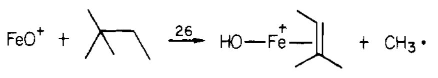
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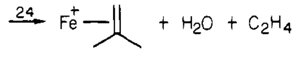
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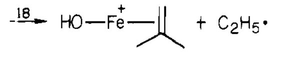
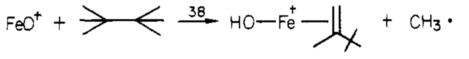

(35)

$\xrightarrow{32}$ other products (see table III) (36)

iron, and completed by elimination of water and ethene to form the iron–isobutene ion. The H_2O elimination product could also arise by initial C–H insertion.

The final compound studied is a highly symmetric, highly branched hydrocarbon, 2,2,3,3-tetramethylbutane. If one postulates C–H bond insertion, there are no β hydrogens to transfer, so these pathways are closed to this particular species and C–C insertions appear to dominate. There are two different C–C bonds in this compound. Insertion into the terminal C–C bonds leads to reactions 37 and 40. Reaction 37 results from insertion into the C–C bond, followed by elimination of the methyl radical and concluded by a β-hydride shift to form the hydroxy–iron–olefin ion. This can transfer another hydrogen to the metal, creating the π-allyl ligand. This species can then eliminate water, creating the product in reaction 40. Products from reactions 38 and 39 result from insertion into the central C–C bond. The hydroxy–iron–isobutene complex is formed by elimination of *tert*-butyl radical and a β-hydride transfer. The Fe^+–isobutene ion is formed by two successive β-hydride transfers and elimination of water and an isobutene ligand.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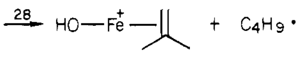
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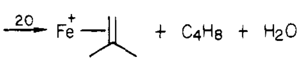
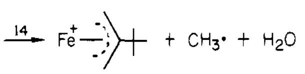

(39)


(40)

Conclusions

In general from the reactions observed, it appears that FeO^+ is more reactive toward alkanes than Fe^+ which is due mainly to the greater reaction exothermicity involved in H_2O loss. The majority of the products observed may be explained by initial C–H insertion and loss of H_2O to produce an activated Fe^+–olefin complex which subsequently decomposes. An alternative mechanism involving C–C insertion, however, cannot be ruled out and is in fact supported by observation of radical-loss products. These radical-loss products dominate for systems in which C–H insertion pathways are inhibited by the absence of β hydrogens. These species consist of stable hydroxyalkene ions which can rearrange to the aquo–π-allyl form under collisional activation.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (Contract DE-AC02-80ER10689) for supporting this research and the National Science Foundation (CHE-8002685) for providing funds for the purchase of the FTMS. We also gratefully thank Marc Wise, Chemistry Department, Purdue University, for construction of the 5.2-cm cubic trapping cell.

Registry No. FeO^+, 12434-84-3; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; C_4H_{10}, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2; 2-methylpropane, 75-28-5; 2-methylbutane, 78-78-4; 2,2-dimethylpropane, 463-82-1; 2,3-dimethylbutane, 79-29-8; 2,2-dimethylbutane, 75-83-2; 2,2,3,3-tetramethylbutane, 594-82-1.

The Ionic Hydrogen Bond and Ion Solvation. 1. $NH^+\cdots O$, $NH^+\cdots N$, and $OH^+\cdots O$ Bonds. Correlations with Proton Affinity. Deviations due to Structural Effects

Michael Meot-Ner (Mautner)

Contribution from the Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Washington, D.C. 20234.

Received May 10, 1982

Abstract: In dimers $BH^+\cdots A$, a linear correlation is found between the bond dissociation energy $\Delta H°_D$ and the difference ΔPA between the proton affinities of the proton donor B and the proton acceptor A. The correlation applies for 48 $-NH^+\cdots O-$ dimers including a series with varying A and constant B, i.e., hydrates of ammonium and pyridium ions ($-NH^+\cdots OH_2$); a series with varying B and constant A, i.e., complexes $CH_3NH_3{}^+\cdots O-$; and other dimers with ΔPA values varying from 9 to 70 kcal mol and bond energies from 27 to 12 kcal mol^{-1}. The correlation $\Delta H°_D$ (kcal mol^{-1}) = $\Delta H°_D(0) - b\Delta PA$ for $-NH^+\cdots O-$ bonds yields the parameters $\Delta H°_D(0) = 30.0$ kcal mol^{-1} and $b = 0.26$. Analogous linear correlations are observed for $-NH^+-\cdots N-$ bonds in a set of 8 ammonium ion dimers, and for $-OH^+\cdots O-$ bonds in a set of 21 oxonium ion hydrates, with parameters $\Delta H°_D(0) = 23.2$, $b = 0.23$ and $\Delta H°_D = 30.4$, $b = 0.30$, respectively. Analogous linear correlations apply also for $-NH^+\cdots S-$ and $-SH^+\cdots O-$ bonds. The correlations are in accord with trends predicted by ab initio calculations of Desmeules and Allen.[1] The correlations are reliable predictors of $BH^+\cdots A$ energies within experimental error limits. Deviations from the correlations help to identify special structural effects. Such effects include multiple hydrogen bonding, intramolecular hydrogen bonding, resonance, and steric crowding.

Introduction

The thermochemistry of numerous hydrogen-bonded dimer ion $BH^+\cdot A$ has been investigated by Kebarle and other workers.[2] Bond dissociation energies ($\Delta H°_D$) and entropies ($\Delta S°_D$) were obtained from the temperature dependence of the equilibrium constants of clustering reactions:

$$BH^+ + A \rightleftarrows BH^+\cdot A$$

The dissociation energies range from 8 to over 30 kcal mol^{-1}. The

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(1) Desmeules, P. J.; Allen, L. C. *J. Chem. Phys.* **1980**, *72*, 4731.

(2) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

ionic hydrogen bonds in such protonated dimer ions are thus much stronger than hydrogen bonds in neutral dimers. The strength of ionic hydrogen bonds results from the combination of electrostatic, polarization, exchange repulsion, charge transfer, and coupling components, of which the first two are most significant in hydrogen bonding.[3,4] The physical factors that contribute to ionic hydrogen-bonding interactions were investigated quantitatively by several theoretical methods.[3,5-7]

A useful qualitative trend relating ionic hydrogen bond strengths ΔH°_D to the proton affinity difference $\Delta PA = PA(B) - PA(A)$ was observed by Kebarle;[6,7] the dissociation energy of the ionic hydrogen bond decreases as the difference between the proton affinities of A and B, i.e., ΔPA, increases. A qualitative justification of this trend is easily provided by viewing the formation of the $BH^+{\cdot}A$ bond as partial proton transfer from BH^+ to A in the complex. Partial proton transfer is facilitated in a series of dimers as BH^+ becomes an increasingly more efficient proton donor, i.e., as the proton affinity (PA) of neutral B decreases. On the other hand, partial proton transfer to A is also facilitated as A becomes an increasingly efficient proton acceptor, i.e., as the proton affinity of A increases. The combination of the two factors leads to the inverse relation between ΔPA and ΔH°_D.[6] This trend was demonstrated by Yamdagni and Kebarle[8] in series of ammonium dimer ions such as $(CH_3)_2NH_2^+{\cdot}NH_3$, $CH_3NH_3^+{\cdot}NH_3$, and $NH_4^+{\cdot}NH_3$. The trend was further demonstrated in series of ammonium ion hydrates $CF_3CH_2NH_3^+{\cdot}H_2O$, $CH_3NH_3^+{\cdot}H_2O$, and $C_2H_5NH_3^+{\cdot}H_2O$,[9] and also in hydrates of pyridinium ions $XpyH^+{\cdot}H_2O$ and substituted anilinium ions $XC_6H_4NH_3^+$.[6] In the latter study Davidson et al.[6a] examined the dependence of ΔH°_D on ΔPA for a limited series of ion hydrates $BH^+{\cdot}H_2O$, which included hydrates of oxonium ions, i.e., $R_2OH^+...OH_2$, as well as the pyridnium hydrates. The trend in these combined, but not extensive series indicated an asymptotic decrease of ΔH°_D, with increasing ΔPA, from 31.5 kcal mol^{-1} for $H_3O^+{\cdot}H_2O$ (ΔPA = 0) to 12 kcal mol^{-1} for $4\text{-}(CH_3)_2NpyH^+{\cdot}H_2O$ (ΔPA = 69.9 kcal mol^{-1}). However, in substituent-protonated anilinium ion hydrates $H_2N\text{–}C_6H_4\text{–}XH^+{\cdot}H_2O$, a linear relation was observed between ΔH°_D and ΔPA.[6b] The relation between $\Delta H^\circ D$ and ΔPA was analyzed theoretically by Desmeules and Allen,[1] who predicted an approximately linear relation over a wide range of ΔPA.

