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Oxonium Ions. Solvation by Single Acetonitrile Molecules in the Gas Phase and by Bulk Solvents¹

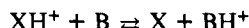
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Abstract: The standard free energies of formation of gaseous complexes between monoprotic oxonium ions and acetonitrile have been obtained by using the ion cyclotron resonance equilibrium constant method for exchange of acetonitrile between the ions. The results show that the "solvation" by a single molecule of acetonitrile in the gas phase reproduces the important diverse effects of molecular structure on oxonium ion solvation by bulk water. It is estimated from the present results that the effects of solvation by bulk water are only about three times as great as the corresponding effects of "solvation" by a single water molecule in the gas phase. Internal charge delocalization from the protonic site of the oxonium ion strongly reduces solvation. Proton transfer between charge-localized and charge-delocalized oxonium ions may be reversed by differential solvation, both with single H-bonding molecules in the gas phase and with bulk solvent. Further evidence for the site of preferred protonation of esters and amides is provided.

Analysis of protonation equilibria for weak oxygen (and other bases) (X) in aqueous mineral acid mixtures, e.g.,



(where B is a Hammett primary aniline base²) has been accomplished by the use of the Bunnett–Olsen relationship.³

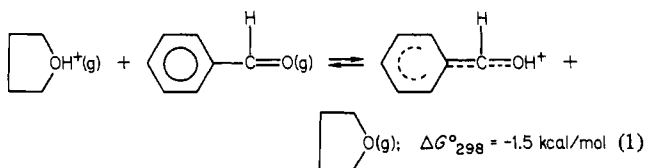
$$\log [(\text{XH}^+)/(\text{X})] + H_0 = \phi(H_0 + \log [\text{H}^+]) + pK_{\text{XH}^+}$$

H_0 is the Hammett acidity function = $(-\log[\dot{a}_{\text{H}^+}/f_{\text{BH}^+}])$, (H^+) is the stoichiometric concentration of H^+ , and pK_{XH^+} is the thermodynamic value for the acid dissociation of XH^+ referred to the standard state of infinite dilution in water. The results of this analysis lead Levi, Modena, and Scorrano^{4b} to conclude that the more internally delocalized the positive charge of the oxonium ion, the weaker is the hydrogen bonding between water and the protonic site, as expressed by the decreased value of the parameter ϕ . The consequence of substantially different ϕ values for two oxygen bases of the same family (cf. Results) may be an inversion of basicity order between dilute and concentrated acid solutions.⁴ Thus, acetophenone, which is intrinsically more basic than acetone, has a smaller ϕ value (cf. Table II) because its conjugate acid has the greater internal charge delocalization, and thus poorer solvation. Therefore, while acetophenone is a stronger base than acetone in concentrated acid solution (or the gas phase), it becomes the weaker base in dilute acid solution because of the greater solvation of the conjugate acid of acetone. The evaluation of the relative free energies and heats of transfer from the gas phase to dilute solutions either in water or fluorosulfuric acid has recently been reported for a small but varied series of oxonium ions.⁵ These results also support the analysis of Levi, Modena, and Scorrano.

Single molecule solvation of gaseous ions by hydrogen bonding has been recently studied by high-pressure mass spectrometry,⁶ flowing afterglow,⁷ and ion cyclotron resonance spectrometry.⁸ It has been clearly established by these means that single molecule solvation of both cations and anions reduces the inherent effects of substitution on ion stabilities.⁹ However, only one previous study^{6c} has compared the effects of single molecule solvation in the gas phase for an extended series of substituted organic ions with the corresponding effects of solvation by bulk water. For relatively weakly solvated 3- and 4-substituted pyridinium ions, it was found that solvation effects of a single gaseous water molecule are only about 20% of that for corresponding effects of bulk water.

In this paper we have employed an extended series of monoprotic oxonium ions and found that the relatively large effects

of oxonium structure on solvation by bulk water are faithfully and discriminately reflected in the gas phase by the relative hydrogen bonding energies of these ions with a single molecule of acetonitrile. For example, the greater charge delocalization (and stabilization by polarization) in the conjugate acid of benzaldehyde leads to greater gas phase basicity than that for tetrahydrofuran⁹ (cf. Table II):



We observe by direct measurement (cf. Experimental Section) a reversal in the position of equilibrium in the gas phase when this proton transfer reaction takes place with both ions bound by

(1) This work has been supported in part by grants from the National Science Foundation (UCI), the Public Health Service (UCI), and CNR (Rome). This work is part of an U.S.A.–Italy Cooperative Science Program and Grant No. 1790 with NATO.

(2) L. P. Hammett, "Physical Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1970.

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

(4) (a) P. Bonvicini, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, *J. Am. Chem. Soc.*, **95**, 5960 (1973); (b) A. Levi, G. Modena, and G. Scorrano, *ibid.*, **96**, 6585 (1974); (c) G. Perdoncin and G. Scorrano, *ibid.*, **99**, 6983 (1977).

(5) R. W. Taft, J. F. Wolf, J. L. Beauchamp, G. Scorrano, and E. M. Arnett, *J. Am. Chem. Soc.*, **100**, 1240 (1978).

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(7) (a) G. I. Mackay and D. K. Bohme, *J. Am. Chem. Soc.*, **100**, 327 (1978); (b) F. C. Fehsenfeld, I. Dotan, D. L. Albritton, C. J. Howard, and E. E. Ferguson, *J. Geophys. Res.*, **83**, C3, 1333 (1978); (c) D. K. Bohme, G. I. Mackay, and S. D. Tanner, *J. Am. Chem. Soc.*, **101**, 3724 (1979).

