Journal of the American Chemical Society / 100:4 / February 15, 1978

Solvent Effects of Water and Fluorosulfuric Acid on Proton Transfer Equilibria and the Energies of Solvation of Gaseous Onium Ions[1]

R. W. Taft,* J. F. Wolf, J. L. Beauchamp,[2] G. Scorrano, and E. M. Arnett

Contribution from the Department of Chemistry, University of California, Irvine, Irvine, California 92717, the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, the Centro CNR Meccanismi di Reazioni Organiche, Istituto di Chimica Organica, 35100 Padova, Italy, and the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. *Received April 8, 1977*

Abstract: Precise relative proton affinities from a recent pulsed ion cyclotron resonance spectroscopy study have made it possible to evaluate the medium effects of water and of fluorosulfuric acid on the standard free energy and/or enthalpy change for reaction 1, $B + NH_4^+ \rightleftharpoons BH^+ + NH_3$, involving a wide variety of onium ions. The large medium effects (up to 50 kcal mol^{-1}) are associated primarily with onium ion solvation, although effects of neutral bases of different types are not negligible. With the use of a thermodynamic cycle, evaluations have been made of the relative heats and free energies (water only) of transfer of onium ions from the gas phase to dilute solution in water and in fluorosulfuric acid. An analysis of the relative onium ion hydration entropies and energies has been carried out which approximately separates the contributions of hydrogen bonding (HB) terms from the sum of "physical" terms associated with differential cavity sizes, solvent structure, van der Waals dispersion forces, and electrostatic interactions. It is shown that these "physical" terms make relatively minor contributions to the differences in the heats of transfer from the gas to aqueous phase for onium ions which have the same hydrocarbon content and substitutional pattern at the central atom. The major contributions to such differential heats of transfer are the differences in the favorable HB terms arising from the association of water clusters with each of the available protonic sites of the onium ions. The energy differential for the HB terms is found to be approximately the same as the corresponding difference in binding energy of single water attachments in the gas phase. The magnitude of electrostatic hydration energy for the aquated ions, $OH_3^+\cdots[(OH_2)_n]_3$ and $NH_4^+\cdots[(OH_2)_n]_4$, has been estimated. There is a marked reduction in solution compared to the gas phase in the stabilization of ammonium and oxonium ions by polarization of hydrocarbon substituents. The strong H-bond donor protons of these ions give rise to ionic polarization of the H-bonded solvent in preference to ionic polarization of the hydrocarbon substituents. The relative free energies of transfer of substituted ammonium and oxonium ions from the gas phase to aqueous solution are shown to contain large unfavorable contributions from such electrostatic polarizability effects. The corresponding relative heats of transfer are much less dependent upon unfavorable polarizability effects because of compensating favorable effects of hydrocarbon substituents on solvent structure and van der Waals dispersion force terms. The relative heats of hydration of gaseous onium ions are determined primarily by favorable HB terms which depend upon the number and kind of acidic protons present. Certain substituents are shown to also exert dipolar electron-withdrawing effects, steric hindrance, and resonance effects on the HB solvation energy terms. In fluorosulfuric acid solutions, the relative heats of solvation of gaseous onium ions depend in particular on the number of protonic sites present, with much less dependence (compared to the results in water) on the type of protonic site. The strong leveling effect on HB terms in this solvent is especially evident in the appreciably smaller solvation energies of oxonium ions in fluorosulfuric acid as compared with aqueous solution. The relative heats of transfer from water to fluorosulfuric acid solutions for substituted ammonium and oxonium ions are found to be dominated by differential HB terms. These heats of transfer also are found to correlate with the Bunnett activity coefficient parameter, φ_e, for indicator bases in H_2SO_4-H_2O media.

Introduction

In this paper we have combined recently obtained precise gas phase basicities[3] and solution basicities[4] for the reaction

$$NH_4^+ + B \rightleftharpoons BH^+ + NH_3 \qquad (1)$$

to evaluate the solvent effects (on both free energy and enthalpy) involved in the formation of oxonium, sulfonium, phosphonium, and carbonium ions (BH^+). The results are placed in perspective with previous evaluations of solvent effects for ammonium ions.[4a-c,5] Two solvent systems, water and the superacid fluorosulfuric acid, are treated in this work. To aid in understanding the solvent effects, the following thermodynamic cycle is used to evaluate the solvation energies of BH^+ relative to NH_4^+:

$$\begin{tikzcd}
NH_4^+ \arrow[d, "\Delta G^0_s(NH_4^+)"', "\Delta H^0_s(NH_4^+)"] & + & B \arrow[d, "\Delta G^0_s(B)", "\Delta H^0_s(B)"'] \arrow[r, "\Delta G^0_{(g)}", "\Delta H^0_{(g)}"'] & BH^+ \arrow[d, "\Delta G^0_s(BH^+)", "\Delta H^0_s(BH^+)"'] & + & NH_3 \arrow[d, "\Delta G^0_s(NH_3)", "\Delta H^0_s(NH_3)"'] \\
NH_{4\,(s)}^+ & + & B_{(s)} \arrow[r, "\Delta G^0_{(s)}", "\Delta H^0_{(s)}"'] & BH_{(s)}^+ & + & NH_{3(s)}
\end{tikzcd}$$

The solvent effects on reaction 1 are defined as follows

$$\delta_s \Delta G^0 \equiv \Delta G^0_{(g)} - \Delta G^0_{(s)} \qquad (2)$$

$$\delta_s \Delta H^0 \equiv \Delta H^0_{(g)} - \Delta H^0_{(s)} \qquad (3)$$

The above cycle then gives

$$-\delta_R \Delta G^0_s(BH^+) \equiv -[\Delta G^0_s(BH^+) - \Delta G^0_s(NH_4^+)] = \delta_s \Delta G^0 - \delta_R \Delta G^0_s(B) \qquad (4)$$

where $\delta_R \Delta G^0_s(B) \equiv \Delta G^0_s(B) - \Delta G^0_s(NH_3)$

$$\text{or } -\Delta G^0_s(BH^+) = -\Delta G^0_s(NH_4^+) + \Delta G^0_{(g)} - \Delta G^0_{(s)} - \Delta G^0_s(B) + \Delta G^0_s(NH_3) \qquad (4a)$$

$$\text{and } -\delta_R \Delta H^0_s(BH^+) \equiv -[\Delta H^0_s(BH^+) - \Delta H^0_s(NH_4^+)] = \delta_s \Delta H^0 - \delta_R \Delta H^0_s(B) \qquad (5)$$

where $\delta_R \Delta H^0_s(B) \equiv \Delta H^0_s(B) - \Delta H^0_s(NH_3)$

$$\text{or } -\Delta H^0_s(BH^+) = -\Delta H^0_s(NH_4^+) + \Delta H^0_{(g)} - \Delta H^0_{(s)} - \Delta H^0_s(B) + \Delta H^0_s(NH_3) \qquad (5a)$$

An analysis of the effects of molecular structure on these solvation parameters is presented which extends or modifies

0002-7863/78/1500-1240$01.00/0

earlier considerations of organic cation solvation.[5,6] Many of the major features of structure–solvation effects in onium ions are discussed in detail. The solvation energies reported herein supersede some previously published values[4a,b,5f] which were based upon earlier less accurate literature values for gas phase proton affinities relative to ammonia (having errors up to 10 kcal mol^{-1}) and upon erroneous standard states for $\delta_R\Delta G^0_{(B)}$ values for some nitrogen bases (those indicated in Table I).

Results

Table I presents a summary of available data for onium ions in aqueous solution. Table II gives a similar summary for data available in the FSO_3H solvent system. It must be reiterated that for the data in Table II the quantity $\Delta H^0_{FSO_3H}$ applies to the following process:[7]

$$NH_4{}^+{}_{(FSO_3H)} + B_{(CCl_4)} \rightleftarrows BH^+_{(FSO_3H)} + NH_{3(CCl_4)} \quad (6)$$

In contrast, the aqueous data of Table I involve water in reaction 1 as the solvent for both neutral bases and their conjugate acids. As a consequence, the FSO_3H solvent effect on reaction 1, i.e., $\delta_{FSO_3H}\Delta H^0$ values of Table II, contain contributions from the differentials in the heats of transfer of the neutral bases from the gas phase to carbon tetrachloride solution rather than to FSO_3H solution. It has been proposed that these contributions are relatively minor.[7] Our present results (cf. Discussion section) support this conclusion.

Discussion

Aqueous Solution Medium Effects. Reaction 1 is in general accompanied by extremely large medium effects in water. The medium effect parameters, $\delta_{aq}\Delta G^0$ and $\delta_{aq}\Delta H^0$, of Table I cover ranges of up to 50 kcal mol^{-1}. This range for all onium ions is appreciably extended over that (~30 kcal mol^{-1}) noted earlier for only nitrogen bases.[5,6f] It is further readily established by the data of Table I that these aqueous medium effects arise largely because of major differences between the solvation energies of the cation. However, differentials in both the free energy and the heat of transfer of different types of neutral bases from the gas phase to dilute aqueous solution are by no means trivial. Values of $\delta_R\Delta G^0_{aq}(B)$ range over 8.3 kcal mol^{-1} for all of the bases in Table I, whereas for nitrogen bases, the range in $\delta_R\Delta G^0_{aq}(B)$ values is only 2.7 kcal mol^{-1}. Thus, for bases of different types, the values of $\delta_{aq}\Delta G^0$ by themselves provide only poor quantitative estimates of the relative cation hydration energies, i.e., of $-\delta_R\Delta G^0_{aq}(BH^+)$ values. This situation is even more pronounced for the nonequality between corresponding values of $\delta_{aq}\Delta H^0$ and $-\delta_R\Delta H^0_{aq}(BH^+)$. The values of $\delta_R\Delta H^0_{aq}(B)$ range in Table I over 9.5 kcal mol^{-1}. Furthermore, note that the orders of increasing $-\delta_R\Delta G_{aq}(BH^+)$ or $-\delta_R\Delta H_{aq}(BH^+)$ values (in the former case, in progressive order from the bottom to the top of Table I) clearly do not correspond to the order of decreasing gas phase basicity, i.e., of ΔG^0_g value.