In the present study we examine the relation between ΔH°_D and ΔPA for extensive series of dimer ions. The present data are sufficiently extensive that the relation can be examined separately for hydrogen bonds of the types $\text{–NH}^+\cdots\text{O–}$ and $\text{–OH}^+\cdots\text{O–}$, over proton affinity differences ranging from 10 to 70 and 0 to 50 kcal mol^{-1}, respectively. More limited series of dimers of the types $\text{–NH}^+\cdots\text{N–}$, $\text{–NH}^+\cdots\text{S–}$, and $\text{–SH}^+\cdots\text{O–}$ are also examined. As we shall observe, each series shows a linear correlation between ΔH°_D and ΔPA over a large range of bonding energies and proton affinity differences.

In a preceding series of studies, we examined the effects of some special structural features of B and A on the ionic hydrogen bond. These studies included entropy effects of steric hindrance,[10] effects of intramolecular hydrogen bonds on clustering,[11] and cluster stabilization by multiple hydrogen bonding.[11] In the present study we shall observe some instances where such structural features cause significant deviation from the ΔH°_D vs. ΔPA correlations.

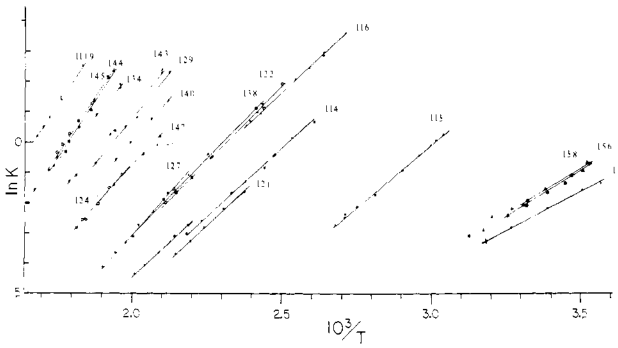

Figure 1. van't Hoff plots for $\text{–NH}^+\cdots\text{O–}$ and $\text{–NH}^+\cdots\text{N–}$ dimers. Numbers refer to reactions in Tables I and II.

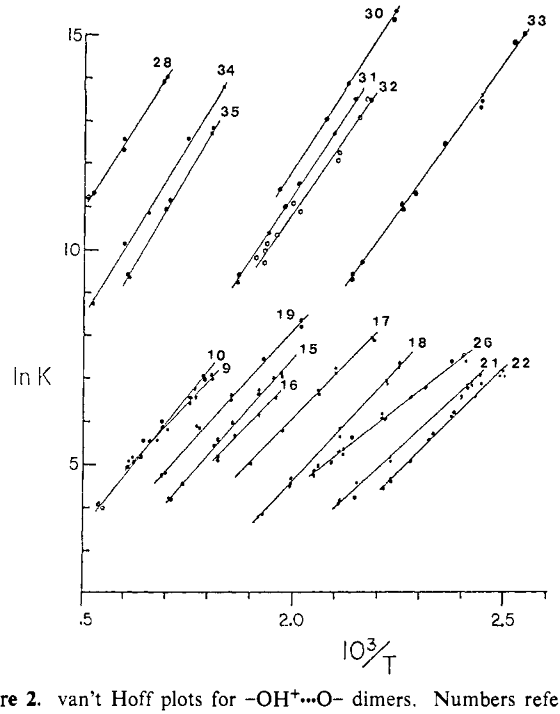

Figure 2. van't Hoff plots for $\text{–OH}^+\cdots\text{O–}$ dimers. Numbers refer to reactions in Table III.

Experimental Section

The measurements were conducted using the NBS pulsed high-pressure mass spectrometer, utilizing the usual techniques;[10] 1-ms ionizing pulses of 500–1000-eV electrons initiate ionic reactions in the reaction mixture. Ions exit the source through a 0.06-mm diameter hole to a low-pressure region ($P \leq 5 \times 10^{-5}$ torr as measured ≈30 cm from the source). The ions are accelerated through this region toward an Einsel lens and the quadrupole mass analyzer, by a field of 8 V/cm, obtained by a +10-V potential applied to the ion source.

Ionization in the source results in rapid primary reactions that generate BH^+ during the ionizing pulse. Subsequently the equilibrium $BH^+ + A \rightleftarrows BH^+\cdots A$ is observed as the normalized ion intensities of BH^+ and $BH^+\cdots A$ become time independent; the equilibrium is observed for 2–5 ms after the ionizing pulse. Equilibrium constants are calculated as K (atm^{-1}) = $(BH^+{\cdot}A)/[P(A)(BH)^+]$, where $P(A)$ is the pressure of A in atm. For hydration studies, trace amounts (0.01 to 0.1%) of B were introduced to the ion source in neat H_2O or 1–20% H_2O in CH_4 of c-C_6H_{12} as carrier gas, with total source pressures of 0.2–1.0 torr. In other systems, trace B and 0.1–20% A in a carrier gas were used. Checks were made in several systems to ensure that K was independent of pressure and composition over the above range. Thus for composition studies, the dimers $CH_3NH_3^+{\cdot}B$ were examined with the concentration of B varied by factors of 2 to 5 over the range of 1 to 10%, for B = CH_3CN, CH_3OH, C_2H_5OH, $HCOOCH_3$, CH_3COOCH_3, $CH_3COO\text{-}i\text{-}C_3H_7$, $(n\text{-}C_6H_{10})_2O$, and CH_3NO_2. Further, in several hydration systems the partial pressure of H_2O was varied between 20 and 100% of the total source pressure (see following paper). In all cases, K remained constant within the usual experimental scatter of ±20%. For pressure studies, P

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[3] Morokuma, K. M. *Acc. Chem. Res.* **1977**, *10*, 299.

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[7] Merlet, P.; Peyerimhoff, S. D.; Buenker, R. J. *J. Am. Chem. Soc.* **1972**, *99*, 8301. For further references to theoretical work, see ref 1.

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[10] Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1983**, *105*, 2956.

[11] Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1983**, *105*, 4906, 4912.

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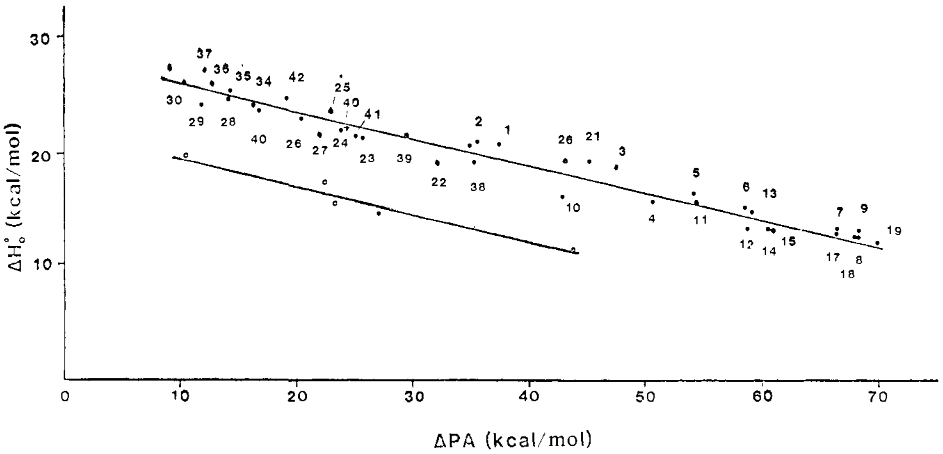

Figure 3. Correlation between $\Delta H°_D$ and ΔPA for $-NH^+\cdots O-$ and $-NH^+\cdots S-$ bonds. Numbers refer to reactions to Table I. The lower line is for $-NH^+\cdots S-$ dimers (M. Mautner, unpublished results).

was varied by a factor of 2 or more between 0.3 and 1.0 torr in most reaction systems, with similar results. Further details of pressure studies and checks of the effects of accelerating voltage are described in the following paper. Materials were obtained from commercial sources and used as purchased.