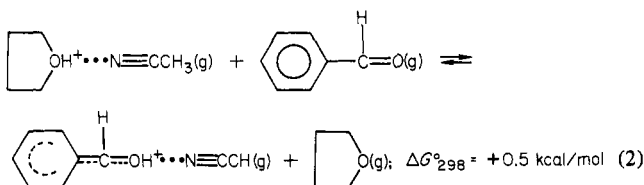
(8) (a) R. T. McIver, Jr., J. A. Scott, and J. M. Riveros, *J. Am. Chem. Soc.*, **95**, 2706 (1973); (b) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4762 (1972); (c) D. H. Aue, H. M. Webb, and M. T. Bowers, Abstracts, Twenty-First Conference on Mass Spectrometry and Applied Topics, San Francisco, May 20–25, 1973, p 183; (d) unpublished results of J. F. Wolf, R. T. McIver, Jr., and R. W. Taft, quoted in R. W. Taft, "Proton Transfer Reactions", E. F. Caldin and V. Gold, Eds., Chapman and Hall, London, 1975, p 31.

(9) For recent discussions of structural effects on gas-phase basicities, cf.: (a) R. W. Taft in "Kinetics of Ion-Molecule Reactions", P. Ausloos, Ed., Plenum Publishing Corp., 1979, pp 271–293; (b) D. H. Aue and M. T. Bowers in "Gas-phase Ion Chemistry", Vol. 2, M. T. Bowers, Ed., Academic Press, New York, 1979, p 1; (c) also R. W. Taft, M. Taagepera, J. L. M. Abboud, J. R. Wolf, D. J. DeFrees, W. J. Hehre, J. E. Bartmess, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **100**, 7765 (1978).

[†] University of California—Irvine.

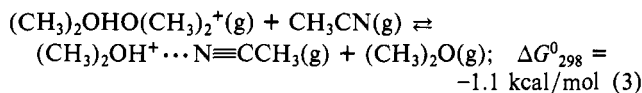
[‡] Istituto di Chimica Organica.

a single molecule of acetonitrile:

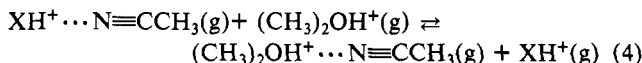


The greater "solvation" of the more charge-localized conjugate acid of tetrahydrofuran reverses the basicity order.

Acetonitrile has been selected for this study because it is a moderately good hydrogen bond acceptor but has a relatively low proton affinity and minimal steric requirements. The standard free energy of binding of acetonitrile to dimethyloxonium ion in the gas phase has been found to be -23.0 kcal/mol. This figure is obtained from the standard free energy of binding (-21.9 kcal/mol) of dimethyl ether to dimethyloxonium ion as obtained by Kebarle,¹⁰ and our result for reaction 3. More highly sub-



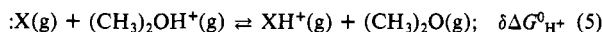
stituted monoprotonic oxonium ions bind acetonitrile less firmly. The standard free energy decrease in binding of acetonitrile to these ions, relative to that for dimethyl oxonium ion, $\delta\Delta G^\circ_{+\text{MeCN}}$, is given by



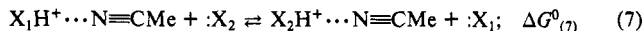
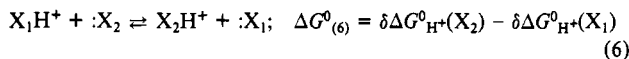
The results are compared with the corresponding relative free energies of transfer, $-\delta\Delta G^\circ_{(\text{aq})}(\text{XH}^+)$, of the oxonium ions from the gas phase to dilute solutions in bulk water. The thermodynamic cycle and methods employed to obtain $-\delta\Delta G^\circ_{(\text{aq})}(\text{XH}^+)$ values are given in detail in ref 5.

Experimental Section

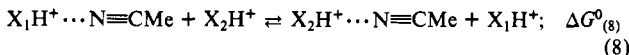
The gas phase basicities of the oxygen bases in this study were determined by the pulsed ion cyclotron resonance method for determination of the equilibrium constant for proton transfer, as previously described in detail.^{11,12} The results reported herein have been corrected for an ICR cell temperature factor which has been shown subsequently to apply. This correction increases the ΔG°_{300} values of ref 12 by a factor of 1.067. The gas phase basicity of the oxygen base, X, relative to that for dimethyl ether is given by reaction 5. These $\delta\Delta G^\circ_{\text{H}^+}$ values are recorded in Table II.