Terms Contributing to the Relative Energetics of Transfer between the Gas Phase and Solution. The solvation energies of organic ions in aqueous solution are difficult to interpret and understand quantitatively because of the unique and complex structures of ions and solvent involved and the various possible modes of charge distribution within the ions. The following terms are generally accepted as probable contributors to the relative heat or free energy of transfer of a cation (compared to $NH_4{}^+$) from the gas phase to solution:[6b,8] (1) the differential energy of creating a cavity in the solvent structure to accommodate the ions (to be referred to as CAV terms); (2) differential hydrogen bonding between the H-bond donor ions and the H-bond acceptor solvent molecules (to be referred to as HB terms); (3) differential Born charging or electrostatic (ELS) solvation of the cationic charge (inversely proportional to the "effective" radius of the "chemically" solvated cations); (4) differential structure-making hydrophobic interactions or ionic solvent structure-breaking interactions[9,10] (STR terms); (5) differential van der Waals dispersion force interactions between the ions and solvent (VWD terms). The ELS terms require additional comment. We include (somewhat arbitrarily) in these terms the effects of hydrocarbon substituents on electrostriction of solvent[11] and on the differential between solution and the gas phase in ion-induced dipole stabilization (differential polarizability effects).[4a,b,12]

Contributions from the CAV, HB, ELS, STR, and VWD terms to the solvation energies of the gaseous onium ions are not mutually exclusive, of course, so that even partial evaluations cannot be expected to be very precise. For present purposes, we shall endeavor to separate the more chemical HB and ELS terms from the sum of the "physical" ELS, CAV, STR, and VWD terms.

The directions of these solvation terms are usefully summarized at this point. Table III lists the expected trends for the introduction of hydrocarbon substituents.

The directions indicated in Table III are either self-evident or are based upon the following considerations. For the ELS term, the oversimplified assumption is made that the "effective" radius of the non-spherically symmetric cation is (somehow) increased by the substituent. Also a negative ELS term will result if there is charge dispersal to the solvent (cf. subsequent discussion). For the HB term, the reduction in the number and hydrogen-bond donor ability of protonic hydration sites leads to a negative term (e.g., $MeNH_3{}^+$ compared to $NH_4{}^+$). Steric hindrance to H-bonding solvation[13] also will lead to a negative HB term in Table III. Hydrocarbon substituents increase the enthalpy of solution (+ term in Table III) by either dispersion force (VWD) or structural (STR) interactions with the solvent. However, overridingly unfavorable entropies of solution[4b,c] lead to corresponding negative terms in $-\delta_R\Delta G^0_{s(BH+)}$.

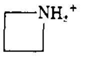
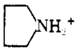
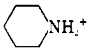
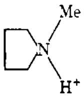
It is noteworthy that all terms of Table III are negative (unfavorable) for the effect of hydrocarbon substituents on the $-\delta_R\Delta G^0_{s(BH+)}$ values, whereas there are positive terms contributing to the $-\delta_R\Delta H^0_{s(BH+)}$values which will reduce (or could even reverse) the negative terms. Evidence that this in fact occurs is provided in Table IV, which compares the effects of methyl and ethyl substituents on the relative free energies and enthalpies of transfer from the gas phase to aqueous solution for oxonium and ammonium ions.

The oxonium ion series suffers from more unfavorable effects of alkyl substituents than does the ammonium ion series. Although these unfavorable effects are greater on the free energy than the enthalpy of solution in both series, the oxonium ion series also shows bigger differences in these quantities. There is greater entropy loss on solution (Table IV) of the more highly hydrated oxonium ions (cf. Table I). We examine further the effects on entropies of solution in the following section.

Effects of Hydrocarbon Substituents on Entropies of Aquation. Table V presents a representative comparison of the effects of hydrocarbon structure on the relative entropies of transfer both for neutral bases ($\delta_R\Delta S^0_{aq(B)}$) and their corresponding conjugate acids ($\delta_R\Delta S^0_{aq(BH+)}$) from the gas phase to aqueous solution. The figures are derived readily from the data of Table I and are relative to NH_3 and $NH_4{}^+$, respectively. The bases in Table V are arranged in order of increasing entropy loss on solution. As expected,[4b,c] this order corresponds to increasing hydrocarbon complexity. For the corresponding onium ions, however, it is clear that no such order prevails.

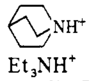
We have found, however, that there is a very close correspondence between the effects of hydrocarbon structure of the entropies of aquation of neutral bases and their conjugate acids for the same class. That is, comparisons must be made for onium ions with the same number and type (NH^+, OH^+, etc.)

Table I. Aqueous Solvent Effects on the Energetics of Proton Transfer Reaction (1) and Energies of Hydration of Gaseous Onium Ions Relative to Ammonium Ions. All Values in kcal mol^{-1}

BH^+	ΔG_g^0[a]	ΔH_g^0[b]	ΔG_{aq}^0[c]	ΔH_{aq}^0[c]	$\delta_{aq}\Delta G^0$	$\delta_{aq}\Delta H^0$	$\delta_R\Delta G_{aq}^0$-(B)	$\delta_R\Delta H_{aq}^0$-(B)	$-\delta_R\Delta G_{aq}^0$-(BH$^+$)	$-\delta_R\Delta H_{aq}^0$-(BH$^+$)
H_3O^+	31.4	32.0	14.2[d]	12.6[e]	17.2	19.4	−2.0[f]	−2.0[g]	19.2	21.4
$MeOH_2^+$	19.3	20.1	15.41	13.1	3.9	7.0	−0.8[h]	−2.1[i]	4.7	9.1
$EtOH_2^+$	14.8	15.6	15.26	12.1	−0.5	3.5	−0.6[h]	−4.1[i]	0.1	7.6
Me_2OH^+	11.0	12.2	15.99	11.9	−5.0	0.3	2.4[h]	−0.9[i]	−7.4	1.2
$MeEtOH^+$	7.5	8.3	15.82	(11.8)[j]	−8.3	−3.5	(2.5)[j]	(−1.7)[j]	−10.8	−1.8
Me_2COH^+	7.2	8.4	16.50	11.8	−9.3	−3.4	0.5[h]	−1.6[i]	−9.8	−1.8
$Me(OEt)COH^+$	3.4	4.2	17.32[w]	11.5[x]	−13.9	−7.3	1.2[h]	−2.3[y]	−15.1	−5.0
Et_2OH^+	3.7	4.9	15.87	11.8	−12.2	−6.9	2.6[h]	−2.6[i]	−14.8	−4.3
Me_2SOH^+	−7.2	−6.0	14.71	14.8	−21.9	−20.8	−5.7[l]	−8.6[i]	−16.2	−12.2
$Me(NMe_2)COH^+$	−12.4	−11.6	13.16[k]	14.9[k]	−25.6	−26.5		−7.6[i]		−18.9
NH_4^+	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
$CF_3CH_2NH_3^+$	1.8	2.0	4.96[m]	4.2[m]	−3.2	−2.2		−1.8[n]		−0.4
$MeNH_3^+$	−9.2	−9.0	−1.92	−0.7	−7.3	−8.3	−0.3	−2.6	−7.0	−5.7
$EtNH_3^+$	−11.9	−11.7	−1.96	−1.2	−9.9	−10.5	−0.2	−4.5	−9.7	−6.0
n-$PrNH_3^+$	−13.5	−13.3	−1.80	−1.4	−11.7	−11.9	−0.1	−4.8	−11.6	−7.1
i-$PrNH_3^+$	−14.4	−14.2	−1.94	−1.5	−12.5	−12.7	−0.1	−4.8	−12.4	−7.9
n-$BuNH_3^+$	−13.9	−13.7	−1.90	−1.5	−12.0	−12.2	0.0	−5.6	−12.0	−6.6
t-$BuNH_3^+$	−16.7	−16.5	−1.96	−1.9	−14.7	−14.6	0.0	−5.6	−14.7	−9.0
$C_6H_5NH_3^+$	−6.7	−6.5	6.34	5.1	−13.0	−11.6		−4.4[o]		−7.2
c-$C_6H_{11}NH_3^+$	−16.4	−16.2	−1.82	−1.9	−14.6	−14.3		−6.4		−7.9
$Me_2NH_2^+$	−16.0	−15.6	−2.09	0.5	−13.9	−16.1	0.0	−4.7	−13.9	−11.4
	−18.2	−17.8	−2.79	−0.1	−15.4	−17.7	−1.6[v]	−5.7	−13.8	−12.0
	−20.0	−19.6	−2.81	−0.5	−17.2	−19.1	−1.2[v]	−6.7	−16.0	−12.4
$Et_2NH_2^+$	−20.8	−20.4	−2.42	−0.3	−18.4	−20.1	0.2	−6.8	−18.6	−13.3
	−2.09	−20.5	−2.56	−0.3	−18.3	−20.2	−0.8[v]	−7.1	−17.5	−13.1
n-$Pr_2NH_2^+$	−22.8	−22.4	−2.39	−0.7	−20.4	−21.7	0.7	−8.7	−21.1	−13.0
Me_3NH^+	−20.6	−19.8	−0.75	3.7	−19.8	−23.5	1.1	−4.7	−20.9	−18.8
$C_6H_5NMe_2H^+$	−18.6	−17.8	5.69		−24.3					
$(allyl)_3NH^+$	−25.3	−24.5	1.32	3.7[p]	−26.6	−28.2				
	−24.1	−23.3	−1.66	3.4	−22.4	−26.7	0.3[v]	−6.6	−22.7	−20.1
	−27.1	−26.3	−2.55[q]	1.3[q]	−24.5	−27.6		−9.5[n]		−18.1
Et_3NH^+	−27.5	−26.7	−2.01	2.2	−25.5	−28.9	1.3	−8.2	−26.8	−20.7
n-Pr_3NH^+	−29.4	−28.6	−1.93	2.0	−27.5	−30.6				
4-CF_3pyrH^+	−8.8	−8.0	9.02	10.3[r]	−17.8	−18.3		−3.1[r]		−15.2
$pyrH^+$	−16.6	−15.8	5.50	7.7	−22.1	−23.5	−0.4[v]	−3.4	−21.7	−20.1
4-$MepyrH^+$	−20.6	−19.8	4.38	6.4	−25.0	−26.2	−0.6[v]	−4.7	−24.4	−21.5
2,6-Di-t-$BupyrH^+$	−26.9	−26.1	5.7[s]		−32.6					
$Me_2PH_2^+$	−12.1	−11.7	7.3[t] (est)		−19.4 (est)					
Me_3PH^+	−22.0	−21.2	0.8[t] (est)		−22.8 (est)					
Me_2SH^+	3.5	4.7	22.14	19.4	−18.6	−14.7	2.8[h]		−21.4	
$C_6H_5CMe_2^+$	−3.3	−2.5	~30.8[u]		−34.1					
$(C_6H_5)_2CMe^+$	−7.7	−6.9	26.8[u]		−34.5					

