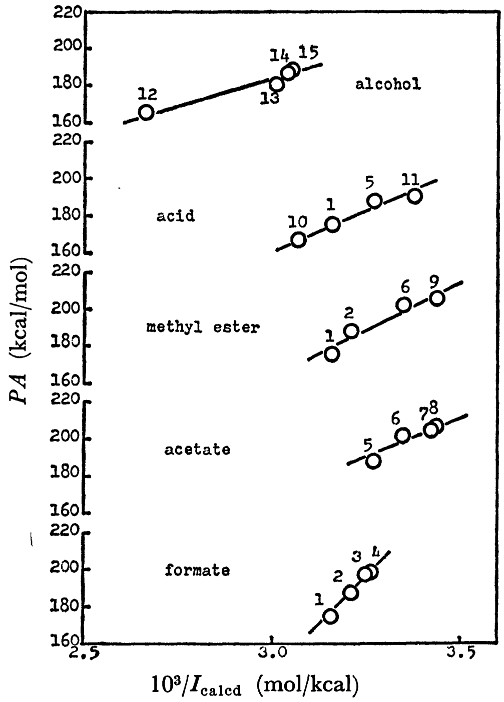


Fig. 1. Plots of *PA* *vs.* $1/I_{calcd}$.

Series	$10^{-5}\,a_1$	$10^{-2}\,b_1$
Formate	2.17	5.09
Acetate	1.01	1.40
Methyl ester	1.01	1.38
Acid	0.79	0.75
Alcohol	0.56	0.15

Table 3. Proton affinities and electronic properties of oxygenated compounds

Series and compound No.	PA[a] kcal/mol	M_O	M_O^{HO}	N_p	$N(s)_{lp}$	$N(p)_{lp}$	$N(p)_{lp}^{HO}$	M_H	ΔE kcal/mol
Formates									
1	175	6.367	1.476	4.581	1.786	1.912	1.467	0.700	293.0
2	188	6.347	1.316	4.583	1.764	1.894	1.298	0.702	310.6
3	198	6.351	1.272	4.587	1.764	1.894	1.248	0.706	315.0
4	198	6.354	1.208	4.590	1.764	1.894	1.174	0.708	316.9
Acetates									
5	188	6.347	1.277	4.562	1.785	1.911	1.253	0.727	276.1
6	202	6.373	1.312	4.598	1.775	1.910	1.287	0.722	320.6
7	205	6.380	1.248	4.798	1.766	1.907	1.207	0.724	335.1
8	207	6.382	1.231	4.616	1.766	1.908	1.189	0.725	337.0
Methyl esters									
1	175	6.367	1.476	4.581	1.786	1.912	1.467	0.700	293.0
2	188	6.347	1.316	4.583	1.764	1.894	1.298	0.702	310.6
6	202	6.373	1.312	4.598	1.775	1.910	1.287	0.722	320.6
9	205	6.381	1.148	4.605	1.776	1.909	1.104	0.725	324.4
Acids									
10	167	6.261	0.917	4.478	1.783	1.904	0.879	0.706	239.7
1	175	6.367	1.476	4.581	1.786	1.912	1.467	0.700	293.0
5	188	6.347	1.277	4.562	1.785	1.911	1.253	0.727	276.1
11	190	6.351	1.114	4.566	1.785	1.904	1.077	0.730	280.5
Alcohols									
12	165	6.335	2.000	4.611	1.724	2.000	2.000	0.629	255.4
13	180	6.298	1.433	4.603	1.695	1.970	1.433	0.635	261.7
14	187	6.315	1.247	4.604	1.711	1.977	1.247	0.652	276.7
15	189	6.318	1.211	4.606	1.712	1.976	1.211	0.654	279.2

a) From Ref. 12.

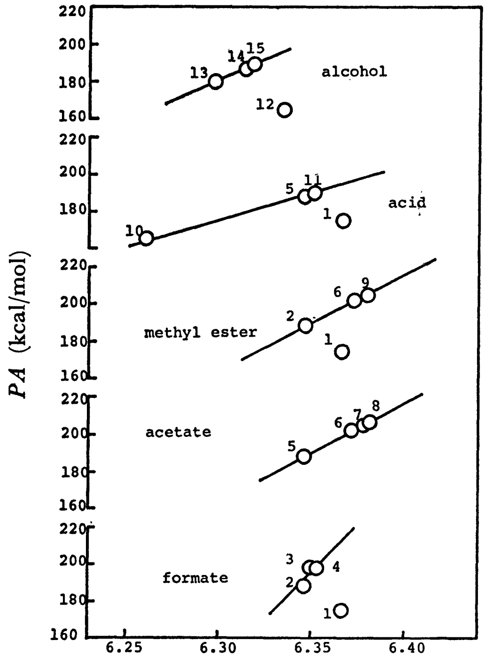


Fig. 2. Plots of PA vs. M_O.

