J. Am. Chem. Soc. 1982, 104, 6255–6261 6255

Formation, Thermochemistry, and Relative Stabilities of Proton-Bound Dimers of Oxygen n-Donor Bases from Ion Cyclotron Resonance Solvent-Exchange Equilibria Measurements

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Abstract: Proton-bound dimers of nearly 30 oxygen n-donor bases have been generated by using ion cyclotron resonance trapped ion techniques and fast bimolecular processes involving the gas-phase ion chemistry of $(CHF_2)_2O$. In mixtures of two oxygen n-donor bases and $(CHF_2)_2O$, base exchange equilibria have been examined and thermochemistry of the processes obtained. Results reveal a remarkable constancy of hydrogen bond energies of 30.8 ± 2 kcal mol^{-1} in symmetric proton-bound dimers regardless of functional group involved or gas-phase basicity. Exceptions to the constant hydrogen bond energy can be explained in terms of either inhibition of resonance by "solvation", relief of ring strain, or steric crowding. In unsymmetric proton-bound dimers, the strength of the hydrogen bond is shown to be directly related to the difference in proton affinity of the two bases involved. In the few cases where data from other techniques are available, excellent agreement is obtained.

Introduction

The development of gas-phase basicity and acidity scales within the past decade has provided chemists with a means of unambiguously correlating structure and stability of naked ions and of assigning true intrinsic electronic substituent effects.[1-4] Earlier attempts to do this on the basis of analogous solution-phase data have had to contend with the often very important role of solvent in the modification of ionic properties.[5] As many studies have shown, the effect of solvation is frequently sufficient to completely reverse orders of stabilities of ions in solution compared to the gas phase.[6] However, when both types of data are available, they may be coupled to provide a quantitative evaluation of *total solvation energetics*.[7]

The study of partially solvated ions in the gas phase provides an opportunity to examine the intermediate case between the naked ion in the dilute gas phase and the fully solvated ion found in solution. Such investigations provide a means, virtually on a per molecule basis, of assessing the reasons for alteration of relative ionic stabilities by coordination with solvent molecules. Quite significantly, Kebarle has recently noted that relative total solvation energetics may be inferred from relative enthalpies of attachment of the first few solvent molecules.[8,9]

The study of these extremely interesting species has been limited largely to high-pressure mass spectrometric (HPMS) experiments where solvated or cluster ions can be readily formed by termolecular processes.[10-19] With the exception of a few cases where unusual bimolecular reaction sequences lead to the production of cluster ions,[20-24] the study of such species has not been routinely possible by ion cyclotron resonance spectroscopy (ICR) because of the low pressures entailed and consequent absence of collisional stabilization processes. However, we have recently presented a very general method involving fast bimolecular ion–molecule reaction sequences of $(CHF_2)_2O$ which allows production of protonated bases coordinated with a single solvent molecule for a wide range of species under the low-pressure conditions involved in ICR.[25,26] These proton-bound dimer species, once produced, may undergo reaction with other solvent species present in the system, and, under thermochemically favorable conditions, a solvent-exchange equilibrium may be established and relative energetics of solvation by single solvent molecules obtained. For example, in mixtures containing $(CHF_2)_2O$ and two bases, B and B*, of comparable base strength the two symmetrical proton-bound dimers BHB^+ and B^*HB^{*+} are produced as well as the unsymmetrical species, BHB^{*+}. At sufficiently long reaction times base-exchange equilibria may be established, eq 1 and 2, and the

$$BHB^+ + B^* \rightleftharpoons BHB^{*+} + B \qquad (1)$$

$$BHB^{*+} + B^* \rightleftharpoons B^*HB^{*+} + B \qquad (2)$$

relative free energies of solvation of both BH^+ and B^*H^+ by B and B* may be obtained. Data such as this for proton-bound dimers are relatively scarce and have been limited to studies of water, methanol, dimethyl ether, acetone, and Me_2SO by Kebarle and a series of four aliphatic alcohols and dimethyl ether by Beauchamp. The present study extends data available for proton-bound dimers to 20 n-donor oxygen bases including water, five alcohols, six ethers, three ketones, two aldehydes, two carboxylic acids, and two esters. In addition to the symmetric

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[†] On sabbatical leave from Marshall University, Huntington, WV.