[a] All positive values are from ref 3; all negative values are from ref 4a with small corrections based upon additional unpublished results; precision is ± 0.2 kcal mol^{-1}. [b] Obtained from $\Delta G_{(g)}^0$ values using corrections for molecular rotational symmetry numbers—cf. ref 3 for justification. [c] Unless otherwise cited, values are from the literature as quoted in ref 4a or 4b (for ammonium ions) and ref 4d or 4e (for oxonium ions). [d] H_2O has been estimated (ref 4d) to have a $\varphi = 1$ and be half-protonated in 84.5% H_2SO_4 (ref 5f), which gives the value cited. If the formal value of $pK_{BH^+} = -1.74$ is used (cf. ref *f*), this leads to a value in reasonable agreement, i.e., $\Delta G_{(aq)}^0 = 15.0$. [e] From the temperature coefficient of the estimated pK_{HB^+} values. Using the formal pK_{BH^+} values gives the same result. This result is also expected on the basis of extrapolation of the $\Delta H_{(aq)}^0$ values for alcohols. [f] J. Hine and R. D. Weimar, Jr., *J. Am. Chem. Soc.*, **87**, 3387 (1965). [g] Obtained from $\Delta H_s = 0$ and $\Delta H_v = 10.52$ kcal. [h] Obtained from J. Hine and P. K. Mookerjee, *J. Org. Chem.*, **40**, 292 (1975). [i] The ΔH_{aq}^1 and ΔH_v values needed to compute ΔH_{aq}^0(B) were taken from Tables 17 and 19 of ref 5f, except for the following: MeOH, $\Delta H_{aq}^1 = -1.74$ (E. M. Arnett and D. R. McKelvey in "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969); Me(OMe)CO, $\Delta H_{aq}^1 = -1.89$ (J. P. Guthrie, *J. Am. Chem. Soc.*, **96**, 3608 (1974); $\Delta H_v = 7.9$ (N. A. Lange, "Handbook of Chemistry", 10th ed, McGraw-Hill, New York, N.Y.); Me_2SO, $\Delta H_v = 7.9$ (W. S. MacGregor, *Ann. N.Y. Acad. Sci.*, 141, 33 (1967)); $Me(NMe_2)CO$, $\Delta H_{aq}^1 = -5.2$ and $\Delta H_v = 10.9$ (J. P. Guthrie, *J. Am. Chem. Soc.*, **96**, 3608 (1974). The values for Me_2O were estimated through data reported in ref 5d concerning the pair Me_2O/Et_2O. [j] Estimated value obtained by assuming a value lying halfway between that for Me_2O and Et_2O. [k] G. Zangrossi, Thesis, Padova, 1976. [l] Computed from data of S. Y. Lam and R. L. Benoit, *Can. J. Chem.*, **52**, 718 (1974). [m] P. Love, R. B. Cohen, and R. W. Taft, *J. Am. Chem. Soc.*, **90**, 2455 (1968). [n] Unpublished results of J. F. Wolf. [o] Reference 5d. [p] J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, *J. Chem. Soc. A*, 1212 (1969). [q] C. A. Grob and M. G. Schlageter, *Helv. Chim. Acta*, **59**, 264 (1976). [r] E. M. Arnett, B. Chawla, L. Bell, M. Taagepera, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, 99, 5729 (1977). [s] D. H. McDaniel and M. Ozcam, *J. Org. Chem.*, 33, 1922 (1968). [t] Estimated measurements in CH_3NO_2 solution: W. A. Henderson and C. A. Streuli, *J. Am. Chem. Soc.*, **82**, 5791 (1960). [u] Cf. J. F. Wolf, P. G. Harch, and R. W. Taft, *J. Am. Chem. Soc.*, **97**, 2904 (1975). [v] Value given is for the correct standard state. An error in the standard state used was made for a value previously given (ref 4b and 4c). The error has been corrected by adding 2.303*RT* log 55.5 to previously tabulated values. [w] D. G. Lee and M. H. Sadar, *J. Am. Chem. Soc.*, 96, 1862 (1974). [x] Estimated value for results in ref *k*; [y] $\Delta H_S{}^1 = -2.5$, E. M. Arnett, J. J. Burke, J. V. Carter, and C. F. Douty, *J. Am. Chem. Soc.*, 94, 7837 (1973); $\Delta H_V = 8.30$, "CRC Handbook of Chemistry and Physics", 57th ed., CRC Press, Cleveland, Ohio.

Table II. Fluorosulfuric Acid Solvent Effects on the Enthalpy Change for Reaction (6) and the Heats of Solution of Gaseous Onium Ions Relative to Ammonium Ion. All Values in kcal mol^{-1}.

BH^+	$\Delta H^0_{(g)}$[a]	$\Delta H_{(FSO_3H)}$[b]	$\delta_{FSO_3H}\Delta H^0$	$\delta_R\Delta H^0(B)$[d]	$-\delta_R\Delta H^0_{FSO_3H}(BH^+)$
H_3O^+	32.0	26.8	+5.2	−2.2	7.4
$MeOH_2^+$	20.1	26.2	−6.1	−2.2	−3.9
$EtOH_2^+$	15.6	24.6	−9.0	−2.7	−6.3
Me_2OH^+	12.2	25.1	−12.9	−0.7	−12.2
Et_2OH^+	4.9	23.8	−18.9	−2.4	−16.5
Me_2COH^+	8.4	24.2	−15.8	−2.9	−12.9
Me_2SOH^+	−6.0	14.7	−20.7	−6.9[e]	−13.8
$Me(OEt)COH^+$	4.2	25.9	−21.7	−4.4	−17.3
$Me(NMe_2)COH^+$	−11.6	11.3	−22.9	−6.5[f]	−16.4
NH_4^+	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
SH_3^+	28.4	38.0	−9.6	−1.1	−8.5
PH_4^+	14.9	29.3	−14.4	1.1	−15.5
$CF_3CH_2NH_3^+$	2.0	3.9[c]	−1.9	−1.5[c]	−0.4
$MeNH_3^+$	−9.0	−3.0	−6.0	−1.4	−4.6
$EtNH_3^+$	−11.7	−3.5	−8.2	−2.1	−6.1
n-$PrNH_3^+$	−13.2	−2.9	−10.3	−3.0	−7.3
i-$PrNH_3^+$	−14.2	−6.0	−8.2	−2.1	−6.1
n-$BuNH_3^+$	−13.7	−2.9	−10.8	−3.4	−7.4
t-$BuNH_3^+$	−16.5	−5.5	−11.0	−2.6	−8.4
$C_6H_5NH_3^+$	−6.5	9.3[c]	−15.8	−5.6[c]	−10.2
$Me_2NH_2^+$	−15.6	−4.5	−11.1	−2.0	−9.1
$Et_2NH_2^+$	−20.4	−4.4	−16.0	−3.9	−12.1
4-CF_3pyrH^+	−8.0	7.2[c]	−15.2	−5.5[c]	−9.7
$CH_3C{\equiv}NH^+$	15.3	29.7	−14.4	−2.1	−12.3
Me_3NH^+	−19.8	−4.2	−15.6	−2.0	−13.6
$pyrH^+$	−15.8	4.7	−20.5	−5.2	−15.3
$C_6H_5NMe_2H^+$	−17.7	5.6	−23.3	−5.7[c]	−17.6
4-$MepyrH^+$	−19.8	4.2[c]	−24.0	−6.9[c]	−17.1
	−26.3	−2.5	−23.8		
Et_3NH^+	−26.7	−5.9	−20.8	−5.0	−15.8
2,6-di-*t*-Bu-$pyrH^+$	−26.1	5.1[c]	−31.2	−8.4[c]	−22.8
Me_3PH^+	−21.2	−1.3	−19.9	−2.0	−17.9
Me_2SH^+	4.7	25.2	−20.5	−2.6	−17.9
Et_2SH^+	−0.3	24.2	−24.5	−5.1	−19.4
$(C_6H_5)_2CMe^+$	−6.9	28.6[g]	−35.5		

[a] Cf. footnotes *a* and *b* of Table I. [b] Cf. ref 5e and 5f and E. M. Arnett and J. F. Wolf, *J. Am. Chem. Soc.*, **95**, 978 (1973); E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, *ibid*, **96**, 3875 (1974). [c] Reference 4b. [d] Cf. ref 5f, Tables 16 and 17, unless otherwise indicated. [e] Value in Table 17 of ref 5f has been corrected using ΔH_v = 12.64 kcal/mol: W. S. MacGregor, *Ann. N.Y. Acad. Sci.*, 141, 3 (1967). [f] Unpublished result of J. F. Wolf. [g] E. M. Arnett, J. V. Carter, and R. P. Quirk, *J. Am. Chem. Soc.*, **92**, 1770 (1970).

of acidic protons. The results of such a comparison are given in Table VI, in which it will be noted that the unfavorable entropy of aquation increases with increasing hydrocarbon complexity both for the neutral base and its conjugate acid. The increased carbon number, Δn_c = no. C's (B_l) − no. C's (B_2), provides a reasonable index of these effects. The effects of hydrocarbon structure in Table VI may be seen to be perhaps slightly larger for the onium ions.