Results and Discussion

1. Linear Correlations between $\Delta H°_D$ and ΔPA. van't Hoff plots for the clustering reactions are presented in Figures 1 and 2. The results, along with related literature data, are summarized in Tables I–III. The tables contain all the available data, to our knowledge, on organic $-NH^+\cdots O-$, $-NH^+\cdots N-$, and $-OH^+\cdots O-$ dimers that are free of special structural effects (see below). However, the tables do include a few examples of such structurally complex dimers. Also omitted from the tables are some $X_{py}H^+\cdots OH_2$ dimers from ref 6 which constitute data essentially similar to data which are already included.

Altogether, the present correlations are based on 76 data points, of which 64 are results from this and the following paper.

Table I and Figure 3 show the data on $-NH^+\cdots O-$ type dimers. The data comprise three series of dimers. The first series (reactants 1–19) are hydrates of ammonium and pyridinium ions, i.e., $R_3NH^+\cdots OH_2$ and $XpyH^+\cdots OH_2$. In this series the neutral ligand is constant and the ionic species varies. In contrast, in the second series the ionic species is constant, $CH_3NH_3^+$, and the ligands comprise several sets of various types of oxygen compounds (reactants 20–47). The third series comprises dimers with various ionic and neutral components.

Figure 3 shows the $\Delta H°_D$ vs. ΔPA correlation for $-NH^+\cdots O-$ type dimers. A linear correlation is observed that includes all the known dimers of this type, with ΔPA values from 9 to 70 and corresponding hydrogen-bonding energies of 27 to 12 kcal mol^{-1}. (Dimers where identifiable structural effects cause significant deviations, indicated by δ_{cor} in the tables, will be discussed below.) The general form of the correlation is

$$\Delta H°_D = \Delta H°_D(0) - b\Delta PA \qquad (1)$$

For $-NH^+\cdots O-$ bonds, the 48 structurally simple dimers in Table I yield

$$\Delta H°_D \text{ (kcal mol}^{-1}) = 30.0 \pm 1.5 - (0.26 \pm 0.03)\Delta PA \qquad (2)$$

The standard deviation of $\Delta H°_D$ experimental values from correlation 2 is 1.1 kcal mol^{-1}. The largest deviation is 2.6 kcal mol^{-1}, and of the 48 dimers only 4 deviate by more than 2 kcal mol^{-1}. The statistics of the correlation are shown in Table IV.

A linear correlation (eq 1) is also observed for $-NH^+\cdots N-$ bonds including amines and pyridines, as shown in Table II and Figure 4. The correlation includes a set of ammoniated ions $-NH^+\cdots NH_3$ and other dimers. The range of ΔPA is limited in these dimers since all nitrogen bases have high proton affinities. Table II also shows several symmetric dimers where ΔPA = 0. For the correlation and in Figure 4, the average $\Delta H°_D$ for the symmetric dimers is used, i.e., ($\Delta H°_d = 23.6$) kcal mol^{-1} for ΔPA = 0. The parameters of the correlation are shown in Table IV. In dimers 15–19 in Table II the neutral ligands are nitriles. These dimers do not fit the correlations for other types of $-NH^+\cdots N-$ bonds.

Table III shows the available data for $-OH^+\cdots O-$ dimers. Figure 5 shows the $\Delta H°_D$ vs. ΔPA correlation for $-OH^+\cdots OH_2$ hydrates. This fairly extensive series covers the monohydration of 20 oxonium ions and covers a ΔPA range from 0 to 55 kcal mol^{-1}. The correlation parameters are shown in Table IV.

In addition to the nitrogen and oxygen dimers covered by Tables I–III, linear correlations (eq 1) are also observed for sulfur compounds, i.e., sulfur ligands in $-NH^+\cdots S-$ dimers and sulfonium ions with oxygen ligands $-SH^+\cdots O-$. For completeness, the correlation lines for these dimers are shown in Figures 1 and 3, and the correlation parameters are given in Table IV. The data will be presented elsewhere.

The correlation parameters in Table IV show high correlation coefficients for all the lines. The standard deviation of $\Delta H°_D$ values from the values calculated from the least-squares equations are not larger than 1.2 kcal mol^{-1}. This turns out to be the same magnitude as the error limits usually associated with the temperature studies that yield the $\Delta H°_D$ values. It should also be noted that the data for the 76 reactions included in the correlations were obtained in two different laboratories, using somewhat different experimental conditions such as pressure, mixture composition, ionization and detection methods, and temperature ranges. All considered, the scatter about the correlation lines is comparable to the precision of $\Delta H°_D$ measurements and to the general magnitude of difference between data obtained by the different laboratories.

2. Generality and Limitations of the Correlations. Empirical relation 1, with the appropriate parameters as given in Table IV, can serve for the prediction of $\Delta H°_D$ in new dimers and possibly for ion–neutral interactions in more complex systems, including biological reactions which involve protonated intermediates. To check the generality of the correlations, the applicability of (1) to available data should be examined. In this section we shall check simple dimers, i.e., dimers with monofunctional, unhindered components. Deviations due to special structural features will be discussed later.

The correlation for $-NH^+\cdots O-$ bonds includes all the structurally simple dimers in Table I. As noted above, the data include sets with a constant ligand H_2O, a constant ion $CH_3NH_3^+$, and various mixed dimers. No type of dimer shows significant deviations. However, taken alone, the subset of $-NH^+\cdots O-$ hydrates (reactions 1–19, Table I) yields correlation parameters somewhat different from the complete set of 48 dimers taken together (Table IV). The difference may be due to experimental scatter and the more limited proton affinity range (from 35 to 68 kcal mol^{-1}) of the hydrates than the complete set. In any event, as part of the complete set, the hydrates fit the correlation within the usual scatter. Thus, correlation 1 in Table IV is generally applicable

Table I. Thermochemistry[a] of -NH⁺···O- and -NH⁺···Halide Bonds. Dissociation of Ammonium and Pyridium Ion Hydrates ($BH^+ H_2O$) and Clusters of $CH_3NH_3^+$ with Oxygen, Sulfur, and Halogen Ligands