In order to obtain the $-\delta\Delta G^\circ_{+\text{MeCN}}$ values for reaction 4, an extensive series of overlapping equilibria were obtained for pairs of oxygen bases (X_1 and X_2 , starting with $\text{X}_1 = \text{O}(\text{CH}_3)_2$) for both of the following type reactions:



From the difference $\Delta G^\circ_{(7)} - \Delta G^\circ_{(6)}$, one obtains $\Delta G^\circ_{(8)}$ for the relative free energy of binding of acetonitrile to the cations X_1H^+ and X_2H^+ :



Reaction 7 was carried out with use of methods similar to those employed for reaction 6, except that the experiments are performed in the presence of a 10–100-fold excess of acetonitrile over the two oxygen bases, X_1 and X_2 . As shown in Figure 1 (which is typical except for the additional formation of a homodimer—cf. below), the conjugate acids, X_1H^+ and X_2H^+ , are rapidly formed and react away to their acetonitrile

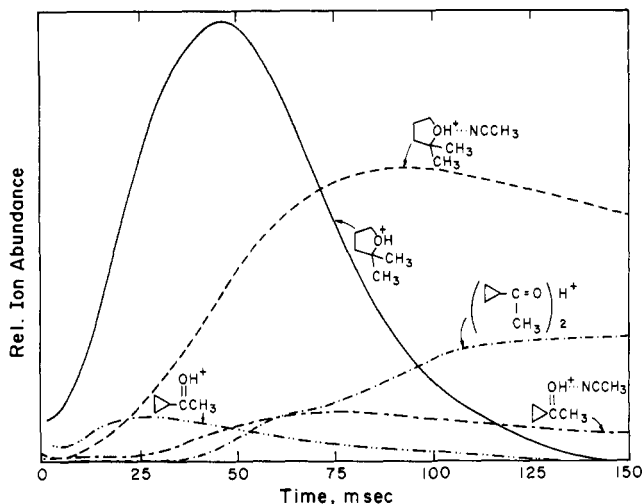


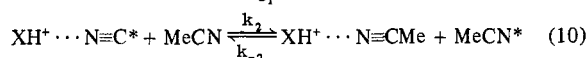
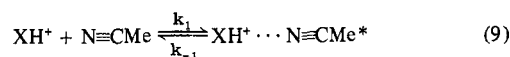
Figure 1. Time plot for the proton transfer reaction between 2,2-dimethyltetrahydrofuran and methyl cyclopropyl ketone in the presence of a large excess of acetonitrile: ordinate, relative ion abundances; abscissa, time (ms). The experimental conditions were CH_3CN , $p = 2.58 \times 10^{-5}$; $\text{CCCC}(\text{CH}_3)_2\text{O}$, $p = 1.35 \times 10^{-6}$; $\text{CCCC}(\text{O})\text{CH}_3$, $p = 8.4 \times 10^{-7}$ (in torr); magnetic field strength = 18.3 kG.

heterodimers, when the oxygen bases are at typical pressures of ca. 2×10^{-7} torr. At acetonitrile pressures of $\sim 10^{-5}$ torr, the relative peak intensity of $[\text{X}_2\text{H}^+\cdots\text{N}\equiv\text{CMe}]/[\text{X}_1\text{H}^+\cdots\text{N}\equiv\text{CMe}]$ reaches a steady state in approximately 200 ms. This quotient obeys the equilibrium constant expression for reaction 7, as a function of the $[\text{X}_1]/[\text{X}_2]$ ratio. A constant magnetic field strength of 12 kG (or greater) was employed in all experiments to ensure a nearly constant ion loss for the two heterodimers. The chemical equilibrium condition was confirmed by the use of multiple overlaps as shown in Figure 2, employing a variety of oxygen bases. The overlap agreement confirms our estimated general precision of $\Delta G^\circ_{+\text{MeCN}}$ values of ± 0.3 kcal/mol.

As the gas phase basicity increases, especially with charge delocalization in the oxonium ion, the proton bound homodimer, X_2H^+ , becomes more thermodynamically stable than the acetonitrile bound oxonium ion.¹³ For example, we have found that the proton bound homodimer of methyl cyclopropyl ketone is 2.5 kcal/mol more stable than the acetonitrile bound conjugate acid of methyl cyclopropyl ketone. Nevertheless, as Figure 1 shows, using the conditions specified above, the proton bound homodimer forms much more slowly than the acetonitrile heterodimer, since $\text{MeCN}/\text{CCCC}(\text{O})\text{CH}_3 = 31$. There is no evidence from the steady state region of Figure 1 that the relative intensity $[\text{X}_2\text{H}^+\cdots\text{N}\equiv\text{CMe}]/[\text{X}_1\text{H}^+\cdots\text{N}\equiv\text{CMe}]$ is appreciably affected by the homodimer formation. Thus in Figure 1 this quotient is 9.3 at 100 ms, 10.1 at 135 ms, and 10.4 at 150 ms, where $\text{X}_2 = \text{CCCC}(\text{CH}_3)_2\text{O}$ and $\text{X}_1 = \text{CCCC}(\text{O})\text{CH}_3$. We obtain, therefore, $\Delta G^\circ_{(7)} = [(-1.99)(323) - (-10^{-3})]/\ln[(8.4)(10)/(13.5)] = -1.2$ kcal/mol with an estimated uncertainty of ± 0.3 kcal/mol.

No homodimer of the 2,2-dimethyltetrahydrofuran or heterodimer of ether and ketone bases could be detected under the conditions of Figure 1, even though the ether has very nearly the same basicity toward the proton as the methyl cyclopropyl ketone (see $\Delta G^\circ_{(6)}$ value of Table I).¹³ Since this result was typical for all our experiments, we suggest that the proton bound homodimers of charge delocalized conjugate acids are particularly stabilized by delocalization of the positive charge into both base molecules. Perhaps this is accomplished through formation of the symmetrical single minimum species as distinguished from the double minimum species formed with most other proton bound dimers.

Mechanistically, the formation of the acetonitrile bound heterodimers appears to occur by bimolecular reactions (no termolecular) at the low pressures of these experiments:



(13) We are indebted to a referee for calling our attention to these considerations.

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

(11) J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **101**, 6046 (1979), and references given therein.