The results of Tables V and VI suggest that a separation is possible of the hydrogen bonding effects (associated with number and type of acidic proton) on $\delta_R\Delta S^0_{aq(BH^+)}$ values from the physical type effects (sum of ELS, CAV, STR, and VWD terms which are associated with hydrocarbon structure). In particular, it appears from Tables V and VI that approximately −8 and −15 eu may be assigned to the latter for the effects of methyl and ethyl substituents, respectively. Applying such approximate "correction" effects to the values of $\delta_R\Delta S^0_{aq(BH^+)}$ in Table V does indeed give entropy contributions (Table VII) which are generally very consistent with the expectations of the H-bond theory.[14]

In Table VII, the entropy contributions for substituted ammonium ions relative to NH_4^+ increase (more favorable entropy of transfer from the gas to aqueous phase) as acidic protons are replaced by the alkyl substituents, since with the expected decreased -NH^+—$(OH_2)_n$ hydration of the ion there is less entropy loss of water. For all oxonium ions relative to NH_4^+, the HB entropy contribution is decreased. Generally this decrease corresponds to that expected from the increased -OH^+—$(OH_2)_n$ hydration, although values for the weakest oxygen bases, H_2O and MeOH, are subject to greater uncertainties (cf. footnotes to Table I). For support of this interpretation, we turn next to evidence from the energetics of onium ion hydration.

Table III. Effect of Hydrocarbon Substituents on Relative Solvation Terms for Gaseous Onium Ions (+ Denotes Increasing Spontaneity or Exothermicity of Solution)

<table>
<tr><th></th><th>CAV</th><th>STR</th><th>VWD</th><th>ELS</th><th>HB</th></tr>
<tr><td>$-\delta_R\Delta H^{g\rightarrow H_2O}_{s(BH^+)}$</td><td>−</td><td>+</td><td>+</td><td>−</td><td>−</td></tr>
<tr><td>$-\delta_R\Delta G^{g\rightarrow H_2O}_{s(BH^+)}$</td><td>−</td><td colspan="2">$\overbrace{\qquad-\qquad}$</td><td>−</td><td>−</td></tr>
</table>

Comparison with Binding Energies of Water Molecules to Gaseous Onium Ions. The relative hydration energies of Table I can in a few instances be directly compared to the relative binding energies of water molecules to the ions in the gas phase. The binding energy of attaching three water molecules to the protonic sites in H_3O^+ (the most highly solvated ion in either Tables I or II) is 76 kcal.[15] The binding energy of attaching four water molecules to NH_4^+ is 58 kcal,[16] i.e., 18 kcal less. Kebarle has shown that these binding energies involve principally H-bonding interactions.[18] In close correspondence to this figure are the values of $-\delta_R\Delta G^0_{aq(BH^+)}$ and $-\delta_R\Delta H^0_{aq(BH^+)}$

Table IV. Effects of Methyl and Ethyl Substituents on the Relative Free Energy and Enthalpy of Transfer for Oxonium and Ammonium Ions[a]

	$\delta\Delta G^0_{(BH+)}$[b]	$\delta\Delta H^0_{(BH+)}$[b]	$\delta\Delta S^0_{(BH+)}$[c]		$\delta\Delta G^0_{(BH+)}$[b]	$\delta\Delta H^0_{(BH+)}$[b]	$\delta\Delta S^0_{(BH+)}$[c]
H_3O^+	(0.0)	(0.0)	(0.0)	NH_4^+	(0.0)	(0.0)	(0.0)
$MeOH_2^+$	−14.5	−12.3	−7.4	$MeNH_3^+$	−7.0	−5.7	−4.4
$EtOH_2^+$	−19.1	−13.8	−17.8	$EtNH_3^+$	−9.7	−6.0	−12.4
Me_2OH^+	−26.6	−20.2	−21.5	$Me_2NH_2^+$	−13.9	−11.4	−8.4
Et_2OH^+	−34.0	−25.7	−27.8	$Et_2NH_2^+$	−18.6	−13.3	−17.8

[a] Negative sign denotes unfavorable g → aq transfer for BH^+. [b] In kcal mol^{-1}. [c] In cal deg^{-1} mol^{-1}.

Table V. Comparison of the Relative Entropies of Transfer from the Gas Phase to Aqueous Solution for Neutral Bases and for Their Corresponding Conjugate Acids (in cal deg^{-1} mol^{-1}).

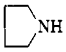
B	$\delta_R\Delta S^0_{aq}$ (B)	$\delta_R\Delta S^0_{aq}$ (BH^+)	B	$\delta_R\Delta S^0_{aq}$ (B)	$\delta_R\Delta S^0_{aq}$ (BH^+)
H_2O	0.0	−7.4	Me_2NH	−15.8	−8.4
$MeNH_2$	−7.7	−4.4	Et_2O	−17.4	−35.2
MeOH	−4.4	−14.8		−18.4	−12.1
Me_2O	−11.1	−28.9	Me_3N	−19.4	−7.0
$EtNH_2$	−14.4	−12.4	Et_2NH	−23.5	−17.8
EtOH	−11.7	−25.2	(n-Pr)$_2$NH	−31.5	−27.2
n-$PrNH_2$	−15.8	−15.1	Et_3N	−31.9	−20.5

Table VI. Comparison of the Differential Entropies of Transfer from the Gas Phase to Aqueous Solution for Pairs Having the Same Type of Conjugate Acids (in cal/deg^{-1} mol^{-1}).

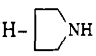
Δn_C	B_1-B_2	$\delta\Delta S^0_{aq}$(B)	$\delta\Delta S^0_{aq}$(BH^+)
0	Et_2NH- 	−5.1	−5.7
1	EtOH-MeOH	−7.3	−10.4
1	$EtNH_2$-$MeNH_2$	−6.7	−8.0
2	Et_2O-Me_2O	−6.3	−6.3
2	Et_2NH-Me_2NH	−7.7	−9.4
2	n-$PrNH_2$-$MeNH_2$	−8.1	−10.7
3	Et_3N-Me_3N	−12.5	−13.5
4	n-Pr_2NH-Me_2NH	−15.7	−18.8

Table VII. Relative Entropy Contributions from H-Bonding Hydration of Gaseous Methyl and Ethyl Substituted Ammonium and Oxonium Ions

BH^+	$\delta_R\Delta S^{HB}_{aq(BH+), cal/deg}$[a]	BH^+	$\delta_R\Delta S^{HB}_{aq(BH+), cal/deg}$[a]
Et_3NH^+	24.	$Et_2OH_2^+$	−5.
Me_3NH^+	17.	$MeOH_2^+$	−7.
$Et_2NH_2^+$	12.	H_3O^+	−7.
$Me_2NH_2^+$	8.	$EtOH_2^+$	−10.
$MeNH_3^+$	4.	Me_2OH^+	−13.
NH_4^+	(0.)		

[a] Relative H-bonding entropy contribution, $\delta_R\Delta S^{HB}_{aq(BH+)}$, obtained from the $\delta_R\Delta S^0_{aq(BH+)}$ value of Table V by subtracting −8 and −15 cal deg^{-1} mol^{-1} for each Me or Et substituent, respectively.

(Table I), which show NH_4^+ to be less energetically hydrated than H_3O^+ by 19-21 kcal.

We believe that it would be naive to conclude from this remarkable correspondence that in aqueous solution only three and four water molecules are involved in chemical binding to H_3O^+ and NH_4^+, respectively. With the abundance of clusters of water molecules associated through an extended network by hydrogen bonds, it seems certain that more (but an uncertain number of) water molecules should be regarded as "chemically" bound to these ions.[17] The equivalence of gas phase and solution hydration energies instead suggests that the additional water molecules in bulk water "share" in the total binding energy available with each protonic hydration site in the onium ion. In the gas phase, this energy is liberated by the interaction on a 1:1 basis between each available protonic site and a water molecule. In solution, the same energy is apparently liberated at each of the available protonic sites by additional hydrogen-bonded water molecules sharing in this total binding energy.

Unfortunately, it is not possible to learn whether the same result applies to other unsubstituted cations, e.g., H_3S^+ or PH_4^+, for lack of needed data in both the gas phase and solution. Comparisons (cf. Table VIII) with substituted oxonium and ammonium ions, however, make it clear that such a direct correspondence does not apply to them as it does for NH_4^+ and H_3O^+ ions.

There is no equality between gas phase energies of attachment of water molecules to substituted onium ions and the corresponding energies of hydration of these ions. This is seen in Table VIII especially in terms of the ΔH^0 values. The ΔH^0 values, however, are evidently more appropriate than the values of ΔG^0 in this comparison since there is much greater translational entropy loss on hydration in the gas phase than in aqueous solution. Consequently, we conclude that the CAV, STR, VWD, HB, and ELS terms contribute in differing degrees to the ΔH^0 and ΔG^0 values of Table VIII for the transfer of gaseous substituted onium ions to aqueous solution.

In order to minimize the contributions from the total of CAV, STR, VWD, and ELS terms and evaluate HB terms, it appears that a key feature is to maintain the same hydrocarbon content and substitutional pattern at the central atom of the onium ion. Grunwald,[20] for example, used tetraphenylphosphonium ion, tetraphenylmethane, and tetraphenylboride ion to separate ELS from non-ELS terms for the solvation energies of the cation and anion. We propose specifically that the difference in solvation energies between two gaseous onium ions having the same hydrocarbon content and substitutional pattern will include minimal (but not necessarily negligible) contributions from the sum of ELS, CAV, STR, and VWD terms.

Table IX lists values of differential free energies and heats of transfer between the gas and aqueous phases for a reasonably extensive variety of pairs of onium ions having the same hydrocarbon content and substitutional pattern (such a pair of ions will be designated as an HCSP pair).