relation between the PA and I_{calcd} values. The approach to a constant PA or I_{calcd} value with increasing chain length of R was observed for all the series investigated, especially for the formates, acetates, and alcohols. This may coincide with the fact that oxygenated compounds with a chain length greater than C_3 have a limited proton affinity.[12]

Electron Density of the Oxygen Atom vs. *Proton Affinity.* The electron density of the oxygen atom of BO in reaction(1), M_O, should be a measure of the proton affinity, because the electron density of such hetero-atoms as nitrogen and oxygen relates directly to the base strength.[29] As expected, the M_O values for the parent molecules are in satisfactory agreement with their PA values with some exceptions (H_2O and HCO_2H). A similar correlation with almost the same degree of accuracy as that in Eq. (4) can be seen from Fig. 2.

In connection with the linear correlation between the M_O and PA values, the electron densities of the oxygen p-orbitals (denoted as N_p; $N_p = N_{p_x} + N_{p_y} + N_{p_z}$) may correlate more directly with the proton affinities. In this respect, the linear correlations between the PA and N_p values throughout the series are found to be more satisfactorily established than those between the PA and M_O values, as may be seen from Table 3.

It is of interest here to notice the contributions of the electron densities of the oxygen s and p lone-pairs in the parent molecule to the proton affinity: the nonbonding lone-pair p-orbital expands perpendicularly to the C–O bond axis in the direction of the plane on which almost all the atoms (except the H atoms of the substituent R) are located. Although the electron densities of the lone-pair s-orbital ($N(s)_{lp}$)

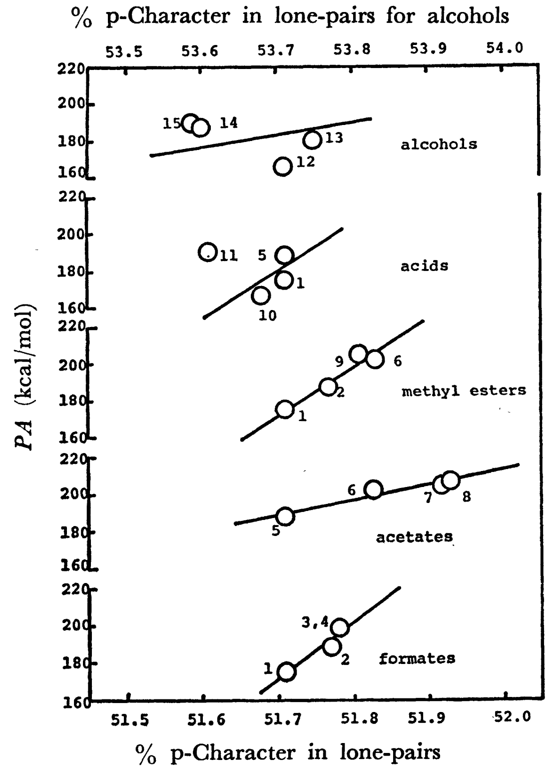


Fig. 3. Plots of % p-character in lone-pairs of parent molecule *vs.* proton affinity.

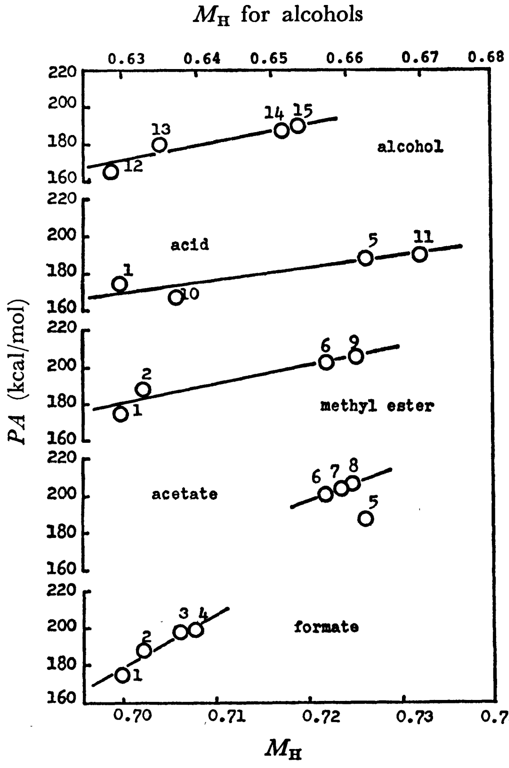


Fig. 4. Plots of *PA* *vs.* M_{H}.