(12) J. F. Wolf, R. G. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).

Table I. Results for Reaction 7 and the Derived Results for Reaction 8 (All Values in kcal/mol at 298 K)

$X_1H^+ + X_2 \rightleftharpoons X_2H^+ + X_1; \Delta G^\circ_{(6)}$					(6)
$X_1H^+ \cdots NCMe + X_2 \rightleftharpoons X_2H^+ \cdots NCMe + X_1; \Delta G^\circ_{(7)}$					(7)
$X_1H^+ \cdots NCMe + X_2H^+ \rightleftharpoons X_2H^+ \cdots NCMe + X_1H^+; \Delta G^\circ_{(8)}$					(8)
X_1	X_2	$\Delta G^\circ_{(6)}^a$	$\Delta G^\circ_{(7)}^b$	$\Delta G^\circ_{(8)}^c$	
<i>n</i> -PrOH	Me ₂ O	-1.9	-1.3	0.6	
<i>n</i> -PrOH	HCO ₂ Et	-2.6	-0.4	2.2	
Me ₂ O	1,4-dioxane	-1.2	-1.1	0.1	
Me ₂ O	HCO ₂ Et	-0.7	+0.8	1.5	
Me ₂ O	CH ₃ CO ₂ CH ₃	-5.2	-2.0	3.2	
1,4-dioxane	CCCC(=O)	-0.3	+0.5	0.8	
CCCC(=O)	CCCCN	-1.3	+0.1	1.4	
HCO ₂ Et	CCCCN	-2.1	-1.2	0.9	
CCCCN	Me ₂ CN	-1.2	-1.2	0.0	
1,4-dioxane	Me ₂ CO	-2.8	-0.7	2.1	
1,4-dioxane	CCCCN	-1.6	-0.5	2.1	
Me ₂ CO	CH ₃ CO ₂ CH ₃	-1.2	-0.5	0.7	
CCCCO	CCCCCO	-0.7	-0.3	0.4	
CH ₃ CO ₂ CH ₃	CCCCC(=O)	-1.4	-1.4	0.0	
CCCCC(=O)	CCCCCO	-0.8	-1.0	-0.2	
CCCCO	CH ₃ CO ₂ Et	-1.4	+0.4	1.8	
Me ₂ CO	C ₆ H ₅ CHO	-4.2	-2.4	1.8	
CCCCO	C ₆ H ₅ CHO	-1.5	+0.5	2.0	
CCCCO	CCCCCO ₂ CH ₃	-3.5	-0.4	3.1	
CCCCCO	CCCCCO ₂ CH ₃	-2.8	-0.2	2.6	
CCCCCO	C ₆ H ₅ CO ₂ CH ₃	-3.7	+0.1	3.8	
Et ₂ O	CCCCCC(=O)	-1.3	-1.1	0.2	
Et ₂ O	<i>n</i> -Pr ₂ O	-2.0	-1.2	0.8	
<i>n</i> -Pr ₂ O	CCCCCC(=O)	-0.7	0.0	0.7	
Et ₂ O	C ₆ H ₅ C(=O)Me	-5.6	-2.0	3.6	
Et ₂ O	C ₆ H ₅ CO ₂ CH ₃	-3.3	-0.1	3.2	
<i>c</i> -C ₆ H ₁₁ C(=O)Me	CCCC(Me)O	-0.7	-0.7	0.0	
CCCC(Me)O	CCCC(=O)Me	-2.0	-0.5	1.5	
CCCC(Me)O	HC(=O)NHMe	-2.7	+0.2	2.9	
<i>i</i> -PrEtO	CCCC(=O)Me	-1.6	-0.7	0.9	
<i>i</i> -PrEtO	HC(=O)NHMe	-2.3	-0.2	2.1	
<i>n</i> -Pr ₂ O	CCCC(=O)Me	-2.4	-1.1	1.3	
<i>n</i> -Pr ₂ O	C ₆ H ₅ C(=O)Me	-3.4	-0.9	2.5	
<i>i</i> -Pr ₂ C=O	CCCC(=O)Me	-0.3	-1.2	-0.9	
CCCC(Me ₂)O	<i>i</i> -Pr ₂ O	-1.0	-0.7	0.3	
CCCC(=O)Me	CCCC(Me ₂)O	-0.3	-1.2	-0.9	
<i>n</i> -Pr ₂ O	<i>i</i> -Pr ₂ CO	-2.1	0.0	2.1	
<i>i</i> -Pr ₂ CO	CCCC(Me ₂)O	-0.6	-2.1	-1.5	
<i>t</i> -BuC(=O)Me	<i>n</i> -Pr ₂ O	-0.3	-1.0	-0.7	
<i>i</i> -Pr ₂ O	<i>p</i> -CH ₃ (C ₆ H ₄)C(=O)CH ₃	-3.3	-0.9	2.4	
<i>p</i> -CH ₃ (C ₆ H ₄)C(=O)CH ₃	(CCC) ₂ C(=O)	-2.2	-1.0 ^d	1.2 ^d	

^a Uncertainty ± 0.2 kcal/mol. ^b Uncertainty ± 0.2 kcal/mol. ^c Uncertainty ± 0.3 kcal/mol. ^d Uncertainty ± 0.5 kcal/mol.