		$\Delta H°_D$	$\Delta S°_D$	$\Delta G°(T)$	ΔPA[b]	δ_{cor}[c]
		$BH^+ \cdot H_2O$				
	ammonium ions					
1	NH_4^+	20.6,[e] 17.2[d]	23.1,[e] 20		37.5	
2	$CF_3CH_2NH_3^+$	21.1[f]	30.0[f]		35.5	
3	$CH_3NH_3^+$	18.4,[e] 18.8[f]	21.8,[e] 26.3[f]		47.6	
4	$C_2H_5NH_3^+$	17.5[f]	25.9[f]		50.5	
5	$(CH_3)_2NH_2$	16.2[e]	22.9[e]		54.1	
6	$(CH_3)_3NH^+$	15.2,[e] 14.5[g]	24.7,[e] 24[g]		58.6	
7	$(C_2H_5)_3NH^+$	13.2[f]	27.0[f]		66.4	
8	$(n\text{-}C_3H_7)_3NH^+$	12.5[f]	30.2[f]		68.1	
9	$(n\text{-}C_4H_9)_3NH^+$	13.0[f]	32.0[f]		68.3	
	pyridinium ions					
10	4-CNpyH⁺	16.0[h]	25.7[h]		42.9	
11	pyH⁺	16.1,[i] 15.0[h]	27.0,[i] 25.5[h]		54.3	
12	2,6-$(CH_3)_2$pyH⁺	13.2[i]	25.9[i]		58.6	
13	4-CH_3pyH⁺	14.7[h]	26.6[h]		19.2	
14	2-*i*-C_3H_7pyH⁺	14.2	28.8[i]		60.7	
15	2-*tert*-C_4H_9pyH⁺	14.2[i]	30.8[i]		60.9	
16	2,6-$(C_2H_5)_2$pyH⁺	13.0[i]	28.6[i]		61.9	
17	2,6-(*i*-$C_3H_7)_2$pyH⁺	12.8[i]	32.1[i]		66.4	
18	2,6-(*tert*-$C_4H_9)_2$pyH⁺	12.5[i]	41[i]		68.0	
19	4-$N(CH_3)_2$pyH⁺	12.0[h]	24.8[h]		69.9	
		$CH_3NH_3^+ \cdot A$				
	alcohols					
20	H_2O	18.4,[e]	21.8[e]		47.6	
21	CF_3CH_2OH	19.1	28.5		45.1	
22	CH_3OH	19.0	24.2		32.2	
23	C_2H_5OH	21.3	(25)[j]	8.9 (496)	25.8	
24	$n\text{-}C_3H_7OH$	22.0	25.6		23.5	
25	$n\text{-}C_4H_9OH$	23.5	(26)[j]	10.6 (495)	23.0	
26	$tert\text{-}C_4H_9OH$	22.9	(26)[j]	10.0 (495)	20.4	
	ethers					
27	$(CH_3)_2O$	21.5	29.3		22.0	
28	$(C_2H_5)_2O$	22.0	25.0		14.0	
29	$(n\text{-}C_3H_7)_2O$	24.0	26.7		11.8	
30	$(n\text{-}C_4H_9)_2O$	25.0	28.0		10.4	
31	$(n\text{-}C_6H_{11})_2O$	27.2	31.4		9.1	
32	$CH_3OCH_2CH_2OCH_3$	30.1	30.1		9.2	5.2
33	$CH_3OCH_2CH_2CH_2OCH_3$	31.2	32.0		0.3	3.2
	ketones					
34	CH_3COCH_3	24.0	23.2		17.4	
35	$C_2H_5COCH_3$	25.2	(25)[j]	11.4 (553)	14.3	
36	$C_2H_5COC_2H_5$	25.9	(26)[j]	11.8 (549)	12.7	
37	$n\text{-}C_3H_7COC_2H_5$	27.0	27.0		12.1	
	acids, esters, amide, nitromethane					
38	$HCOOH$	19.0	24.2		35.3	
39	$CF_3COOC_2H_5$	21.4	(26)[j]	9.4 (450)	29.5	
40	CH_3COOH	22.0	24.3		23.9	
41	$HCOOCH_3$	21.4	(24)[j]	10.3 (459)	25.2	
42	$HCOO\text{-}n\text{-}C_4H_9$	24.5	(26)[j]	12.5 (461)	19.3	
43	CH_3COOCH_3	23.5	24.8		16.8	
44	$CH_3COO\text{-}i\text{-}C_3H_7$	30.0	35.2		12.1	4.9
45	$n\text{-}C_4H_9COO\text{-}n\text{-}C_3H_7$	30.0	34.8		10.1	4.5
46	$HCONH_2$	30.0	30.0		15.7[l]	5.7
47	CH_3NO_2	20.5	23.0		34.9	
		Other -NH⁺···O- Dimers				
48	$c\text{-}C_6H_{11}NH_3^+ \cdot (C_2H_5)_2O$	22.0[k]	31.8[k]		21.0	
49	$c\text{-}C_6H_{11}NH_3^+ \cdot (n\text{-}C_3H_7)_2O$	25.4[k]	31.2[k]		18.9	
50	$(CH_3)_3NH^+ \cdot CH_3CON(CH_3)_2$	27.2[k]	24.1[k]		8.3	
51	pyH⁺·$(n\text{-}C_3H_7)_2O$	23.5	(31)	8.0 (500)	18.5	
52	$c\text{-}C_6H_{11}NH_3^+ \cdot$ $CH_3OCH_2CH_2CH_2OCH_3$	28.4[k]	35.0[k]		16.2	4.2
53	$c\text{-}C_6H_{11}NH_3^+ \cdot c\text{-}C_8H_{15}O_4$ (12-crown-4)	37.2[k]	34.8[k]		1.7	12.1
54	$HCNH^+ \cdot H_2O$	29.8[g]			4.9	
55	$CH_3CNH^+ \cdot H_2O$	24.8	28.4		22.7	
		-NH⁺···Halogen Dimers				
56	$CH_3NH_3^+ \cdot CH_3F$	11.8	23.3		64.1	
57	$CH_3NH_3^+ \cdot CH_3Cl$	10.7	20.6		46.1	
58	$CH_3NH_3^+ \cdot CH_3Br$	11.2	21.0		48.4	

(*Footnotes for Table I*)

[a] ΔH°_D, ΔG°, ΔPA, and δ_{cor} in kcal mol^{-1} (4.18 kJ mol^{-1}), ΔS° in cal mol^{-1} K^{-1} (=4.18 J mol^{-1} K^{-1}). Data from present work unless indicated otherwise. $\Delta G^\circ(T)$ values given for reactions measured at one temperature. T in Kelvin. [b] Proton affinities from evaluated tabulation by S. G. Lias, *J. Phys. Chem. Ref. Data*, to be submitted for publication. [c] δ_{cor} shows deviation from value predicted by correlation 1, Table IV; $\delta_{cor} = \Delta H^\circ_D - (30.0 - 0.26\Delta PA)$ kcal mol^{-1}. δ_{cor} values are given only for dimers which are not included in the least-squares correlation analysis because of structural effects. [d] Payzant, J. D.; Cunningham, A. J., Kebarle, P. *Can. J. Chem.* 1973, *51*, 3242. [e] Following paper. For ΔH°_D adjusted values (assuming constant ΔS°_D values) are quoted. [f] Lau, Y. K.; Kebarle, P. *Can. J. Chem.* 1981, *59*, 151. [g] Quoted in Taft, R. W. *Prog. Phys. Org. Chem.*, in press. [h] Davidson, W. R.; Sunner, J.; Kebarle, P. *J. Am. Chem. Soc.* 1979, *101*, 1675. [i] Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* 1983, *105*, 2956. [j] Estimated on the basis of homologous compounds. [k] Meot-Ner (Mautner), M., submitted for publication. [l] PA($HCONH_2$) = 198.8 kcal mol^{-1} (M. Meot-Ner, unpublished results).

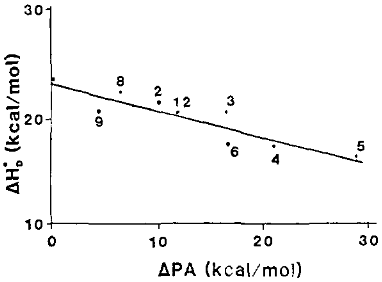

Figure 4. Correlation between ΔH°_D and ΔPA for $-NH^+\cdots N-$ bonds. Numbers refer to reactions in Table II. For ΔPA = 0, average ΔH°_D of symmetric dimers is used.

to all $-NH^+\cdots O-$ bonds measured so far. Interestingly, the hybridization of neither the proton donor N nor the proton acceptor O seems to matter, since the series includes ions where the proton is bonded to N lone pairs with hybridization sp^3, sp^2, and sp nitrogen, i.e., R_3NH^+, NH^+ (i.e., pyridines), and $RCNH^+$, and ligands with sp^3 and sp^2 oxygen lone pairs, i.e., in R_2O and $RC{=}O$.

Table I shows ΔH°_D values for the complexes of $CH_3NH_3^+$ with three methyl halides. The ΔH°_D values are similar, although ΔPA for the CH_3F complex is significantly different from those for the CH_3Cl and CH_3Br complexes. The polarizabilities and dipole moments of the three ligands are similar, and the weak bonds here may be purely electrostatic.

The $-NH^+\cdots N-$ bonds in Table II include a series of ammoniated ammonium ions and a set of mixed dimers. Only one dimer, $(C_2H_5)_3NH^+\cdot 2Fpy$, shows stronger bonding than predicted by the correlation, possibly owing to a bonding interaction involving the fluorine atom. Thus the correlation is applicable to all the dimers involving amines and pyridines. However, cyanide ligands (Table II, 17–31) show substantially stronger bonding than predicted by the $-NH^+\cdots N-$ correlation, possibly owing to the high dipole moment of these ligands (3.9–4.4 × 10^{-18} esu cm; 1–2 × 10^{-18} esu cm for the other nitrogen ligands in Table II).