and of the lone-pair p-orbital ($N(\mathrm{p})_{\mathrm{lp}}$) are not linearly well related to the *PA* values (see Table 3), the % p-character in the lone-pairs, which is defined by $10^2 N(\mathrm{p})_{\mathrm{lp}}/(N(\mathrm{s})_{\mathrm{lp}}+N(\mathrm{p})_{\mathrm{lp}})$, correlates directly with the proton affinity, as shown by Fig. 3. Unfortunately, the % p-character of the lone-pairs of the alcohols, which are not completely accurate because of an unsufficient estimation of the $N(\mathrm{p})_{\mathrm{lp}}$ values, showed marked deviations from the straight line. This linear relationship between the % p-character of the lone-pairs and the *PA* value coincides with the fact that nitrogen and oxygen bases with a high s-character of their lone-pairs have small *PA* values.[30)]

Bearing in mind that the *PA* values correlate well with the I_{calcd} values, the electron density of the oxygen atom or of the nonbonding lone-pair p-orbital at the HOMO (denoted respectively as $M_{\mathrm{O}}^{\mathrm{HO}}$ and $N(\mathrm{p})_{\mathrm{lp}}^{\mathrm{HO}}$) may correlate directly with the *PA* values. However, as may be seen from Table 3, the *PA* values depend inversely on the $M_{\mathrm{O}}^{\mathrm{HO}}$ values which correspond roughly to the $N(\mathrm{p})_{\mathrm{lp}}^{\mathrm{HO}}$ values. This suggests that the proton affinity cannot be explained simply by the electron density at the HOMO of the parent molecule, that is, electrons at lower MOs (next to the HOMO, *etc.*) may participate in the protonation reaction.

We will now examine the possibility of a correlation between the proton affinities and the electron densities about the proton of the protonated compounds, M_{H}. As can be seen from Fig. 4, there exists a sufficiently linear correlation between them throughout the series. This is well explained by the following reasons: (a) the proton affinity correlates with the proton 1s chemical shift,[19)] and (b) the proton chemical shift has also a correlation with the M_{H} values, as has been found in the NMR results for halomethanes.[31)]

Calculated Proton Affinity. As shown in Table 3, the calculated proton affinities, ΔE, obtained from Eq. (2) are larger than the experimental proton affinities and increase with an increase in the chain length of the alkyl substituent (R). The *PA* values of all the oxygenated compounds investigated are roughly linearly correlated with the ΔE values:

$$PA = 0.388\Delta E + 75.65\ \mathrm{kcal/mol} \qquad (5)$$

However, Eq. (5) is incomplete, because a least-squares error analysis of the relation expressed by Eq. (5) has a maximum relative error of 8.2%. As shown in Fig. 5, completely linear lines can be obtained from the plots of *PA* *vs.* ΔE for each series and can be expressed by the following equation with a maximum error of 3%:

$$PA = a_2\Delta E + b_2\ \ \mathrm{kcal/mol} \qquad (6)$$

where a_2 and b_2 are constants specified in Fig. 5. The slopes of the straight lines are almost unity for the formates, methyl esters, and alcohols but are smaller than unity for the acids and acetates. In the latter two compounds, an overestimation can be seen for the effect of the substituents (R) on the calculated proton affinities, that is, a change in the ΔE values with an increase in the carbon number of the substituents is more significant than that in the corresponding *PA* values, while, in the other series, the difference between the ΔE values corresponds almost exactly to that between the *PA* values (see Table 3). Therefore, in the acids and acetates, the settled geometries, especially for those of the substituents, appear incomplete in the approximate INDO-MO method.

Bond Index of $E_{\mathrm{OH^+}}$ vs. *Proton Affinity.* Now, we examine the total bond energy ($E_{\mathrm{OH^+}}$) and the resonance

TABLE 4. TOTAL BOND ENERGIES AND THEIR PARTITIONING TERMS FOR THE OXYGEN-PROTON BONDS IN THE PROTONATED COMPOUNDS

Series and compound No.	$-E_{OH^+}$/eV	% O(p)−H$^+$(s)[a] overlap population	$-E^R_{OH^+}$/eV	$-E^K_{OH^+}$/eV	$E^V_{OH^+}+E^J_{OH^+}+E^N_{OH^+}$/eV
Formates					
1	19.363	60.53	21.326	6.101	8.065
2	19.698	50.49	21.299	6.078	7.678
3	19.738	59.58	21.311	6.094	7.667
4	19.752	59.62	21.317	6.099	7.664
Acetates					
5	19.756	60.59	21.529	6.233	8.006
6	19.964	59.64	21.396	6.153	7.584
7	19.930	59.85	21.371	6.152	7.593
8	19.936	59.88	21.374	6.156	7.594
Methyl esters					
1	19.363	60.53	21.326	6.101	8.065
2	19.698	59.49	21.299	6.078	7.678
6	19.964	59.64	21.396	6.153	7.584
9	19.988	59.69	21.404	6.163	7.997
Acids					
10	19.445	60.12	21.460	6.149	7.580
1	19.363	60.53	21.326	6.101	8.065
5	19.756	60.59	21.529	6.233	8.006
11	19.788	60.65	21.540	6.244	7.834
Alcohols					
12	19.432	55.98	21.420	5.845	7.793
13	19.374	52.73	21.618	5.749	7.881
14	19.542	53.59	21.612	5.811	7.863
15	19.568	53.62	21.614	5.818	8.165

a) Defined by % O(p)-H$^+$(s) overlap population=oxygen-p and hydrogen-s overlap populations in the O-H$^+$ bond×10^2/total overlap population in the O-H$^+$ bond.