In 200 ms, a great many collisions, e.g., (9) or (10), occur. However, with use of estimates of solvent exchange rates as an order of magnitude less than the collision rate,^{13,14} it does not appear that equilibrium 7 is

being directly established under our operating conditions. Thus, the heterodimers detected are both hot ($XH^+ \cdots N \equiv CMe^*$) as well as thermalized ($XH^+ \cdots N \equiv CMe$). The convincing thermodynamic consistency of our results (Figures 2 and 4) can be rationalized, however, by the proposal that the pair of nonthermalized acetonitrile bound heterodimers are formed in the steady states of reactions 9 and 10 in the same or very nearly the same relative amounts as the thermalized ones. Applying the steady state approximation to reactions 9 and 10 for two

(14) (a) S. G. Lias and P. Ausloos, "Ion-Molecule Reactions", ACS, Washington, 1975, p 182; (b) J. L. Beauchamp, M. C. Caserio, and T. B. McMahon, *J. Am. Chem. Soc.*, **96**, 6243 (1974); (c) K. Tanaka, G. I. MacKay, and D. K. Bohme, *Can. J. Chem.*, **56**, 193 (1978).

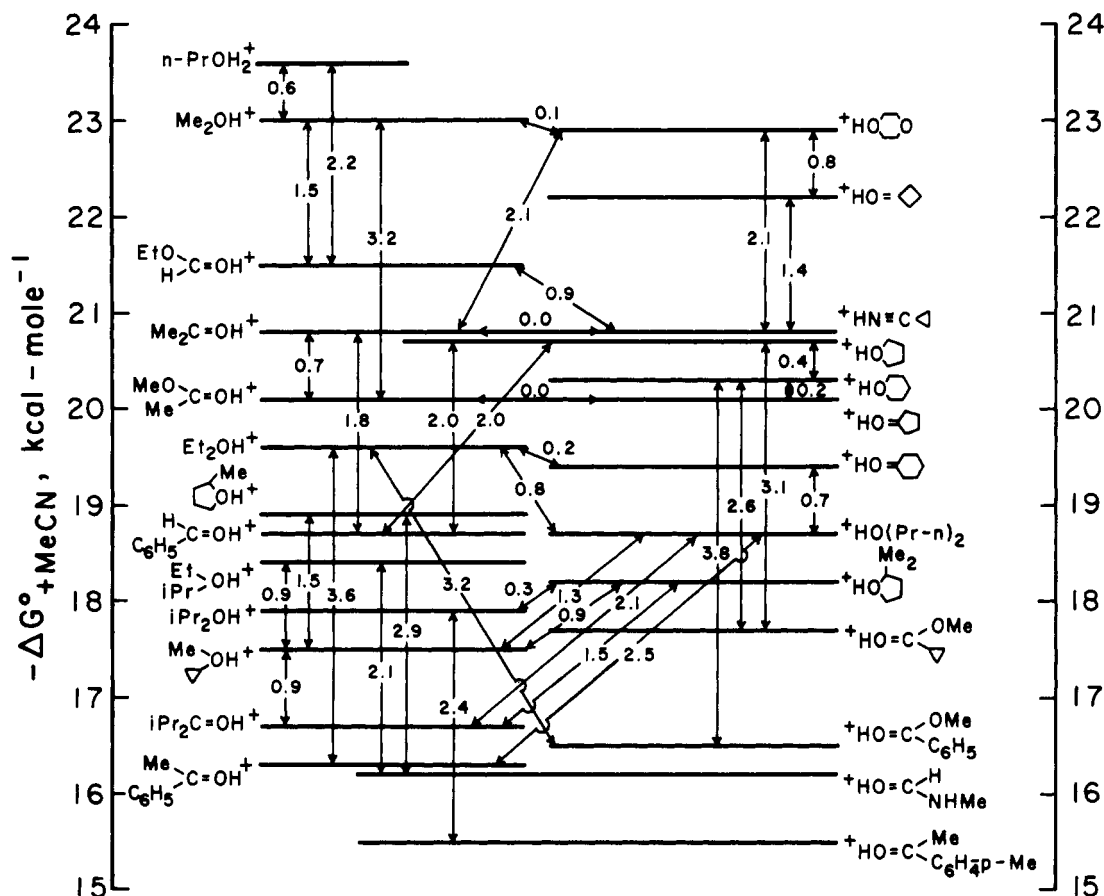


Figure 2. Relative free energies (kcal/mol) of binding of acetonitrile to oxonium ions obtained from multiple stair-stepping overlaps for reactions corresponding to equation 8.

bases, X_2 (with primed rate constants) and X_1 (with un-primed constants), one obtains

$$\frac{[X_2H^+ \cdots N \equiv CMe^*]/[X_2H^+]}{[X_1H^+ \cdots N \equiv CMe^*]/[X_1H^+]} = \frac{K_{(1)'}(MeCN)/[1 + k_2'/k_{-1}'(MeCN)]}{K_{(1)}(MeCN)/[1 + k_2/k_{-1}(MeCN)]}$$

The equilibrium condition for $(9) + (10) = (8)$ gives

$$\frac{[X_2H^+ \cdots N \equiv CMe]_e / [X_2H^+]_e}{[X_1H^+ \cdots N \equiv CMe]_e / [X_1H^+]_e} = \frac{K_{(1)'} k_2' k_{-2}}{K_{(1)} k_2 k_{-2}'}$$

where $K_{(1)} = k_1/k_{-1}$ and $K_{(1)}' = k_1/k_{-1}'$. The proposal that the rate constant ratios k_{-1}/k_2 and k_{-2}/k_2 have little or no dependence upon the base structure X_1 or X_2 seems reasonable in terms of the related structures and large numbers of degrees of freedom in each pair of heterodimers. It leads to the result that

$$\frac{[X_2H^+ \dots N \equiv CMe^*]/[X_2H^+]}{[X_1H^+ \dots N \equiv CMe^*]/[X_1H^+]} \approx \frac{[X_2H^+ \dots N \equiv CMe]_e/[X_2H^+]_e}{[X_1H^+ \dots N \equiv CMe]_e/[X_1H^+]_e} \approx \frac{K_{(1)}'}{K_{(1)}}$$

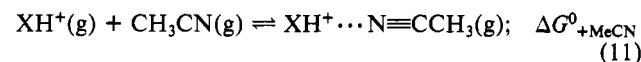
Further experimental work is in progress to test this assumption.