Using the observed heats of attachments of successive water molecules to H_3O^+ and NH_4^+ in the gas phase (cf. footnote *b* of Table IX for the figures used), one may estimate the differential heats of attachment of the appropriate number of water molecules to each pair of the HCSP ions of Table IX. The results (given as calcd value in Table IX) do agree roughly with the corresponding values of either $\delta\Delta G^{0g\rightarrow H_2O}_{(BH+)}$ or $\delta\Delta H^{0g\rightarrow H_2O}_{(BH+)}$. The calculated values are too crude to indicate a preference for the latter values (which presumably do not contain, as do the former ones, the entropy contributions already discussed).

There may be major sources of error affecting the agreement of values in Table IX arising from the failure of substituent effects to cancel in the differential binding energies both in the gas phase and in solution. The few direct determinations

Table VIII. Differentials in Gas Phase Attachment Energies and in Corresponding Hydration Energies of Substituted Onium Ions

Process[a]	$-\Delta G^{0h}$	$-\Delta H^{0h}$	ΔS^{0g}
$Me_2OH^+ + Me_3NH^+\cdots OH_2 \rightleftarrows Me_2OH^+\cdots OH_2 + Me_3NH^+$	7.3[b]	8.[c] (est)	−2.
$Me_2OH^+ + Me_3NH^+(aq) \rightleftarrows Me_2OH^+(aq) + Me_3NH^+$	13.5[d]	20.0[d]	−22.
$OH_3^+ + Me_2OH^+\cdots OH_2 + 2H_2O \rightleftarrows OH_3^+(OH_2)_3 + Me_2OH^+$	32.0[e]	53.4[e]	−72.
$OH_3^+ + Me_2OH^+(aq) + (aq) \rightleftarrows OH_3^+(aq) + Me_2OH^+$	26.6[d]	20.2[d]	+22.
$NH_4^+ + Me_3NH^+\cdots OH_2 + 3H_2O \rightleftarrows NH_4^+(OH_2)_4 + Me_3NH^+$	22.3[f]	43.[c,f]	−70.
$NH_4^+ + Me_3NH^+(aq) + (aq) \rightleftarrows NH_4^+(aq) + Me_3NH^+$	20.9[d]	18.8[d]	+7.

[a] If not otherwise indicated, reactants and products are in the gas phase. [b] References 18 and 19. [c] ΔH^0 estimated from ΔG^0 using a value of ΔS^0 typically found in ref 15, 16, and 18. [d] From Table I. [e] References 15 and 18. [f] References 16 and 19. [g] Cal deg^{-1} mol^{-1}. [h] kcal mol^{-1}.

Table IX. Differential Free Energies and Heats of Transfer from the Gaseous to Aqueous Phase for HCSP Pairs of Onium Ions (in kcal mol^{-1})

B_1H^+-B_2H^+	$-\delta\Delta G^{g\rightarrow H_2O}_{(BH^+)}$[a]	$-\delta\Delta H^{g\rightarrow H_2O}_{(BH^+)}$[a]	Calcd[b]
OH_3^+-NH_4^+	~19.2	~21.4	20.
$MeOH_2^+$-$MeNH_3^+$	11.7	14.8	13.
$EtOH_2^+$-$EtNH_3^+$	9.8	13.6	13.
$C_6H_5NMe_2H^+$-$C_6H_5CMe_2^+$	15.[c]		20.
Me_2OH^+-Me_2SH^+	14.0		17.[d]
Me_2OH^+-$Me_2NH_2^+$	6.5	12.6	3.
Et_2OH^+-$Et_2NH_2^+$	3.8	9.0	3.
Me_2COH^+-Me_2SOH^+	6.4	10.4	

[a] A positive value denotes greater solvation energy for the left-hand onium ion. [b] Calculated using for 1st OH^+, 37; 2nd OH^+, 22; 3rd OH^+, 17; and for 1st NH^+, 20; 2nd NH^+, 14; 3rd NH^+, 12; 4th NH^+, 10. (These are values reported for H_3O^+ and NH_4^+ in ref 15, 16, 18, 19, and 21, or interpolated from them.) [c] Obtained from data of Table I assuming $\delta_R\Delta G^0_{(B)}$ to be 5 kcal mol^{-1} greater for *N,N*-dimethylaniline than α-methylstyrene. [d] Estimated on the basis that the attachment of the first water to SH^+ is approximately the same as that for NH^+.

Table X. Heats of Hydration of Unsubstituted Onium Ions, and Their Approximate "Chemical" and "Physical" Solvation Components

Onium ion	$-\Delta H^0_{aq}(BH^+)$	HB[BH^+; $(H_2O)_n$][a]	Total physical solv terms[a] (TPST)
H_3O^+	102.[b]	76.	26.
NH_4^+	81.	56.	25.
H_3S^+	(70.)[c]	(50.)[c]	(20)
PH_4^+	(50.)[c]	(30.)[c]	(20)

[a] These interaction energies have been arbitrarily given as positive quantities, i.e., $-\Delta H^0_{aq}(BH^+) \equiv HB[BH^+;(H_2O)_n] + TPST$ in kcal mol^{-1}. [b] Combining this figure with the recent proton affinity value of H_2O (ref 3a) gives the enthalpy of solution for $H^+_{(g)}$ as −272 kcal mol^{-1}. [c] Crude estimates.

available regarding this cancellation of substituent effects in the calculated gas phase values indicate that this assumption may involve substantial imperfections, e.g.

$$Me_2OH^+\cdots OH_{2(g)} + Me_3NH^+_{(g)} \rightleftarrows Me_2OH^+_{(g)} + Me_3NH^+\cdots OH_{2(g)}$$

ΔH^0_{obsd} = 9.0 kcal mol^{-1},[18,19] as compared with 17.0 kcal[15,16] for the same process with unsubstituted H_3O^+ and NH_4^+. Further, imperfect cancellation of the hydrocarbon substituent effects on the heats of solutions of the HCSP ions is to be expected, especially for ELS terms arising from differential polarizability effects of the hydrocarbon substituents (cf. subsequent discussion).

In general, the more highly substituted the ammonium or oxonium ion, the poorer is the prospect for cancellation of substituent effect contributions to the differential binding and solvation energies for the HCSP pair of onium ions. It will be noted in Table IX that for such ions there is generally poorer quality of agreement between the calculated and the corresponding solution values.

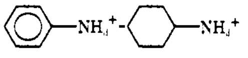
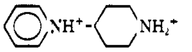
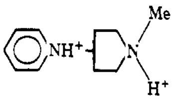
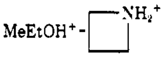
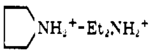
In spite of this difficulty, we believe that the rough agreement between the results in Table IX supports our three premises. First, there are only small contributions from CAV, STR, VWD, and ELS terms in the differential heats of transfer from the gas to aqueous phases for onium ions having the same hydrocarbon content and substitutional pattern at the central atom. Second, the major contributions to such differential heats of transfer are the differences in the total HB binding energies of water clusters associated with the available protonic sites in the onium ions. Third, there is near equality between the difference in HB binding energies of water clusters in solution and the corresponding difference in HB binding energies of water attachments in the gas phase.

Estimates of Absolute Hydration Energies. The enthalpy of transfer of gaseous NH_4^+ to dilute aqueous solution has been estimated to be 81 kcal mol^{-1}.[6e] Combining this figure with the relative enthalpy values, $\delta_R\Delta H^0_{aq(BH^+)}$ from Table I provides approximate absolute values for the enthalpies of hydration of each BH^+. Using these values together with our estimate of the HB terms, [BH^+; $(H_2O)_n$], obtained in the previous section, a rough evaluation is made (Table X) of the total of the contributions from ELS, CAV, STR, and VWD terms (TPST) to the enthalpies of hydration for the unsubstituted gaseous onium ions.

It appears significant that the sum of ELS, CAV, STR, and VWD terms (which we call the total physical solvation) is about the same figure, 26 kcal mol^{-1}, for both H_3O^+ and NH_4^+. The lack of aqueous solution data unfortunately prevents a similar evaluation for H_3S^+ and PH_4^+ ions. However, the available data (Tables I and IX) do suggest a major decrease (as given in Table X) in the HB hydration terms for these ions compared to H_3O^+ and NH_4^+, respectively.

The Born equation for ELS solvation can be appropriately applied only to the "chemically" hydrated ion. That is, for the most successful application of this equation, one needs to know the effective radius of the "chemically" hydrated (not the anhydrous) ion and that there is little or no chemical binding of the hydrated ion to the solvent. The tetrahydrate of K^+, $[K(OH_2)_4]^+$, has been estimated[22] to have a radius of 3.5 Å compared to 1.33 Å for the anhydrous ion.[23,24] The binding energy of four water molecules to K^+ in the gas phase is 59 kcal mol^{-1}.[21] The enthalpy of hydration of $K^+_{(g)}$ is greater than this binding energy by 27 kcal mol^{-1}.[21,28] Using the above radius for $K(OH_2)_4^+$, the Born equation gives essentially this same figure for the ELS hydration energy contribution. Since the nonelectrostatic contribution to the solvation enthalpies for the alkali metal ions is thought to be small (~4 kcal),[26] this agreement accords with the idea that four water molecules are "chemically" bound to K^+ in dilute aqueous solutions. Various

Table XI. Differential Free Energies and Heats of Transfer of Closely Related Gaseous Ions into Water (in kcal mol^{-1})

B_1H^+–B_2H^+ [a]	$-\delta\Delta G^{g\rightarrow H_2O}_{(BH^+)}$ [b]	$-\delta\Delta H^{g\rightarrow H_2O}_{(BH^+)}$ [b]	Calcd [c]
$4CF_3pyrH^+$–$4CH_3pyrH^+$		6.3	
$CF_3CH_2NH_3^+$–$CH_3CH_2NH_3^+$		5.6	
$(allyl)_3NH^+$–$(n\text{-}Pr)_3NH^+$	~0.9 [d]	~2.4 [d]	
		0.7	(0) [e]
	−4.2	−7.0	(−6) [e]
	1.0	0.0	(0) [e]
	3.0	10.2	3
	2.6	0.9	0