energy ($E^R_{OH^+}$), which indicates the covalent bond strength, for the O–H$^+$ bond of the protonated species, in connection with the relation to the proton affinity. It can be seen from Table 4 that the absolute values of E_{OH^+}, which correspond to the bond strength of O–H$^+$, are about twice as large as the proton affinities. This may be mainly attributed to the approximations in the INDO-MO method. It is also noteworthy that index of E_{AB} indicates a static property of the A–B bond and cannot be directly compared with experimental energies such as the dissociation energy.[22] However, good correlations are observed in each series with some exceptions (H_3O^+ and $HCO_2H_2^+$) if both the kinds of energies, *PA* and E_{OH^+}, are plotted against each other. In this respect, it is also noticeable that the % O(p)-H$^+$(s) overlap population defined in Table 4 correlates well with the *PA* values with some exceptions (H_3O^+ and $HCO_2H_2^+$). This coincides with the fact that the % p-character in the oxygen lone-pairs of the parent molecule plays a predominant role in the proton affinity.

In regard to the $E^R_{OH^+}$ values, the slopes of the straight lines obtained from the plots of *PA vs.* $E^R_{OH^+}$ were not constantly positive throughout the series. This may be due to the fact that the resonance energy $E^R_{OH^+}$ is not meaningful for such an ionic oxygen-proton bond in the protonated species. In this respect, the contributions of the electronic exchange term ($E^K_{OH^+}$) and the repulsive electrostatic interactions ($E^V_{OH^+}+E^J_{OH^+}+E^N_{OH^+}$) to the proton affinity are here noted. As may be seen from Table 4, the negative $E^K_{OH^+}$ values become more negative with an increase in the *PA* values, while the positive values of the repulsive terms ($E^V_{OH^+}+E^J_{OH^+}+E^N_{OH^+}$) decrease with an increase in the *PA* values. These observations are in harmony with the fact that the more negative the $E^K_{OH^+}$ value becomes (or the smaller the above sum of the repulsion terms becomes), the stronger becomes the O–H$^+$ bond. There exists on approximate relation between them with some exceptions (H_3O^+ and $HCO_2H_2^+$). Then, we can say that the above exchange and repulsion terms can also be useful as a measure of the *PA* value.

In conclusion, it is worthy of emphasis that the experimental gas-phase proton affinities for the oxygenated compounds investigated cannot be compared directly with the calculated proton affinities or the bond energies obtained by the INDO calculations, but are in satisfactory agreement with them. The proton affinities can also be predicted with a sufficient accuracy from the first ionization potentials and the electron densities of the oxygen atoms of the parent molecules.

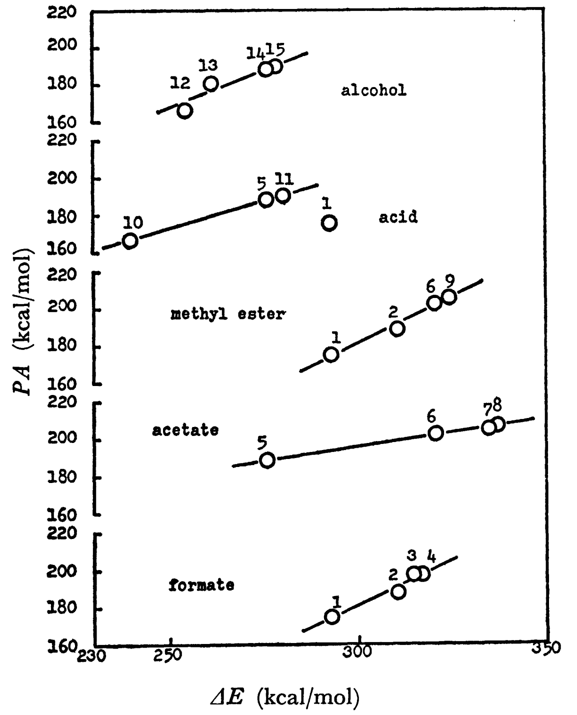


Fig. 5. Plots of PA vs. ΔE.

Series	a_2	$10^{-2}\ b_2$
Formate	0.98	−1.12
Acetate	0.30	1.05
Methyl ester	0.98	−1.12
Acid	0.57	0.32
Alcohol	0.88	−0.54

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