In order to confirm that our results for relative acetonitrile binding energies are reliable, *ab initio* calculations have been carried out at the STO-3G level of approximation for the ketones: acetone, methyl cyclopropyl ketone, and dicyclopropyl ketone.¹⁵ Previous calculations of relative binding energies have given satisfactory agreement with experiment.^{6c,16,17} The calculated values of $-\Delta E_{0, \text{MCN}}^{\text{rel}}$ (relative to acetone)

compared with our experimental $-\delta\Delta G^0_{+\text{MeCN}}$ values (cf. Table II) are in kcal/mol: 0.0, 0.0; -3.7, -3.3; and -6.9, -6.5, respectively.

Results

Table I gives the values of $\Delta G^{\circ}_{(6)}$, $\Delta G^{\circ}_{(7)}$, and $\Delta G^{\circ}_{(8)}$ for pairs of bases (X_1 and X_2) used to obtain the multiple overlap diagram shown in Figure 2. Figure 2 gives rounded values of the standard free energies of binding (± 0.3 kcal/mol) of a single acetonitrile molecule to the indicated monoprotonic oxonium ion, reaction 11.



The diagram has been obtained from $\Delta G^{\circ}_{(8)}$ values of Table I, starting with $X_1 = \text{O}(\text{CH}_3)_2$ and using the $\Delta G^{\circ}_{+\text{MeCN}}$ value of -23.0 kcal/mol obtained for dimethyloxonium ion (cf. reaction 3 and related discussion). It will be noted that overlaps in Figure 2 are in excellent agreement irrespective of whether X_1 or X_2 gives the more charge delocalized oxonium ion for reaction 8 in the spontaneous direction (cf. Table I). These results offer very strongly confirmatory evidence that true equilibrium values have been achieved.

Table II summarizes the values of $\Delta G^0_{+\text{MeCN}}$ (second column) obtained in this study. Also listed in Table II are: the gas phase basicities relative to dimethyl ether, $\delta\Delta G^0_{\text{H}^+}$ values (first column); the relative acetonitrile binding energies, $-\delta\Delta G^0_{+\text{MeCN}}$, for reaction 4 (third column); the corresponding relative standard free energies of transfer of the oxonium ion from the gas phase to dilute solution in bulk water, $-\delta\Delta G^0_{(\text{aq})}(\text{XH}^+)$ values (fourth column); and the values of the Bunnett-Olsen ϕ parameter (fifth column) for activity coefficient behavior in the $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ binary system.

Discussion

The gas phase basicities of the oxygen bases used in this study increase from dimethyl ether over the large range of 19.2 kcal/mol (14 ΔpK_a units). The substituent effects involved in these basicity increases have been discussed elsewhere in terms of polarizability,

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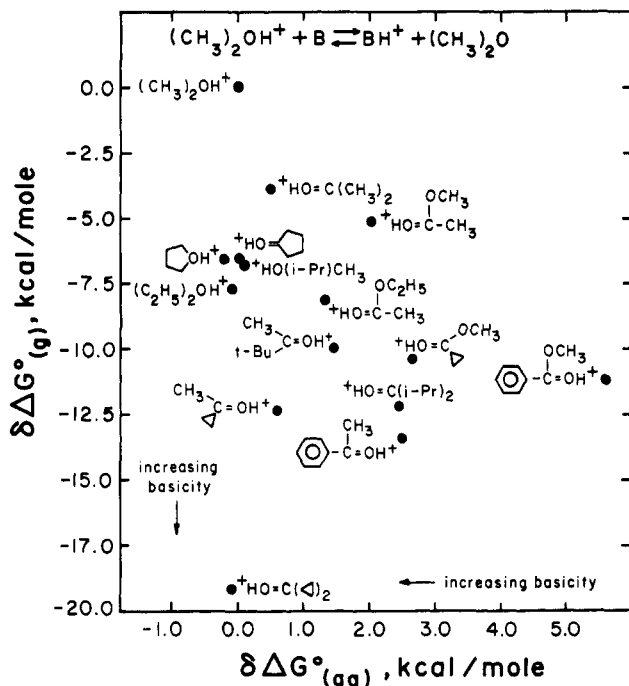
(16) M. Taagepera, D. J. DeFrees, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, **102**, 424 (1980).