[a] Substituents present have approximately the same polarizability (cf. ref 3b). [b] A positive value denotes greater solvation energy for the left-hand onium ion. [c] Calculated as in footnote *b* of Table VI. [d] Obtained from data of Table I, assuming the same $\delta_R\Delta G^0_{eq}(B)$ and $\delta_R\Delta H^0_{eq}(B)$ values for triallylamine and tri-*n*-propylamine. [e] Assumes the same $NH^+\cdots OH_2$ binding energy for unsaturated as saturated substituents.

methods of estimating hydration numbers are in general in support of this conclusion.[27]

An effective radius for $H_3O^+\cdots[(H_2O)_n]_3$, or $NH_4^+\cdots[(H_2O)_n]_4$ near the 3.5 Å value for $[K(OH_2)_4]^+$ seems to be a reasonable figure. On this basis, the results of our separation of HB and TPST terms (Table X) appear consistent. That is, are a figure in the region of 25–30 kcal mol^{-1} for the ELS hydration term for the "chemically" hydrated NH_4^+ and H_3O^+ ions appears to be a realistic one. Also, the enthalpies of hydration of −23 to −38 kcal mol^{-1} obtained by Ladd[28] for the presumably chemically inert $(n\text{-}Pr)_4N^+$, $(Et)_4N^+$, and Me_4N^+ ions seem also to be in reasonable accord.

ELS Terms from Polarizability Effects. Evidence has been recently summarized[12] favoring the idea that the large polarizability effects of hydrocarbon substituents which stabilize gas phase onium ions are largely dissipated for ammonium and oxonium ions in aqueous solution. The marked reduction in solution of the stabilization of these ions by polarization of the hydrocarbon substituents is pictured to be the consequence of the dispersal of charge to the medium which accompanies the hydrogen bonding between the solvent and the strong H-bond donor protons, $-NH^+$ and $-OH^+$. In effect, ionic polarization of the H-bonded solvent then takes priority over ionic polarization of the hydrocarbon substituents.

The picture of charge dispersal from oxonium and ammonium ions through hydrogen bonding is supported by both theoretical calculations[29,30] and indirect experimental evidence.[31] The simple electrostatic model for the polarizability effect,[32] $-\alpha e^2/2r^4$, indicates that this effect falls off with inverse *fourth* power of the distance, *r*, between the center of polarizability and the center of positive charge. Consequently, charge dispersal by H-bonding will increase the effective distance, *r*, and markedly reduce the polarizability effect.

The prerequisites for large ELS terms contributing to the relative solvation energies, $-\delta_R\Delta G^0_{aq}(BH^+)$ and $-\delta_R\Delta H^0_{aq}(BH^+)$ values of Table I (or $-\delta_R\Delta H^0_{FSO_3H}(BH^+)$ values of Table II) are substituted onium ions with strong H-bond donor protons and good H-bond acceptor solvents. When these prerequisites are not met, polarizability effects of hydrocarbon substituents on proton transfer energetics are nearly as large in solution as in the gas phase.[13,33]

As illustrated in Table III, the unfavorable contributions of hydrocarbon substituents to the sum of CAV, STR, and VWD terms tend to be compensated between entropy effects (e.g., in Table VI) and enthalpy effects. Thus these terms tend to make large favorable contributions to $-\delta_R\Delta H^0_{aq}(BH^+)$, and relatively small unfavorable contributions to $-\delta_R\Delta G^0_{aq}(BH^+)$ values. Important consequences follow, which can be depicted only on a qualitative basis at present.

Values of $-\delta_R\Delta G^0_{aq(BH^+)}$ have major contributions from favorable HB terms (which decrease as protons are replaced by hydrocarbon substituents), and from unfavorable polarizability effects (ELS terms, cf. Table III and Discussion) which for oxonium and ammonium ions also decrease with increasing numbers of polarizable hydrocarbon substituents. Thus, unless the number and kind of proton in BH^+ is held constant, these two major contributions will be complementary and values of $-\delta_R\Delta G^0_{aq(BH^+)}$ will be complex.

Values of $-\delta_R\Delta H^0_{aq(BH^+)}$ have major favorable contributions from the HB terms and from the sum of CAV, STR, and VWD terms as well as the unfavorable polarizability effect ELS terms (for oxonium and ammonium ions). The latter two contributions are opposed and tend to cancel since they have a qualitatively similar dependence upon the hydrocarbon structure. Thus, $-\delta_R\Delta H^0_{aq(BH^+)}$ values are primarily dependent upon the number and kind of acidic protons, i.e., the favorable HB terms. Table I clearly shows $-\delta_R\Delta H^0_{aq(BH^+)}$ values to be markedly superior to $-\delta_R\Delta G^0_{aq(BH^+)}$ values in reflecting this feature of ion structure.

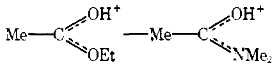
The polarizability effects of hydrocarbon substituents may be best estimated from the values of $-\delta_R\Delta G^0_{aq(BH^+)}$ for onium ions, which have the same number and kind of acidic proton. With this prescription, HB terms tend to remain constant as does also the opposed enthalpy and entropy contributions from the total of CAV, STR, and VWD terms. Thus, for example, the 7.7 or the 7.4 kcal less favorable $-\delta_R\Delta G^0_{(aq)}(BH^+)$ values for $t\text{-}BuNH_3^+$ compared to $MeNH_3^+$ or Et_2OH^+ compared to Me_2OH^+, respectively, are primarily due to the differential polarizability effects (ELS terms). As required for consistency,[4a] it will be noted that there are only very small differences in $\Delta G^0_{(aq)}$ values (for reaction 1 in aqueous solution) for both members of each of these pairs of onium ions. This (or similar) evaluation of polarizability effects cannot be accepted as quantitative, since, in addition to contributions arising from inexact compensation of CAV, STR, and VWD terms, there may also be some smaller contributions from dipolar inductive effects and from steric effects on the HB terms.

Dipolar Substituent Effects on HB Terms. The best current method of eliminating polarizability effect ELS terms in the solvation energies is to limit the comparison of onium ions to those ions having substituents of essentially the same polarizability.[5d] In Table XI, differences in the free energies and enthalpies of transfer from the gas phase to aqueous solution are given for a number of pairs of onium ions which are so related.

Since there are only minimal contributions to these differences in hydration energies from CAV, STR, VWD, and ELS terms, we believe that HB terms predominate. The effect of a CF_3 substituent compared to a Me substituent is to substantially increase the solvation energy, both in aliphatic ammonium ions and in 4-substituted pyridinium ions. This result is attributable to the electron-withdrawing CF_3 dipolar substituent effect, which increases the HB term.[8] Similar, but appreciably smaller, electron-withdrawing effects for aryl and alkenyl substituted ammonium ions compared to their aliphatic substituted counterparts are also indicated by the HB terms in Table XI.

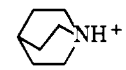
Steric and Resonance Effect Contributions. These contributions are difficult to evaluate because of the current lack of data on appropriate model compounds. However, the 2.6 kcal

Table **XII.** Differential Heats of Transfer of HCSP Pairs of Onium Ions into Fluorosulfuric Acid (in kcal mol^{-1})

B_1H^+-B_2H^+	$-\delta H^{g\rightarrow FSO_3H}_{(BH^+)}$	Calcd[a]	B_1H^+-B_2H^+	$-\delta\Delta H^{g\rightarrow FSO_3H}_{(BH^+)}$	Calcd[a]
OH_3^+-NH_4^+	7.4	7.0	NH_4^+-PH_4^+	15.5	16.0
$MeOH_2^+$-$MeNH_3^+$	0.7	1.0	Me_3NH^+-Me_3PH^+	4.3	4.0
$EtOH_2^+$-$EtNH_3^+$	−0.2	1.0	NH_4^+-SH_3^+	8.5	8.0
Me_2OH^+-$Me_2NH_2^+$	−3.1	−5.0	$Me_2NH_2^+$-Me_2SH^+	8.8	10.0
Et_2OH^+-$Et_2NH_2^+$	−4.4	−5.0	$Et_2NH_2^+$-Et_2SH^+	7.3	10.0
OH_3^+-SH_3^+	15.9	15.0	SH_3^+-PH_4^+	7.0	8.0
Me_2OH^+-Me_2SH^+	5.7	5.0	Me_2COH^+-Me_2SOH^+	0.9	0.0
Et_2OH^+-Et_2SH^+	2.9	5.0		−0.9	0.0

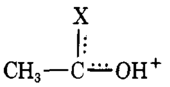
[a] Calculated using 17.0 for each -OH$^+$, 12.0 for each -SH$^+$, 11.0 for each -NH$^+$, 7.0 for each -PH$^+$.

greater enthalpy of solution of



than Et_3NH^+ (Table I) must surely be attributed largely to the greater steric hindrance to the $NH^+\cdots(OH_2)_n$ H-bonding for Et_3NH^+. The value of $\delta_{aq}\Delta G^0$ for 2,6-di-*tert*-butylpyridinium ion is 10.5 kcal more negative than that for pyridinium (Table I). The much poorer solubility in water of the 2,6-di-*tert*-butylpyridine means that the corresponding difference in $-\delta_R\Delta G^0_{aq}(BH^+)$ values will be substantially more negative yet. Even so, until results for an appropriate model compound are available to evaluate the polarizability effect and other contributions due to the *tert*-butyl groups, a quantitative assessment of the apparent steric hindrance to solvation cannot be made.