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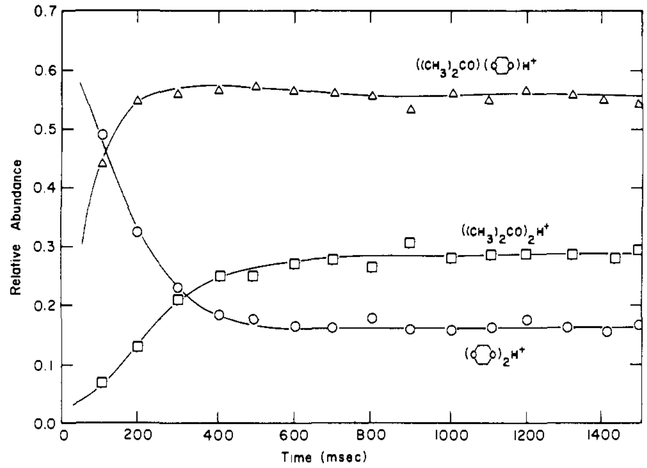


Figure 1. Variation of relative ionic abundances with time for a 17:16:1 mixture of $(CHF_2)_2O$–dioxane–$(CH_3)_2CO$ at a total pressure of 2.0 × 10^{-6} torr following a 6-ms 70-eV electron beam pulse.

proton-bound dimers for these bases, over 30 unsymmetric proton-bound dimers have also been observed and hydrogen bond energies in these species correlated with differences in base strength of the constituent bases.

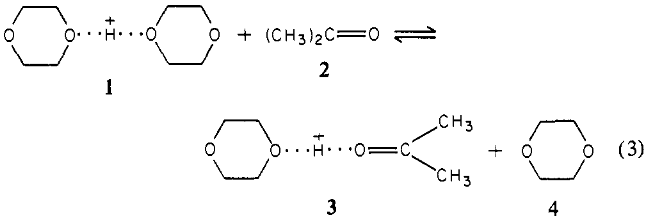
Experimental Section

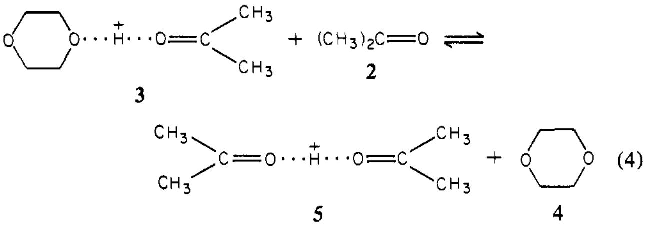
Materials. Commercial samples of most compounds were used. Bis(difluoromethyl) ether, $(CHF_2)_2O$, was obtained from PCR Inc. All samples were purified by several freeze–pump–thaw cycles before use.

Instrumentation. All experiments were conducted at ambient temperature (25 °C) using an ICR spectrometer of conventional Varian V-5900 design, extensively modified to permit both drift and trapped-ion experiments. Details of design and operation of the trapped-ion ICR technique[27] as well as conventional ICR single and double-resonance experiments have been described in detail previously.[28,29]

Procedure. A typical determination of solvent exchange equilibrium constants involved preparation of a mixture of bases of accurately known partial pressures using a Validyne AP-10 absolute pressure gauge attached to a monel vacuum line. This mixture was then leaked into the ICR cell region to a pressure of approximately 10^{-6} torr. An approximately equal amount of $(CHF_2)_2O$ was then also admitted to the system through a separate inlet-leak valve arrangement. When one of the bases involved was methanol, a mixture of $(CHF_2)_2O$ and water was used to enhance relative abundances of the desired proton bound dimers. The detailed mechanism by which proton-bound dimers are produced in $(CHF_2)_2O$ mixtures has been described in detail previously.[25,26]

Steady-state abundances of the three possible proton bound dimers in a mixture containing two bases were usually obtained from the same experiment. Typical data are represented by those shown in Figure 1 for a mixture of dioxane and acetone. Equilibrium constants for the two possible solvent-exchange equilibria, eq 3 and 4, are given by eq 5 6.


(3)


(4)

$$K_3 = \frac{[3]}{[1]}\frac{[4]}{[2]} \tag{5}$$

$$K_4 = \frac{[5]}{[3]}\frac{[4]}{[2]} \tag{6}$$

Relative abundances of proton-bound dimers at equilibrium are obtained from mass-corrected steady-state intensities, and neutral pressure ratios are given by the manometrically determined partial pressures.