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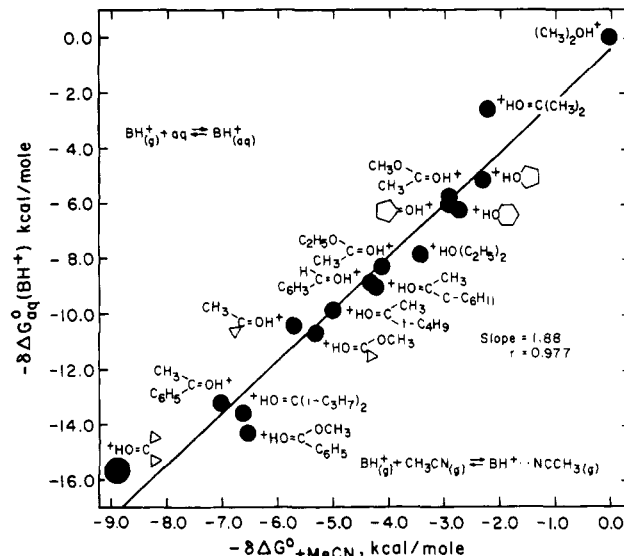
Table II. Relative Free Energies of Formation of Gaseous Monoprotonic Oxonium-Acetonitrile Complexes and Their Relationship to Relative Free Energies of Transfer of the Oxonium Ions from the Gas Phase to Dilute Aqueous Solutions

oxonium ion, XH^+	$\delta \Delta G^\circ_{H^+}$	$-\Delta G^\circ_{+MeCN}^a$	$-\delta \Delta G^\circ_{+MeCN}^b$	$-\delta \Delta G^\circ_{(aq)}(XH^+)^c$	ϕ^d
$(CH_3)_2OH^+$	(0.0)	23.0	(0.0)	(0.0)	0.82
$CCOCCOH^+$	-1.2	22.9	-0.1		
$(CH_3)_2COH^+$	-4.0	20.8	-2.2	-2.6	0.75
$CCCCOH^+$	-6.7	20.7	-2.3	-5.2	0.78
$CCCCCOH^+$	-7.4	20.3	-2.7	-6.2	(0.78)
$CCCCC(=O)^+$	-6.6	20.1	-2.9	ca. -6.0	0.73
$CH_3(CH_2O)COH^+$	-5.2	20.1	-2.9	-5.8	0.61
$(C_2H_5)_2OH^+$	-7.8	19.6	-3.4	-7.9	0.78
$CH_3(C_2H_5O)COH^+$	-8.1	18.9	-4.1	-8.3	0.54
$c-C_6H_4C(Me)OH^+$	-9.7	18.8	-4.2	-9.0	0.61
$c-C_6H_5CHOH^+$	-8.2	18.7	-4.3	-8.9	0.46
$n-Pr_2OH^+$	-10.0	18.7	-4.3		
$Me(t-Bu)COH^+$	-9.7	18.1	-4.9	-9.9	0.55
$CCCC(OMe)OH^+$	-10.2	17.7	-5.3	-10.7	0.40
$CCCC(Me)OH^+$	-12.4	17.5	-5.5	-10.4	0.55
$i-Pr_2COH^+$	-12.1	16.7	-6.3	-13.6	0.54
$c-C_6H_5C(OMe)OH^+$	-11.1	16.5	-6.5	-14.3	0.24
$c-C_6H_5C(Me)OH^+$	-13.4	16.3	-6.7	-13.2	0.40
$H(MeNH)C=OH^+$	-13.1	16.2	-6.8		
$p-Me(C_6H_4)C(Me)OH$	-17.0	15.5	-7.5		
$(CCC)_2COH^+$	-19.2	14.3	-8.7	-15.7	0.58

^a For reaction 9 in kcal/mol, ± 0.3 , except $(CCC)_2C=OH^+$, ± 0.5 , in kcal/mol. ^b Relative free energy of formation of gaseous oxonium ion-acetonitrile complex. ^c Relative free energy of transfer of the oxonium ions from the gas phase to dilute solutions in bulk water. Values obtained through the thermodynamic cycle given in ref 5. Solution basicities have been obtained by the methods given in ref 4. The standard free energies of solution in water of the gaseous oxygen bases have been obtained from ref 22. Estimated uncertainty is ± 0.5 kcal/mol. ^d Values of the Bunnett-Olsen parameter, obtained as in ref 3 and 4.

**Figure 3.** Comparison of gas phase and aqueous basicities of oxonium ions: ordinate, $\delta \Delta G^\circ_{(g)}$ (kcal/mol); abscissa, $\delta \Delta G^\circ_{(aq)}$ (kcal/mol).

inductive, and resonance effects.^{9,12} In Figure 3 are plotted the gas phase basicities relative to dimethyl ether (i.e., $\delta \Delta G^\circ_{H^+}$ values for reaction 5 vs. the corresponding aqueous solution relative basicities. In general, aqueous solution basicities tend to decrease (not increase) relative to that for dimethyl ether. The few oxygen compounds which are more basic than dimethyl ether in water are limited to effects of less than 0.5 kcal/mol. Except for methyl benzoate, the entire basicity range in aqueous solution covers only to 3.0 kcal/mol ($\sim 2 \Delta pK_a$ units). Figure 3 shows that there is

**Figure 4.** Correlation of the relative free energies of bulk aequation of gaseous monoprotic oxonium ions with their relative free energies of binding with a single molecule of acetonitrile: ordinate, $-\delta \Delta G^\circ_{(aq)}(BH^+)$ (kcal/mol); abscissa, $-\delta \Delta G^\circ_{+MeCN}$ (kcal/mol).

little or no correlation of the corresponding relative basicities between the two phases, even among the same family of oxygen bases. The present results therefore confirm and extend the evidence that aqueous medium effects on oxonium ion formation are relatively large and highly specific.⁵

In Figure 4, we have plotted values of $-\delta \Delta G^\circ_{+MeCN}$, the standard free energies of formation of the gaseous monoprotic oxonium-acetonitrile complexes relative to that for dimethyloxonium ion, vs. values of $-\delta \Delta G^\circ_{(aq)}(BH^+)$, the corresponding relative free energies of transfer of these oxonium ions from the gas phase to dilute solutions in bulk water. The remarkable linear relationship of Figure 4 is a striking illustration of the effectiveness of single

hydrogen-bond acceptor molecule "solvation" in reproducing the large diverse effects of molecular structure on the oxonium ion solvation by bulk water. This result takes on particular significance in view of the importance of oxonium ions in many aspects of life processes.