In the series of substituted oxonium ions



$$CH_3—\overset{\overset{X}{\vdots}}{C}\cdots OH^+$$

where X = CH_3, OEt, and NMe_2,[34] there is in this order increasing internal delocalization of the positive charge (resonance effect). The enthalpies of aquation of the gaseous cations decrease in this order by X = CH_3 → OEt, 3.2 kcal and X = OEt → NMe_2, 13.9 kcal. These large substituent effects appear to indicate that HB terms do decrease as the H-bond donor ability of the OH^+ hydration site becomes less due to the internal delocalization of the positive charge.[35] However, here too data for appropriate model compounds are required to make more certain assessments.

Medium Effects on Process 6. Fluorosulfuric Acid Solution Results. The solvent effects of FSO_3H on the proton transfer process 6, $\delta_{FSO_3H}\Delta H^0$ values of Table II range over 41 kcal mol^{-1}. As in water (Table I), the FSO_3H effects are associated predominantly with differences in onium ion solvation energies. Neutral base effects, however, are not trivial, as shown by the range of 9.5 kcal mol^{-1} for $\delta_R\Delta H_{(B)}$ values of Table II.

Relative Heats of Transfer of Onium Ions from the Gas Phase to Fluorosulfuric Acid Solution. The heats of solvation of onium ions relative to NH_4^+, $-\delta_R\Delta H_{FSO_3H}(BH^+)$ values of Table II, increase with increasing number and H-bond donor ability of the protonic solvation sites in the ion. There are no exceptions to this rule within one's ability to apply it. The use of onium ions with the same hydrocarbon content and substitutional pattern at the central atom to minimize any CAV, STR, and ELS terms in the enthalpies of solvation in the fluorosulfuric acid is especially rewarding. In Table XII are given differences in $-\delta_R\Delta H^{g\rightarrow FSO_3H}_{(BH^+)}$ values for an extensive variety of HCSP pairs of cations. The differences in heats of solution for these pairs of onium ions are given to relatively good approximation by the number and kind of protonic sites in the ions. This agreement is shown by calculated values in Table XII which are based upon the following HB term assignments: 17.0 kcal for each -OH$^+$, 12.0 kcal for each SH$^+$, 11.0 kcal for each NH$^+$, and 7.0 kcal for each PH$^+$. Better agreement yet can be achieved if the binding energy associated with each kind of proton site is decreased with successive solvations, i.e., for example, 1st NH$^+$ > 2nd NH$^+$ > 3rd NH$^+$. However, in the absence of gas phase attachment energies for FSO_3H molecules, the number of parameters required is unwarranted.

Table XIII. Differential Heats of Transfer Closely Related Gaseous Onium Ions into Fluorosulfuric Acid (in kcal mol^{-1})

B_1H^+-B_2H^+[a]	$-\delta\Delta H^{g\rightarrow FSO_3H}_{(BH^+)}$
4-CF_3pyrH$^+$-4CH_3pyrH$^+$	7.4
$CF_3CH_2NH_3^+$-$CH_3CH_2NH_3^+$	5.7
$CH_3C{\equiv}NH^+$-CH_3CH_2-NH_3^+	−6.2

[a] Substituents in these bases pairs have approximately the same polarizability (cf. ref 3b).

In fluorosulfuric acid solution, the solvation energies depend in particular on the number of protonic sites present in the onium ion, with much less dependence (compared to the results in water) on the type of protonic site. Thus, the results in Table XII show that two (or three) NH$^+$ sites lead to greater heats of solvation in FSO_3H than does a single OH$^+$ site and that two OH$^+$ sites are essentially equivalent to three NH$^+$ sites.

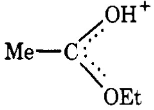
Similar results are obtained for pairs of onium ions having substituents with similar polarizabilities (Table XIII). The enthalpy of solution in fluorosulfuric acid is 6 kcal greater for $CH_3CH_2NH_3^+$, with three -H$^+$ protons, than for $CH_3C{\equiv}NH^+$ with a single (but more acidic) NH$^+$ proton. Table XIII does show that the dipolar electron-withdrawing CF_3 substituent substantially increases the solvation energy of NH$^+$ protonic sites in FSO_3H solution.

Comparison of Relative Enthalpies of Solution of Gaseous Onium Ions in Water and in Fluorosulfuric Acid. HB Terms. The range of $-\delta_R\Delta H^0_{aq}(BH^+)$ values (Table II) is only about 30 kcal mol^{-1} compared to about 50 kcal mol^{-1} for $-\delta_R\Delta H^0_{aq}(BH^+)$ values (Table I) for the same onium ions. The HB solvation terms from Tables IX and XII show substantial reductions in FSO_3H compared to H_2O. The solvent FSO_3H is revealed as a less selective one than water in H-bonding solvation of the onium ion protonic sites. This result is one that is strongly suggested by the nature of these solvents, namely, that the much greater acid strength of FSO_3H would be accompanied by poorer H-bond accepting power. In Table XIV are given the HB solvation terms for the unsubstituted onium ions derived from Tables IX and XII for H_2O and FSO_3H solvent systems. The greatest reduction in HB solvation energy terms for FSO_3H compared to water is for the most highly solvated cation, i.e., H_3O^+. This feature (and others) of the leveling of HB terms which occurs in FSO_3H compared to H_2O is clearly evident through the comparative results of Table XIV.

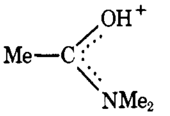
Table XIV. Approximate HB(BH^+;s) Terms in the Heats of Solvation of Unsubstituted Onium Ions in H_2O and FSO_3H Solutions (in kcal mol^{-1})

	HB[BH^+;$(H_2O)_n$]	HB(BH^+;FSO_3H)	Δ
H_3O^+	76	51	25
NH_4^+	56	44	12
SH_3^+	~50	36	~14
PH_4^+	~30	28	~2

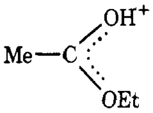
One additional feature which evidently results from the poorer H-bond acceptor ability of FSO_3H compared to H_2O as solvent is worthy of special note. The onium ions, Me_2COH^+ and Me_2SOH^+, have nearly equal solvation enthalpies in FSO_3H, as do also the pair



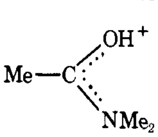
and



(cf. Table XII and ref 34 and 35). However, in aqueous solution the heat of solvation of Me_2COH^+ is 10.4 kcal greater than that of Me_2SOH^+ and, likewise, that for

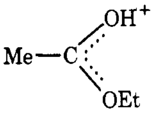


is 13.9 kcal greater than the value for

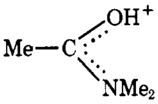


(Table I). The $-\delta_R\Delta H^0_{FSO_3H}(BH^+)$ values for all four of these onium ions are leveled to essentially the same 4-5 kcal/mol range as for the saturated Me_2OH^+ and Et_2OH^+ oxonium ions (cf. Table II).

Evidently, while the delocalization of charge internally within the ion reduces the OH^+ H-bond donor ability (and consequently, the solvation energies in both solvents), in fluorosulfuric acid the effects are of small magnitude. In contrast, it seems apparent that in water there is an interesting competition between effects of internal delocalization of charge vs. external dispersal of charge by hydrogen bonding. If the stabilization by internal delocalization of charge is only moderate or small, then the HB[BH^+;$(H_2O)_n$] terms are also relatively large, approaching that for the dialkyloxonium ions of similar hydrocarbon content, as for Me_2COH^+ and



However, if the internal delocalization of charge produces major stabilization of the ion, as with $Me_2S\overset{\cdots}{-}OH^+$ and



then HB[BH^+;$(H_2O)_n$] terms are also relatively small.

In the next section we examine the differences in the relative heats of solution between water and fluorosulfuric acid of onium ions with "saturated" substituents.

Relative Heats of Transfer of Onium Ions from Water to Fluorosulfuric Acid. From the values of $-\delta_R\Delta H^0_{aq}(BH^+)$ of Table I and the corresponding values of $-\delta_R\Delta H^0_{FSO_3H}(BH^+)$ of Table II, one obtains the heat of transfer of BH^+ relative to NH_4^+ from water to fluorosulfuric acid, $-\delta_R\Delta H^{H_2O\rightarrow FSO_3H}_{(BH+)} = -\delta_R\Delta H^0_{FSO_3H}(BH^+) + \delta_R\Delta H^0_{aq}(BH^+)$. These results are examined in Table XV for unsubstituted H_3O^+ and NH_4^+ and for onium ions with saturated hydrocarbon or fluorocarbon substituents.

Surprisingly, in view of possible complex STR terms in water, the relative heats of transfer from water to fluorosulfuric acid (Table XV) are not reliably different within the combined experimental errors for oxonium or ammonium ions which have the same number of substituents. That is, the differential heats of solvation seem to depend principally upon the HB features of structure, i.e., number and principally the type of protonic solvation sites. The results are, in kcal mol^{-1}, relative to NH_4^+: H_3O^+, 14.0; ROH_2^+, 13.5 ± 0.5; R_2OH^+, 12.8 ± 0.6; RNH_3^+, −0.3 ± 0.4; $R_2NH_2^+$, −1.8 ± 0.6; R_3NH^+, −4.8 ± 0.2 (average values and errors are given). These remarkable results further emphasize the importance of making comparisons in enthalpies of solvation between ions which have the same or nearly the same hydrocarbon content and substitution pattern when transfer energies from the gas phase are considered. We have shown earlier that this requirement is even more important for the corresponding free energies of aquation. However, for transfers between solvents in which HB(BH^+;s) terms are similar, ELS terms due to changes in stabilization of onium ions by polarizable substituents are small. Thus, much wider variations in structural features of the onium ions are permitted with some degree of assurance that ELS, CAV, VWD, and STR terms make small contributions to the energies of transfer between such solvents.