The $-OH^+\cdots O-$ correlation involves all oxonium ion hydrates $-OH^+\cdots OH_2$ for which data are available. Significant deviations are shown only by the hydrates of protonated acids and of difunctional ions, for structural reasons that will be described below. Table III also includes a set of organic $-OH^+\cdots O-$ type dimers where the neutral ligand is other than H_2O (28–42). Of these, only two dimers, both with CH_3COOH as the ligand, show significantly weaker bonding than predicted. While the hydration of protonated acids may be weakened because of resonance affects (see below), the reasons for weak attachment by the acid as a neutral ligand is not evident.

Table III also shows data on three dimers $O_2H^+\cdots O_2$, $CO_2H^+\cdots CO_2$, and $H_2OH^+\cdot CO_2$, which involve small inorganic ions and molecules. The bonding energies are smaller by 5–10 kcal mol than the predicted values. The weak attachment may be related to the low polarizability (1.9 and 2.7 × 10^{-24} cm^3) and zero dipole moment of these ligands vs. the larger polarizability (4–15 × 10^{-24}cm^3) and significant dipole moments (1–2 × 10^{-18}esu cm) of the other ligands in Table III. The applicability of the correlation to such small inorganic ligands remains to be investigated.

A special class of ΔH°_D vs. ΔPA correlations is the symmetric dimer BH^+B. Since in symmetric dimers ΔPA = 0, the correlations predict that ΔH°_D should remain constant within each class $-XH^+\cdots X-$, regardless of the identify of B. For $-NH^+\cdots N-$ symmetric dimers, observations by Yamdagni and Kebarle,[8] extended by Meot-Ner and Sieck,[10] show ΔH°_D to be indeed constant at 23 ± 1.4 kcal mol^{-1} for dimers that range from $(NH_3)_2H^+$ to dimers of such large (and hindered) species as $((n\text{-}C_4H_9)_3N)_2H^+$ and $(2,6\text{-di-}i\text{-}C_3H_7)py_2H^+$. Similarly, ΔH°_D of $-OH^+\cdots O-$ dimers is constant at 32 ± 1.5 kcal mol^{-1} for dimers ranging from $(H_2O)_2H^+$ to dimers of a large variety of alcohols, ethers, and ketones.[13] Therefore, in general the special class of symmetric dimers fits the ΔH°_D vs. ΔPA correlation.

The data discussed so far show that ΔH°_D vs. ΔPA correlations are widely applicable in organic dimers and hydrates of protonated N, O, and S bases. In section 4 we shall observe cases where significant deviations from these correlations occur owing to identifiable structural features that affect the ionic hydrogen bond.

3. Physical Interpretation of the Correlations. The energies, geometries, and charge density changes associated with the ionic hydrogen bond were investigated in a theoretical ab initio 4-31G level study of Desmeules and Allen.[1] Figure 18 of that paper represents the theoretical correlation between ΔPA and bond energy (E_0) for dimers of simple second-row (2···) and third-row (3···) hydrides including combinations ($2H^+\cdots 2$), ($3H^+\cdots 2$), and ($2H^+\cdots 3$), i.e., protonated dimers formed from NH_3, H_2O, H_2S, HCl, FH, and PH_3. The ($2H^+\cdots 2$) combinations calculated by the authors are the symmetric dimers $H_3O^+\cdot H_2O$, $H_2F^+\cdot HF$, and $NH_4^+\cdot NH_3$ and the mixed dimers $H_3O^+\cdot HF$, $NH_4^+\cdot HF$, and $NH_4^+\cdot H_2O$. The present correlations also concern ionic hydrogen bonds involving the second- and third-row electron donors N, O, and S, and we shall compare the theoretical relations between E_0 and ΔPA with the empirical correlations of ΔH°_D vs. ΔPA.

The theoretical results on the symmetric dimers such as $H_3O^+\cdot H_2O$ indicate special effects due to significant covalent bonding, but the three mixed dimers, with a range of ΔPA from 40 to 100 kcal mol^{-1}, yield a linear correlation with $\Delta H^\circ_D(0)$ = 35 kcal mol^{-1} and b = 0.18. The treatment by the authors assumes implicitly that a single correlation line should apply to all ($2H^+\cdots 2$) combinations, regardless of the nature of proton donor and acceptor atoms, and the theoretical results indicate that an approximately linear correlation would apply over a wide range of ΔPA. The experimental observations confirm the first assumption in part, since the correlation lines for the $-NH^+\cdots O-$ and $-OH^+\cdots O-$ bonds are roughly overlapping, and the data for the two types of dimers could be combined into a single correlation line with a scatter not much larger then in the individual lines. The conclusion from both experiment and theory is that $-NH^+\cdots O-$ bonds are not significantly weaker inherently than $-OH^+\cdots O-$ bonds; i.e., for a given ΔPA, ΔH°_D, or E_0 values for the two types of bonds are comparable. On the other hand, in contrast with the theoretical prediction, experimental $-NH^+\cdots N-$ bonds, although also of the type ($2H^+\cdots 2$) yield a correlation with $\Delta H^\circ_D(0)$ which is lower by 6 kcal mol^{-1} than for the other ($2H^+\cdots 2$) dimers. The only experimental ($2H^+\cdots 2$)-type dimer with F as electron donor, i.e., $CH_3NH_4^+\cdot CH_3F$, does not fit well either the $-NH^+\cdots O-$ or the $-NH^+\cdots N-$ ($2H^+\cdots 2$) correlations.

The theoretical ($3H^+\cdots 2$) and ($2H^+\cdots 3$) correlation lines overlap with each other, are roughly parallel to the ($2H^+\cdots 2$) line, and give intercepts lower by ≈12 kcal mol^{-1} than the ($2H^+\cdots 2$) line. These theoretical trends are in qualitative agreement with experiment in that the $-SH^+\cdots O-$ and $-NH^+\cdots S-$ correlations overlap, are parallel with the other lines, and give intercept lower

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[13] Larsen, J. W.; McMahon, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 6255.

Table II. Thermochemistry[a] of -NH$^+$···N- Bonds. Dissociation Enthalpies and Entropies of Dimers BH$^+$···A

	BH$^+$	A	$\Delta H°_D$	$\Delta S°_D$	$\Delta H°(T)$	ΔPA[a]	δ_{cor}[b]
1	NH_4^+	NH_3	24.8	25.8		0	
2	$CH_3NH_3^+$	NH_3	21.4[d]	26.0[d]		10.1	
3	$(CH_3)_2NH_2^+$	NH_3	20.6[d]	28.4[d]		16.6	
4	$(CH_3)_3NH^+$	NH_3	17.3	23.9		21.1	
5	$(C_2H_5)_3NH^+$	NH_3	16.3	29.6		28.9	
6	pyH$^+$	NH_3	17.3	22.5		16.8	
7	$CH_3NH_3^+$	CH_3NH_3	21.7[d]	23.6[d]		0	
8	$(CH_3)_2NH_2^+$	CH_3NH_3	22.4[d]	29.2[d]		6.5	
9	$(CH_3)_3NH^+$	$(CH_3)_2NH$	20.5[d]	28.5[d]		4.5	
10	$(CH_3)_3NH^+$	$(CH_3)_3N$	22.6, 22.5[d]	32.0[d]		0	
11	$(C_2H_5)_3NH^+$	$(C_2H_5)_3N$	23.8[e]	41.0[e]		0	
12	$(C_2H_5)_3NH^+$	py	20.4	(28)	9.0 (408)	11.9	
13	$(C_2H_5)_3NH^+$	2-Fpy	20.8	31.0		22.2	3.2
14	$(n\text{-}C_4H_9)_3NH^+$	$(n\text{-}C_4H_9)_3N$	24.4[e]	56.5[e]		0	
15	pyH$^+$	py	24.6[e]	28.2[e]		0	
16	2,6-$(i\text{-}C_3H_7)_2$pyH$^+$	2,6-$(i\text{-}C_3H_7)_2$py	23.6[e]	48.4[e]		0	
17	$CH_3NH_3^+$	CH_3CN	24.5	25.8		24.9	7.5
18	$CH_3NH_3^+$	$n\text{-}C_3H_7CN$	28.1	(28)[f]	10.0 (581)	20.4	10.0
19	$CH_3NH_3^+$	C_6H_5CN	29.4	31.2		18.2	10.8
20	HCNH$^+$	HCN	30.0[g]	32[g]		0	6.8
21	CH_3CNH^+	CH_3CN	30.2[g]	29[g]		0	7.0

[a] ΔH in kcal mol^{-1}, ΔS in cal mol^{-1} K^{-1}, T in Kelvin. Data from present work unless indicated otherwise. ΔG values given for reactions measured at room temperature. [b] δ_{cor} shows deviation from value predicted by correlation 3, Table IV; i.e., $\delta_{cor} = \Delta H°_D - (23.2 - 0.25\Delta PA)$ kcal mol^{-1}. δ_{cor} values are given only for dimers which are not included in the least-squares analysis because of structural effects. [c] Payzant, J. D.; Cunningham, A. J.; Kebarle, P. *Can. J. Chem.* 1973, *51*, 3292. [d] Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* 1973, *95*, 3509. [e] Mautner (Meot-Ner), M.; Sieck, L. W. *J. Am. Chem. Soc.* 1983, *105*, 2956. [f] Estimated on the basis of homologous compounds. [g] Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* 1978, *100*, 4694.