Equilibria were usually obtained between 400 and 800 ms at total base pressures between 1.0 × 10^{-6} and 3.0 × 10^{-6} torr, and ion intensity ratios monitored for at least twice as long as the time necessary to reach steady state. Double-resonance and time-delayed ion ejection experiments were carried out to confirm that a true dynamic equilibrium existed rather than an artificial static steady state. Each equilibrium constant determination is an average of several experiments in which neutral base pressure ratios were varied by at least a factor of 3. Calculated equilibrium constants thus obtained were all found to agree to within ±15%.

Results

Free-energy changes, $\Delta G°_1$, and $\Delta G°_2$, derived from experimentally determined equilibrium constants via eq 7 for eq 1 and

$$\Delta G° = -RT \ln K \tag{7}$$

2, respectively, are summarized in Table I. In each case B* is the base of higher proton affinity. Maximum uncertainty in the reported $\Delta G°$ values is ±0.2 kcal mol^{-1}.

Values of $\Delta H°_1$ and $\Delta H°_2$ are also given in Table I, based on eq 8 and statistical thermodynamic estimates of the entropy

$$\Delta G° = \Delta H° - T\Delta S° \tag{8}$$

changes, $\Delta S°$, for solvent exchange. Overall entropy changes for each equilibrium have been approximated by the sum of rotational and translational entropy changes calculated from the statistical thermodynamic formulas, eq 9 and 10, where σ is the rotational

$$\Delta S°_{\text{rot}_1} = -R \ln \frac{\sigma_{BHB^{*+}}\sigma_B}{\sigma_{BHB^+}\sigma_{B^*}} \tag{9}$$

$$\Delta S°_{\text{trans}_1} = \frac{3}{2}R \ln \frac{m_B m_{BHB^{*+}}}{m_{B^*} m_{BHB^+}} \tag{10}$$

symmetry number and m is molecular weight. Contributions to the overall entropy change due to changes in translational entropy for equilibria such as eq 1 and 2 have been ignored by previous authors;[23,24] however, for bases B and B* of appreciably different molecular weight, such changes can be significant.

Contributions to overall entropy changes due to rigid rotation, internal rotation, and vibration should also be included for complete accuracy. However, geometries of proton-bound dimers and frequencies of vibrational and rotational motion are essentially unknown, making such calculations impossible. In a few cases, such as $H_5O_2^+$,[12] $N_2H_7^+$,[15] and $((CH_3)_2O)_2H^+$,[16,17] absolute entropies may be derived from temperature-variation experiments of Kebarle and absolute entropies of the constituent base and conjugate acid. For $H_5O_2^+$,[30,31] $N_2H_7^+$,[32] and $(CH_2O)_2H^+$,[33] accurate geometries are also known from ab initio calculations, and for $H_5O_2^+$ vibrational frequencies have been assigned[34] for solid salts containing this unit. Using such data we have carried out statistical thermodynamic calculations for absolute entropies of $H_5O_2^+$, $N_2H_7^+$, and $(CH_2O)_2H^+$ and compared these with experimentally determined entropies. These calculations revealed that for proton-bound dimers, contributions to the total entropy from internal rotation and low frequency vibration along the hydrogen bond must be significant. However, in each of the cases examined, the contributions appeared to be roughly constant since

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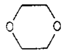
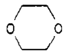
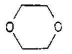
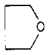
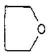
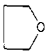
Table I. Thermochemistry of Proton-Bound Dimer Solvent-Exchange Equilibria