The heats of transfer between water and fluorosulfuric acid for onium ions with "saturated" substituents correlate with indicator activity coefficient (solvation) behavior observed in the H_2O-H_2SO_4 binary system. The Bunnett-Olsen treatment[36] makes it possible to express this behavior in H_2O-H_2SO_4 mixtures in terms of the parameter φ_e:

$$\varphi_e = \frac{\log (f_{(XH^+)}/f_X) - \log (f_{BH^+}/f_B)}{-H_0 - \log (C_{H^+})}$$

where f's depend upon the free energy of transfer from dilute

Table XV. Heats of Transfer of BH^+ Relative to NH_4^+ from Water to Fluorosulfuric Acid (in kcal mol^{-1})

BH^+	$-\delta_R\Delta H^{H_2O\rightarrow FSO_3H}_{s(BH+)}$	φ_e	BH^+	$-\delta_R\Delta H^{H_2O\rightarrow FSO_3H}_{s(BH+)}$	φ_e
H_3O^+	14.0	1.0	*n*-$PrNH_3^+$	0.2	~0.0
$MeOH_2^+$	13.0	0.87	*i*-$PrNH_3^+$	−1.8	~0.0
$EtOH_2^+$	13.9	0.86	*n*-$BuNH_3^+$	+0.8	~0.0
Me_2OH^+	13.4	0.82	*t*-$BuNH_3^+$	−0.6	~0.0
Et_2OH^+	12.2	0.78	$Me_2NH_2^+$	−2.3	−0.05
NH_4^+	0.0	~0.0	$Et_2NH_2^+$	−1.2	−0.05
$MeNH_3^+$	−1.1	~0.0	Me_3NH^+	−5.2	−0.4
$CF_3CH_2NH_3^+$	0.0	~0.0	Et_3NH^+	−4.9	−0.4
$CH_3CH_2NH_3^+$	0.1	~0.0	4-CF_3pyrH^+	−5.5	−0.4
			pyrH^+	−4.8	−0.4
			4-MepyrH^+	−4.4	−0.4

aqueous solution to concentrated acid solution of the general base X and its conjugate acid XH^+, or the Hammett aniline indicator B and its conjugate acid BH^+ (for which $\varphi_e \equiv 0$). Values of φ_e from ref 4e and 5f are listed in Table XV and are shown to correlate with $-\delta_R\Delta H_{(BH^+)}^{H_2O\rightarrow FSO_3H}$ values. This correlation evidently follows from the greater variation in solvation energies of XH^+ than of X (since strictly φ_e values depend upon both XH^+ and X) and in approximately proportionally reduced $HB(BH^+;s)$ terms in the transfer between water and concentrated H_2O–H_2SO_4 mixtures as compared with the corresponding transfer between water and FSO_3H solutions.

Finally, we wish to note that the conclusions reached in this work are further supported by evidence on solvation effects observed recently for excited state BH^+ species.[37]

References and Notes

(1) This work has been supported in part by grants from the National Science Foundation (UCI, UP, CIT), the Public Health Service (UCI), the Energy Research and Development Administration (CIT), and CNR (Rome).

(2) Camille and Henry Dreyfus Teacher-Scholar (CIT), 1971–1976.

(3) (a) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977); (b) R. H. Staley, M. Taagepera, W. G. Henderson, I. Koppel, J. L. Beauchamp, and R. W. Taft, *ibid.*, **99**, 326 (1977).

(4) The following references give rather extensive summaries from the literature. Other values are cited specifically in Table I. (a) R. W. Taft, in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975, Chapter 2; (b) E. M. Arnett, *ibid.*, Chapter 3; (c) F. M. Jones III and E. M. Arnett, *Prog. Phys. Org.Chem.*, **11**, 263 (1974); (d) P. Bonvicini, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, *J. Am. Chem. Soc.*, **95**, 5960 (1973); (e) G. Perdoncin and G. Scorrano, *ibid.*, in press.

(5) (a) E. M. Arnett, *Acc. Chem. Res.*, **6**, 404 (1973); (b) E. M. Arnett, F. M. Jones III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4724 (1972); (c) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972); (d) R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *ibid.*, **95**, 3811 (1973); (e) E. M. Arnett and J. F. Wolf, *ibid.*, **97**, 3262 (1975); (f) E. M. Arnett and G. Scorrano, *Adv. Phys. Org. Chem.*, **13**, 83 (1976).

(6) (a) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949); (b) C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 1572 (1969); **74**, 3900 (1970); **75**, 388, 3606 (1971); (c) ref 4b,c; (d) R. P. Bell, "The Proton in Chemistry", Cornell University Press, Ithaca, N.Y., 1975; (e) J. E. Gordon, "The Organic Chemistry of Electrolyte Solutions", Wiley, New York, N.Y., 1975, Chapter 2; (f) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 318 (1976).

(7) Cf. E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, *J. Am. Chem. Soc.*, **96**, 3875 (1974).

(8) E. M. Arnett, B. Chawla, L. Bell, M. Taagepera, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5729 (1977); cf. also W. F. Reynolds, P. G. Mezey, W. J. Hehre, R. D. Topsom, and R. W. Taft, *ibid.*, **99**, 5821 (1977).

(9) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

(10) E. M. Arnett and D. R. McKelvey in "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 6.

(11) Cf. S. D. Haman, "Physico-Chemical Effects of Pressure", Academic Press, New York, N.Y., 1957, p 151.

(12) J. F. Wolf, J. M. Abboud, and R. W. Taft, *J. Org. Chem.*, **42**, 3316 (1977).

(13) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957).

(14) According to this theory an average of about 5 eu per NH^+ is lost, but $-\delta_R\Delta S_{aq}^{HB}(BH^+)$ is nonlinear in the number of and dependent upon the size of the substituent groups. Also, greater entropy loss for H-bond hydration of OH^+ than NH^+ is expected. Reference 6e, pp 213–214, gives a recent summary.

(15) (a) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Am. Chem. Soc.*, **89**, 6393 (1967); (b) M. De Paz, A. G. Guidoni, and L. Friedman, *J. Chem. Phys.*, **52**, 687 (1970).

(16) J. D. Payzant, A. Cunningham, and P. Kebarle, *Can. J. Chem.*, **51**, 3242 (1973).

(17) Cf. M. D. Newton and S. Ehrenson, *J. Am. Chem. Soc.*, **93**, 4971 (1971).

(18) K. Hiraoka, E. P. Grimsrud, and P. Kebarle, *J. Am. Chem. Soc.*, **96**, 3359 (1974).

(19) $\Delta G^0 = -7.3$ kcal/mol for $Me_3NH^+ + H_2O \rightarrow Me_3NH^+\cdots OH_2$, private communication from P. Kebarle to D.H.A. as quoted in ref 6f, footnote 33.

(20) E. Grunwald, G. Baughman, and G. Kohnstam, *J. Am. Chem. Soc.*, **82**, 5801 (1960).

(21) P. Kebarle in "Ions and Ion-Pairs in Organic Reactions", M. Szwarc, Ed., Wiley-Interscience, New York, N.Y., 1972.

(22) (a) G. W. Brady and J. T. Krause, *J. Chem. Phys.*, **27**, 304 (1957); (b) G. W. Brady, *ibid.*, **28**, 464 (1958).

(23) L. Pauling, "Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1944, p 346.

(24) Frank (ref 9) adds an increment of 2.8 Å for "waters of the first hydration shell".

(25) For comparison, figures arrived at in the same manner (ref 21) are for $Li(OH_2)_4^+$, 35 kcal; $Na(OH_2)_4^+$, 33 kcal; $Rb(OH_2)_4^+$, 27 kcal; $Cs(OH_2)_4^+$, 24 kcal.

(26) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

(27) Cf. ref 6e, p 217, for a recent summary.

(28) M. F. C. Ladd, *Z. Phys. Chem.* (*Frankfurt am Main*), **72**, 91 (1970).

(29) M. De Paz, S. Ehrenson, and L. Friedman, *J. Chem. Phys.*, **52**, 3362 (1970).

(30) R. E. Burton and J. Daly, *Trans. Faraday Soc.*, **67**, 1219 (1971).

(31) Cf. ref 6e, pp 209–215.

(32) Cf. J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Am. Chem. Soc.*, **93**, 3914 (1971).

(33) E. M. Arnett and J. F. Wolf, *J. Am. Chem. Soc.*, **95**, 978 (1973).

(34) For references regarding evidence on the protonation sites of esters and amides in solution and in the gas phase, cf. ref 3a.

(35) A. Levi, G. Modena, and G. Scorrano, *J. Am. Chem. Soc.*, **96**, 6585 (1974).

(36) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899 (1966).

(37) B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, submitted.

Vinyl Ether Hydrolysis. 10. Methyl α-Cyclopropylvinyl Ether. A Search for a Change in Reaction Mechanism[1]

A. J. Kresge* and W. K. Chwang

Contribution from the Department of Chemistry, Scarborough College, University of Toronto, West Hill, Ontario M1C 1A4 Canada. *Received August 10, 1977*

Abstract: The rate of hydrolysis of methyl α-cyclopropylvinyl ether catalyzed by H_3O^+, H_2O, seven carboxylic acids, six monohydrogen phosphonate anions, two ammonium ions, and biphosphate ion was measured in wholly aqueous solution at 25 °C. These data, the isotope effect on the H_3O^+ reaction, and a lack of isotopic exchange of the substrate in D_2O solution all point to an unchanging rate-determining proton transfer mechanism for this reaction. It is inferred from this constancy of mechanism that the second step of this reaction, hydration of the alkoxycarbonium ion intermediate, is subject to general base catalysis. The combined carboxylic acid and phosphonate anion catalytic coefficients give a curved Brønsted relation from which the Marcus theory parameters $\Delta G_0^{\ddagger} = 6$ kcal/mol and $w^r = 4$ kcal/mol are derived.

The acid-catalyzed hydrolysis of simple vinyl ethers occurs through electrophilic addition of H^+ to a carbon–carbon double bond (eq 1); the alkoxycarbonium ion thus formed then reacts with water to give a hemiacetal or hemiketal intermediate (eq 2), which itself undergoes rapid decomposition to alcohol and aldehyde or ketone products (eq 3).

In very nearly all examples of this reaction, the carbon protonation step is rate determining, i.e. in these cases, reversal

0002-7863/78/1500-1249$01.00/0