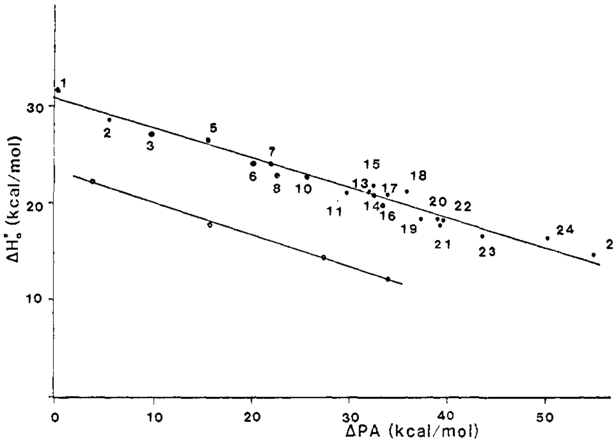


Figure 5. Correlation between $\Delta H°_D$ and ΔPA for $-OH^+\cdots OH_2$ dimers (●, upper line) and $-SH^+\cdots O-$ dimers (○, lower line). Numbers refer to reactions in Table III.

than the $-NH^+\cdots O-$ and $-OH^+\cdots O-$ (although not $-NH^+\cdots N-$) lines. Indeed, an interesting feature of the experimental correlation lines is that the slopes are all comparable, and thus the dependence of $\Delta H°_D$ on ΔPA does not seem to be significantly affected by the nature of BH$^+$ and A or by the absolute magnitude of $\Delta H°_D$. This trend is also a feature of the theoretical lines, and, indeed, the slopes of the theoretical lines, ≈0.20, are close to the experimental slopes, ≈0.25.

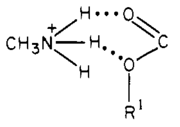
In summary, the major features of the theoretical correlation lines are that they are roughly linear over a wide range of ΔPA and that the slopes of the different correlation lines are comparable. The experimental results are in qualitative agreement with both predictions.

Desmeules and Allen[1] show correlations between ΔPA, $\Delta H°_D$, and partial proton transfer in the hydride dimers as measured by the elongation of the A–H$^+$ bond. The qualitative agreement between theory and the present data suggests that, in the present organic dimers too, increasing bond strength and decreasing ΔPA should correlate with increasingly efficient partial proton transfer as measured by A–H$^+$ bond elongation.

4. Deviations due to Special Structural Features. One use of the present correlations is to identify and quantify special structural effects that lead to significant deviations from these correlations. This section will examine several such structural effects.

The magnitude of the deviations is listed under δ_{cor} (Tables I–III). Significant enhancement of stabilities is observed in dimers where the ligand is a polyfunctional ether (Table I: 32, 33, 52, 53). The data are from a more extensive study which showed that polyethers and crown ethers engage in polydentate bonding with ammonium ions; i.e., three oxygens of a polyether can each bond to the three protons in the complex RNH_3^+ polyether. The multiple interaction can lead to unusually stable complexes, with $\Delta H°_D$ up to 45 kcal mol^{-1}. Similar effects of multiple bonding are observed in dimer ions of nucleic bases.

Other cases of multiple bonding apparently occur in dimers of $CH_3NH_3^+$ with some esters. The present data show an abrupt change from dimers including small esters (Table I: 41–43) to larger, more highly polarizable esters (Table I: 44, 45). In analogy with the polyether complexes, the thermochemistry suggests polydentate bonding with these ligands, where the larger polarizabilities may increase the proton affinities of both oxygen functions to stabilize sufficiently two hydrogen bonds (ion **1**). Double hydrogen bonding is suggested also with $HCONH_2$ (Table I: 46) (ion **2**). However, in **2** the strong bond may also result from the high dipole moment (3.25 × 10^{18} esu cm) of $HCONH_2$.



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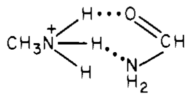


2

The large entropy changes with these ligands also support the constrained structures **1** and **2**. Comparison with the smaller ethers indicates that the second bond contributes about 6 kcal mol^{-1} to the stability of the complex, and the elimination of internal rotation by this second bond causes an entropy change of 10 cal mol^{-1} K^{-1}. With these values, the second bond should be stable below about 600 K, but open at higher temperatures. This is near the temperature range of the present measurements. Thus, the stability of the second hydrogen bond is marginal under the present conditions, which may explain the abrupt onset of the phenomenon with a small structural change in the ligands. Similarly, it is possible that the other esters will also form doubly bonded dimers, and thus exhibit $\Delta H°_D$ values that deviate from the correlation

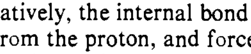
Table III. Thermochemistry[a] of $-OH^+\cdots O-$Bonds. Dissociation Enthalpies and Entropies of Hydrates $BH^+\cdot H_2O$ and Other Clusters $BH^+\cdot A$

	$BH^+\cdot H_2O$	A	ΔH°_D	ΔS°_D	ΔPA^b	$\delta_{cor}{}^c$
1	H_3O^+		31.6^d	24.4^d	0	
2	H_2COH^+		$28.5,^e\ 28.9^f$		5.2	
3	$HCF_2CH_2OH_2{}^+$		$\sim 27^f$		9.6	
4	$HCOOH_2{}^{+\,m}$		24.1^g	$(26)^g$	12.2	−2.6
5	$CH_3OH_2{}^+$		$27.3,^e\ \sim 25^f$	25.2^e	15.4	
6	CH_3CHOH^+		$25.2,^e\ \sim 23^f$	25.0^e	20.1	
7	$C_2H_5OH_2{}^+$		24^h	26^h	21.8	
8	$H(OCH_3)COH^+$		$22.0,^e\ 22.3^f$	25.0^e	22.4	
9	$CH_3COOH_2{}^{+\,m}$		$20.1,^e\ 21.9^f$	21.0^e	23.7	−2.2
10	$(CH_3)_2OH^+$		$22.6,^j\ 24.0$	$26.5,^j\ 28.9$	25.6	
11	$(CH_3)_2COH^+$		21.0^e	20.5^e	29.6	
12	$C_6H_5COOH_2{}^{+\,m}$		19^i		31.7	−1.8
13	$HCOH^+NH_2$		21.2^l	27.2^l	31.9^o	
14	$c\text{-}C_4H_8O_2H^+$(1,4-dioxane)		20.9	25.8	32.3	
15	$c\text{-}C_4H_8OH^+$(THF)		21.8	28.8	32.3	
16	$c\text{-}C_5H_{10}OH^+$(THP)		19.5	25.2	33.2	
17	$(C_2H_5)_2OH$		20.9	30.0	33.7	
18	$(n\text{-}C_3H_7)_2OH^+$		21.3	33.8	35.8	
19	$CH_3(c\text{-}C_3H_5)COH^+$		18.2^e	26.8^e	37.4	
29	$CH_3(C_6H_5)COH^+$		18.3^e	29.1^e	38.9	
21	$(i\text{-}C_3H_7)_2OH^+$		17.8	29.4	39.1	
22	$(n\text{-}C_6H_{11})_2OH^+$		18.2	31.8	39.4^o	
23	$(c\text{-}C_3H_5)_2COH^+$		16.6^e	26.0^l	43.5^k	
24	$CH_3COH^+N(CH_3)_2$		16.5^l	26.3^l	50.3	
25	$C_6H_5COH^+N(CH_3)_2$		15.1^l	26.4^l	56	
26	$CH_3OH^+CH_2CH_2OCH_3$		15.1^l	21.3^l	38.4	−3.1
27	$CH_3OH^+CH_2CH_2CH_2OCH_3$		9	(22)	47.3	−7.0
28	$(CH_3)_2OH^+$	$(CH_3)_2O$	$29.5,\ 30.7^d$	$27.0,\ 29.6^d$	0	0.2
29	$(C_2H_5)_2OH^+$	$(C_2H_5)_2O$	29.8	33.2	0	−0.6
30	$(n\text{-}C_3H_7)_2OH^+$	$(n\text{-}C_3H_7)_2O$	30.2	37.4	0	−0.2
31	$(n\text{-}C_4H_9)_2OH^+$	$(n\text{-}C_4H_9)_2O$	30.5	38.7	0	0.1
32	$(n\text{-}C_6H_{11})_2OH^+$	$(n\text{-}C_6H_{11})_2O$	29	36	0	−1.4
33	$(i\text{-}C_3H_7)_2OH^+$	$(i\text{-}C_3H_7)_2O$	27.0	39.1	0	−3.4
34	$c\text{-}C_4H_8OH^+$	$c\text{-}C_4H_8O$	32.6	32.2	0	1.2
35	$c\text{-}C_5H_{10}OH^+$	$c\text{-}C_5H_{10}O$	32.6	32.2	0	1.2
36	$c\text{-}C_6H_{12}OH^+$	$c\text{-}C_6H_{12}O$	33.2	34.7	0	2.6
37	$(CH_3)_2COH^+$	$(CH_3)_2CO$	30.1^n	30.4^n	0	−0.3
38	$(CH_3)_2SOH^+$	$(CH_3)_2SO$	30.8^n	22.9^n	0	0.4
39	$(CH_3)_2SOH^+$	$(CH_3)_2CO$	24.1^n	24.5^n	15.2	−1.7
40	$(CH_3)_2OH^+$	CH_3OH	26.3^j	27.1^j	10.2	−1.0
41	$CH_3COH^+N(CH_3)_2$	CH_3COOH	18.4^l	24.7^l	26.6	−3.9
42	$(c\text{-}C_3H_5)_2COH^+$	CH_3COOH	22.4	34.9	19.8	−2.5
43	O_2H^+	O_2	20^h	27^h	0	−10.4
44	CO_2H^+	CO_2	20.1^p	24.2^p	0	−10.3
45	H_3O^+	CO_2	14.4^p	20.7^p	35.0	−5.4