	B	B*	ΔG°_1	ΔH°_1	ΔG°_2	ΔH°_2	ΔPA^a
1.	H_2O	CF_3CH_2OH	−1.36	−1.4	+0.22	−1.3	1.9
2.	H_2O	CF_3CO_2H	+0.85	+0.8	+0.57	−1.0	3.0
3.	HCO_2H	MeOH			−1.44	−1.7	2.1
4.	MeOH	MeCHO	~−1.3	−1.0	−1.02	−1.6	2.8
5.	MeOH	EtOH	−2.60	−2.3	−1.83	−2.4	4.5
6.	MeCHO	EtOH			−0.31	−0.8	1.7
7.	MeCHO	$MeCO_2H$	−0.94	−0.6	−0.02	−0.5	3.0
8.	EtOH	$MeCO_2H$	+0.28	+0.6	+0.54	−0.0	1.3
9.	EtOH	PrOH	−1.14	−0.8	−0.61	−1.1	2.1
10.	EtOH	BuOH	−1.34	−1.1	−0.63	−1.3	2.6
11.	$MeCO_2H$	Me_2O	−2.16	−1.6	−1.07	−1.4	2.1
12.	PrOH	BuOH	−0.41	−0.1	+0.31	−0.2	0.5
13.	PrOH	Me_2O	−0.79	−0.3	−0.05	−0.4	1.3
14.	Me_2O	EtO_2CH	−0.71	−0.5	+0.82	+0.2	1.1
15.	Me_2O		−1.19	−1.0	−0.27	−1.0	1.2
16.	EtO_2CH		−1.24	−0.9	+0.10	−0.4	0.1
17.		Me_2CO	−2.35	−1.7	−1.31	−1.5	2.6
18.	Me_2CO	MeO_2CMe	−0.20	+0.1	+0.87	+0.3	1.5
19.	Me_2CO		−2.19	−1.9	−1.03	−1.5	2.5
20.	Me_2CO	MeEtCO	−1.52	−1.2	−0.49	−1.0	3.1
21.	Me_2CO	Et_2O	−1.75	−1.4	−0.50	−1.0	3.5
22.	Me_2CO	Et_2CO	−2.12	−1.9	−1.04	−1.7	4.6
23.		Et_2O	+0.21	+0.6	+0.50	+0.1	1.0
24.		Et_2CO	−0.46	−0.1	+0.43	−0.1	2.1
25.	MeEtCO	Et_2CO	−1.00	−0.7	−0.17	−0.7	1.5
26.	Et_2O	Et_2CO	−0.86	−0.5	−0.18	−0.7	1.1
27.	Et_2O	nPr_2O	−1.39	−1.1	−0.04	−0.6	1.9
28.	Et_2O	iPr_2O	−1.31	−1.0	−0.07	−0.6	5.6

[a] $\Delta PA = PA(B^*) - PA(B)$. Proton affinity data from refs 1 and 2.

good agreement between experimentally determined entropy changes and those based on eq 9 and 10 were obtained. In view of this result and the conclusions drawn elsewhere that hydrogen bonds in proton-bound dimers of oxygen n-donor bases are of comparable length and bond energy, it would appear to be logical to expect roughly constant contributions to absolute entropies from internal rotation about the O···H···O bond and low-frequency vibration association with it. Thus we believe that ΔS° values determined from eq 9 and 10 are accurate to within ±1 cal K^{-1} mol^{-1} and we assign an uncertainty of ±0.5 kcal mol^{-1} to the ΔH° values reported.

Discussion

A measure of the relative stabilities of symmetric proton-bound dimers in the gas phase may be obtained from a calculation of the energetics involved in the double replacement reaction, eq 11.

$$BHB^+ + 2B^* \rightleftharpoons B^*HB^{*+} + 2B \qquad (11)$$

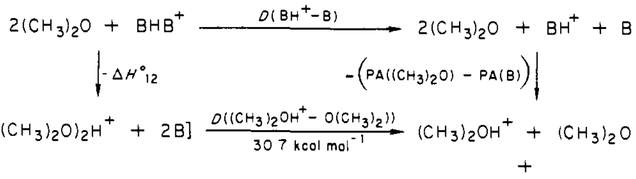
A stability ladder for proton-bound dimers is shown in Table II. For each pair of bases examined the ΔG° values given in the table are obtained from the sum of ΔG°_1 and ΔG°_2 for that pair of bases in Table I, which in turn are obtained from the directly measured equilibrium constants. Following the example of Beauchamp,[24] we have chosen the proton-bound dimer of dimethyl ether as an arbitrary reference point, and included in Table II are values of ΔG°_{12} and ΔH°_{12} for eq 11, where B* is dimethyl ether, eq 12.

$$BHB^+ + 2(CH_3)_2O \rightleftharpoons [(CH_3)_2O]_2H^+ + 2B \qquad (12)$$

Also included are the differences in proton affinity of dimethyl ether and B, ΔPA. From these data the hydrogen bond energy for symmetric proton bound dimers, eq 13, may be obtained using