The order of oxonium ion structures along the correlation line of Figure 4 corresponds to decreasing hydrogen-bonding energies of either bulk water or a single acetonitrile molecule as the protonic charge of the oxonium ion is increasingly reduced by internal electron-releasing polarizability, inductive, and (particularly) resonance effects of substituents at the oxygen atom. The slope of the linear correlation of Figure 4 indicates that a single acetonitrile molecule has about half the effectiveness of bulk water. The correlation equation is: $-\delta\Delta G^0_{\text{(aq)}}(\text{XH}^+) = 0.5 + 1.88(-\delta\Delta G^0_{+\text{MeCN}})$; SD = ± 0.9 kcal/mol; $r = 0.977$.

Gas phase "solvation" energies for hydrogen bonding of a single water molecule to the monoprotic oxonium ions are presently unavailable except for the value for $(\text{CH}_3)_2\text{OH}^+$ ($-\Delta G^0_{+\text{H}_2\text{O}} = 14.6$ kcal/mol).¹⁰ However, it is reasonable to assume a linear free energy relationship between corresponding values of $\Delta G^0_{+\text{MeCN}}$ and $\Delta G^0_{+\text{H}_2\text{O}}$. If the slope is assumed to be equal to the ratio $-\Delta G^0_{+\text{H}_2\text{O}}/-\Delta G^0_{+\text{MeCN}} = 14.6/23.0 \approx 0.6$ for $(\text{CH}_3)_2\text{OH}^+$, the other $\Delta G^0_{+\text{H}_2\text{O}}$ values may be estimated. These estimates indicate that the relative solvation effects of bulk water on monoprotic oxonium ions are only three times as large as the corresponding effects of a single water molecule in the gas phase. Kebarle¹⁸ has previously noted that the solvation energies of inorganic and a few organic ions are well reproduced by the interactions of the first solvent molecules. The present series of organic oxonium ions also appears to be one in which the largest part of the aqueous solvent effects on protonic acid-base equilibria can be generally reliably represented in terms of the formation of specific ion-molecule complexes involving only a few solvent molecules.^{7,9a}

A recent theoretical study of aqueous solvent effects on the basicities of primary ammonium ions has indicated that hydrogen bonding of a single water molecule to each of the three protonic sites of the ammonium ions can account almost quantitatively for the observed effects.¹⁶ In contrast, Kebarle has shown that the aqueous solvent effects on the basicities of 3- and 4-substituted pyridines cannot be accounted for by pyridinium ion solvation by only a few water molecules.^{6c} A similar result is indicated by theoretical calculations for the aqueous medium effects on the basicities of meta- and para-substituted phenoxide ions.^{6c,19}

These contrasting results suggest that in addition to hydrogen-bonding solvation effects in all of the nitrogen and oxygen acid-base series, there are aqueous dielectric constant effects²⁰ that are of major importance in determining the reduction factors of substituent effects in solution compared to the gas phase. It is further suggested that the substantial reduction of internal ion-dipole interactions by an aqueous dielectric constant effect involves two important considerations: (a) the presence of a large number (perhaps ten or more) of water molecules and (b) the ability of this aggregation of solvent to assume an effective position between the ionic and dipolar centers. The presently available facts can be accounted for if condition b applies for the aromatic acid-base series,^{6c} but does not apply for the ammonium or oxonium ion series. Additional experimental and theoretical investigations are needed to critically test these conclusions.

The $-\delta\Delta G^0_{\text{(aq)}}(\text{BH}^+)$ values for the relative free energies of transfer of the oxonium ions from the gas phase to water (Table II) are potentially complex quantities containing contributions from differential energies of creating a cavity in the solvent structure, differential van der Waals dispersion force interactions, differential solvent structure making or breaking interactions, and differential electrostatic solvation energies, as well as differential H-bonding energies.⁵ However, it has been shown for hydrogen-bond donor cations having the same number and kind of protons that there are strong enthalpy-entropy compensations for the former terms.⁵ Thus, values of $-\delta\Delta G^0_{\text{(aq)}}(\text{BH}^+)$ measure to good approximation the relative hydrogen-bonding solvation energies of bulk water.

The structures that have been assigned to the conjugate acids of esters and amides are strongly supported by the $\delta\Delta G^0_{+\text{MeCN}}$ values of Table II and the results in Figure 4. Protonation at the alternate sites of these compounds would give charge-localized cations which would have stronger than observed binding of acetonitrile (and water) molecules.

The Bunnett-Olsen ϕ parameters for the $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ binary system which are listed in Table II give the activity coefficient (solvation) behavior for the monoprotic oxonium ions relative to their conjugate bases. Within the same families of compounds, the ϕ values parallel corresponding values of $\Delta G^0_{+\text{MeCN}}$, in accord with the present and earlier^{4,21} conclusions regarding the nature of these parameters.

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