[a] ΔH°, ΔPA, and δ_{cor} in kcal mol^{-1}, ΔS° in cal $mol^{-1}\ K^{-1}$. Data from present work unless indicated otherwise. [b] Proton affinities from evaluated tabulation by S. G. Lias, NBS Circular, to be published. [c] δ_{cor} shows deviation from value predicted by correlation 4, Table IV; i.e., $\delta_{cor} = \Delta H^\circ_D - (30.4 - 0.30\Delta PA)$ kcal mol^{-1}. δ_{cor} values are given only for dimers that are not included in least-squares correlation analysis because of structural effects. [d] Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 7939. [e] Following paper in this issue. [f] Berman, D. W. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1981. Quoted in Taft, R. W. *Prog. Phys. Org. Chem.* 1983, 14. [g] From $\Delta G^\circ_{582} = -9.2$, assuming $\Delta S = 26$ (cal $mol^{-1}\ K^{-1}$). [h] Kebarle, P. *Am. Rev. Phys. Chem.* **1977**, *28*, 445. [i] Davidson, W. L.; Sunner, J.; Kebarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1675. [j] Hiraoka, K.; Grimsud, E. P., Kebarle, P. *Ibid.* **1979**, *96*, 3359. [k] PA from value quoted in Taft (see footnote *f*). [l] Meot-Ner (Mautner), M. *J. Am. Chem. Soc.*, submitted for publication. [m] Not included in correlation (see text) because of structural effects. [n] Lau, Y. K.; Saluja, P. P. S.; Kebarle, P. *J. Am. Chem. Soc.* **1980**, *102*, 7429. [o] PA from M. Mautner, unpublished results ($PA(HCONH_2) = 198.8$ kcal mol^{-1}). [p] Meot-Ner (Mautner), M.; Field, F. H. *J. Chem. Phys.* **1977**, *66*, 4527.

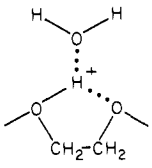
at sufficiently low temperatures.

An opposite, dimer weakening effect is observed in the hydration of a polyfunctional oxonium ion (Table III: 25). In



$$CH_3\dot{O}H^+CH_2CH_2\dot{O}CH_3$$

a weak internal hydrogen bond must be displaced by H_2O to form the hydrate. Alternatively, the internal bond remains intact but delocalizes charge from the proton, and forces the formation of an unfavored T-shaped complex **3**. A more efficient internal



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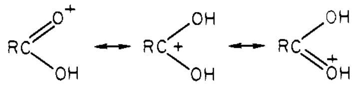
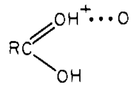
hydrogen bond causes further weakening of the hydrate (Table III: 27).

More minor hydrogen-bond weakening effects are observed in the hydrates $RCOOH^+\cdot H_2O$, which show systematic deviations of ≈2 kcal mol^{-1} from the correlation line (Figure 5). Larsen and McMahon[13] observed similar bond weakening effects in symmetric dimers $(RCOOH)_2H^+$, and attributed the effect to the weakening resonance **4a** ↔ **4b** ↔ **4c** when the dimer is formed (**5**). The



4a 4b 4c



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present systematic deviations suggest such effects for the hydrates; however, the magnitude of the effect is within the error limits.

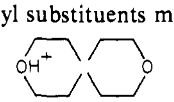
Another structural effect that was investigated recently is that of steric crowding in hydrates and dimers of protonated alkylamines and alkylpyridines.[10] Table III presents some new data

Table IV. Correlation between $\Delta H°_D$ and ΔPA for $-XH^+\cdots Y-$ Bonds. Parameters for the Least-Squares Lines $\Delta H°_D = a - b \times \Delta PA$[a]

	bond	a	σ_a[b]	b	σ_b[b]	$\sigma_{\Delta H°_D}$[b]	N[c]	coefficient[d]
1	$-NH^+\cdots OH_2$[b]	30.0	± 1.5	0.26	± 0.03	1.2	19	0.923
2	$-NH^+\cdots O-$[f]	28.3	± 0.3	0.23	± 0.01	1.1	48	0.979
3	$-NH^+\cdots N-$[g]	23.2	± 0.7	0.25	± 0.05	1.2	8	0.897
4	$-OH^+\cdots OH_2$[h]	30.4	± 0.4	0.30	± 0.01	0.8	20	0.979
5	$-SH^+\cdots OH_2$[i]	22.7	± 0.3	0.26	± 0.01	0.3	4	0.998
6	$-NH^+\cdots S-$[i]	22.3	± 0.9	0.26	± 0.03	0.8	5	0.970

[a] All enthalpies in kcal mol^{-1}. [b] Standard deviation of intercept (σ_a), of slope (σ_b), and standard deviation ($\sigma_{\Delta H°_D}$) values from calculated values based on least squares equation. [c] Number of points in correlation. [d] Correlation coefficient. [e] Based on hydrates 1-19, Table I. [f] All points in Table I, except where δ_{cor} values are indicated. [g] All points in Table II. For ΔPA = 0 the average $\Delta H°_D$ for symmetric dimers, i.e., 23.6 kcal mol is used. Dimers with cyanides not included in correlation. [h] All hydrates in Table III, except where δ_{cor} values are indicated. [i] Mautner, M., unpublished results.

on hydrates and dimers of protonated ethers with large alkyl substituents. As in the amine systems, molecular models show that the alkyl substituents may assume conformations (**6**) that



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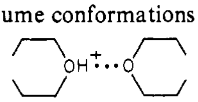

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would prohibit optimal hydrogen bonding, and thus cause $\Delta H°_D$ values lower than predicted by the $-OH^+\cdots O-$ correlation. On the other hand, constraining the substituents in conformations favorable to the hydrogen bond (**7**) may yield the optimal $\Delta H°_D$ values, but should lead to entropy terms unfavorable for dimer formation. The data show $\Delta H°_D$ values both for the hydrates and the dimers which are consistent with the correlation, even for large ethers such as $(n\text{-}C_4H_9)_2OH^+$ and $(n\text{-}C_6H_{11})_2OH^+$. However, in the bulky dimers large $\Delta S°_D$ terms are observed. The present data support the conclusion obtained for hindered amines and pyridines:[10] as long as there exist conformations that allow optimal hydrogen bonding geometry, the enthalpy of the bond is not affected by steric crowding, even if in most possible conformations the bond is blocked. However, steric crowding of the hydrogen bond can lead to substantial entropy effects.

In one special case, the dimer $((i\text{-}C_3H_7)_2O)_2H^+$, steric crowding seems to weaken[13] the bond by ≈3 kcal mol^{-1} (Table III: 33). Molecular models show that in this dimer interference between the alkyl groups may slightly stretch the hydrogen bond even in the optimal conformation.

A further structural application of the $\Delta H°_D$ vs. ΔPA correlations is the identification of protonation sites on the basis of clustering properties. For example, the attachment energy of H_2O to $XC_6H_5NH_2{\cdot}H^+$ is substantially lower for ring-protonated anilinium ions than the value predicted from a $\Delta H°_D$ vs. ΔPA correlation for nitrogen-protonated ions.[6b] In a similar manner, we found that $\Delta H°_D$ for the dimers $(\text{pyrrole})_2H^+$, $(\text{furan})_2H^+$, and $(CH_2{=}CHOCH_3)_2H^+$ is lower than 20 kcal mol^{-1}, and thus substantially lower than $\Delta H°_D$ for symmetric ammonium and oxonium dimer ions.[11] Thus the deviation from the $\Delta H°_D$ vs. ΔPA correlation indicates that the corresponding monomer ions are carbon-protonated, charge-delocalized carbonium ions.

The examples in this section show that deviations from the linear correlations (eq 1) are useful to detect and quantify structural effects that affec the ionic hydrogen bond.

The present results suggest that the strength of positive ionic hydrogen bonds in onium ions can be predicted within the experimental error limits from the ΔPA of the components. Such correlations may be especially useful for systems where direct measurements are not accessible, such as ionic hydrogen bonds between various groups, or ionized functional groups and substrates or solvents in macromolecules, e.g., peptides, enzyme cavities, DNA, etc.

In the following paper we shall examine some common trends that can be used to estimate the entire inner-shell specific solvation of onium ions by several hydrogen-bonding solvent molecules.

Acknowledgment. This work was supported in part by a grant from the Department of Energy, Office of Basic Energy Sciences.

Registry No. NH_4^+, 14798-03-9; $CF_3CH_2NH_3^+$, 54930-25-5; $CH_3NH_3^+$, 17000-00-9; $C_2H_5NH_3^+$, 16999-99-8; $(CH_3)_2NH_2^+$, 17000-01-0; $(CH_3)_3NH^+$, 16962-53-1; $(C_2H_5)_3NH^+$, 17440-81-2; $(n\text{-}C_3H_7)_3NH^+$, 50985-90-5; $(n\text{-}C_4H_9)_3NH^+$, 19497-26-8; 4-CNpyH$^+$, 37449-63-1; pyH$^+$, 16969-45-2; 2,6-$(CH_3)_2$pyH$^+$, 17033-11-3; 4-CH_3pyH$^+$, 16950-21-3; 2-*i*-C_3H_7pyH$^+$, 76065-75-3; 2-*t*-C_4H_9pyH$^+$, 62907-59-9; 4-OCH_3pyH$^+$, 33613-95-5; 2,6-*i*-$(C_3H_7)_2$pyH$^+$, 74570-68-6; 2,6-$(t\text{-}C_4H_9)_2$pyH$^+$, 62907-61-3; 4-$N(CH_3)_2$pyH$^+$, 55277-36-6; H_2O, 7732-18-5; CF_3CH_2OH, 75-89-8; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; $n\text{-}C_3H_7OH$, 71-23-8; $n\text{-}C_4H_9OH$, 71-36-3; $t\text{-}C_4H_9OH$, 75-65-0; $(CH_3)_2O$, 115-10-6; $(C_2H_5)_2O$, 60-29-7; $(n\text{-}C_3H_7)_2O$, 111-43-3; $(n\text{-}C_4H_9)_2O$, 142-96-1; $(n\text{-}C_6H_{11})_2O$, 88211-03-4; $CH_3OCH_2CH_2OCH_3$, 110-71-4; $CH_3OCH_2CH_2CH_2OCH_3$, 17081-21-9; CH_3COCH_3, 67-64-1; $C_2H_5COCH_3$, 78-93-3; $C_2H_5COC_2H_5$, 96-22-0; $n\text{-}C_3H_7COC_2H_5$, 589-38-8; HCOOH, 64-18-6; $CF_3COOC_2H_5$, 383-63-1; CH_3COOH, 64-19-7; $HCOOCH_3$, 107-31-3; HCOO-n-C_4H_9, 592-84-7; CH_3COOCH_3, 79-20-9; CH_3COO-i-C_3H_7, 108-21-4; n-C_4H_9COO-n-C_3H_7, 141-06-0; $HCONH_2$, 75-12-7; CH_3NO_2, 75-52-5; c-$C_6H_{11}NH_3^+$, 29384-28-9; $CH_3CON(CH_3)_2$, 127-19-5; 12-crown-4, 294-93-9; $HCNH^+$, 21107-92-6; CH_3CNH^+, 20813-12-1; CH_3F, 593-53-3; CH_3Cl, 74-87-3; CH_3Br, 74-83-9; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3N$, 75-50-3; py, 110-86-1; 2-Fpy, 372-48-5; $(n\text{-}C_4H_9)_3N$, 102-82-9; 2,6-$(i\text{-}C_3H_7)_2$py, 6832-21-9; CH_3CN, 75-05-8; $n\text{-}C_3H_7CN$, 109-74-0; C_6H_5CN, 100-47-0; HCN, 74-90-8; H_2COH^+, 18682-95-6; $HCF_2CH_2OH^{2+}$, 69798-82-9; $HCOOH_2^+$, 16961-31-2; $CH_3OH_2^+$, 38684-25-2; CH_3CHOH^+, 18682-96-7; $C_23H_5OH^{2+}$, 18639-79-7; $H(OCH_3)COH^+$, 39014-35-2; $CH_3COOH_2^+$, 18639-92-4; $(CH_3)_2OH^+$, 17009-82-4; $(CH_3)_2COH^+$, 43022-03-3; $C_6H_5COOH_2^+$, 56446-76-5; $HCOH^+NH_2$, 50785-80-3; c-$C_4H_8O_2H^+$, 71815-79-7; c-$C_4H_8OH^+$, 27659-93-4; c-$C_5H_{10}OH^+$, 27659-94-5; $(C_2H_5)_2OH^+$, 17009-83-5; $(n\text{-}C_3H_7)_2OH^+$, 17009-84-6; $CH_3(c\text{-}C_3H_5)COH^+$, 70058-20-7; $CH_3(C_6H_5)COH^+$, 39922-13-9; $(i\text{-}C_3H_7)_2OH^+$, 17009-86-8; $(n\text{-}C_6H_{11})_2OH^+$, 88269-09-4; $(c\text{-}C_3H_5)_2COH^+$, 70058-21-8; $CH_3COH^+N(CH_3)_2$, 52754-55-9; $C_6H_5COH^+N(CH_3)_2$, 88001-10-9; $CH_3OH^+CH_2CH_2OCH_3$, 38095-34-0; CH_3OH^+-$CH_2CH_2CH_2OCH_3$, 38095-35-1; $(i\text{-}C_3H_7)_2O$, 108-20-3; c-C_4H_8O, 109-99-9; c-$C_5H_{10}O$, 142-68-7; c-$C_6H_{12}O$, 592-90-5; $(CH_3)_2SO$, 67-68-5; O_2, 7782-44-7; CO_2, 124-38-9; c-$C_6H_{12}OH^+$, 88211-04-5; $(CH_3)_2SOH^+$, 26428-06-8; $CH_3COH^+N(CH_3)_2$, 52754-55-9; O_2H^+, 71722-67-3; CO_2H^+, 638-71-1; H_2, 1333-74-0; $(C_2H_5)_3N$, 121-44-8.