$$BHB^+ \xrightarrow{D(BH^+-B)} BH^+ + B \qquad (13)$$

Scheme I



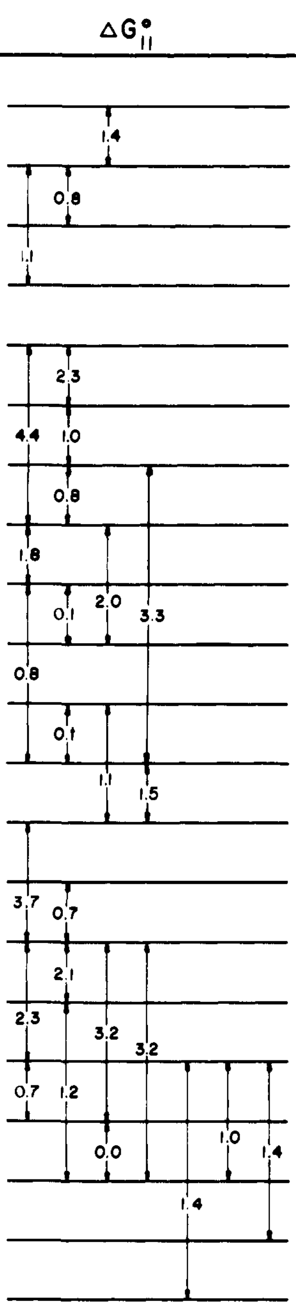
the thermochemical cycle in Scheme I, the known thermochemistry of the dimethyl ether proton bound dimer,[16,17] and the proton affinities of the bases used,[1,2] eq 14. The symmetric proton-bound

$$D(BH^+-B) = \Delta H_{12} + 30.7 + PA((CH_3)_2O) - PA(B) \qquad (14)$$

dimer hydrogen bond energies thus obtained are symmarized in Table III. It should be noted from Table II that no direct link from H_2O, CH_2O, CF_3CO_2H, and CF_3CH_2OH to dimethyl ether has been determined. In these cases the known thermochemistry of $H_5O_2^+$ has been used to calculate values of ΔH°_{12} and ΔG°_{12} and the hydrogen bond energies in Table III.

A comparison of the data obtained here with that of other investigators provides a check of the consistency and accuracy of our technique. For example, the value of ΔG°_{12} for methanol of 6.9 kcal mol^{-1} is in excellent agreement with the value of 7.0 kcal mol^{-1} obtained by Kebarle in an HPMS study of exchange equilibria in methanol–dimethyl ether[16] and in good agreement with the value of 6.2 kcal mol^{-1} also obtained by Kebarle in a study of the actual clustering equilibria in methanol and dimethyl ether.[17] The value obtained from the exchange equilibrium would be expected to be the more accurate, and this is the value in best agreement with our data.

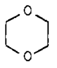
Table II. Stability Ladder for Proton-Bound Dimers



Compound	ΔG°_{12} [a]	ΔH°_{12} [a]	ΔPA [a][b]
Trifluoroacetic acid	19.4	18.6	16.8
Water	(18.0)	(18.9)	19.8
Formaldehyde	17.2	17.6	15.5
Trifluoroethanol	16.9	16.2	17.9
Methanol	6.9	7.2	7.9
Acetaldehyde	4.3	4.3	5.1
Acetic acid	3.3	3.1	2.1
Ethanol	2.5	2.5	3.4
n-Propanol	0.8	0.6	1.3
n-Butanol	0.6	0.2	0.8
Ethyl formate	0.1	-0.3	-1.1
Dimethyl ether	(0.0)	(0.0)	(0.0)
Dioxane	-1.3	-1.9	-1.2
Methylacetate	-4.3	-4.7	-5.3
Acetone	-5.0	-5.2	-3.8
Methylethyl ketone	-7.0	-7.4	-6.9
Diethyl ether	-7.3	-7.7	-7.3
Tetrahydrofuran	-8.1	-8.5	-6.3
Diethyl ketone	-8.2	-8.8	-8.4
i-Propyl ether	-8.7	-9.4	-12.9
n-Propyl ether	-8.7	-9.4	-9.2

[a] All values in kcal mol^{-1}. [b] $\Delta PA = PA((CH_3)_2O) - PA(B)$.

Table III. Hydrogen Bond Strengths in Symmetric Proton-Bound Dimers[a]

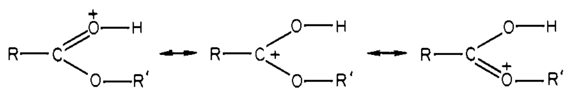
water and alcohols		ethers		aldehydes and ketones		acids and esters	
H_2O	31.6[b]	$(CH_3)_2O$	30.7[c]	CH_3CHO	31.5	CH_3CO_2H	29.7
CF_3CH_2OH	32.4	$(C_2H_5)_2O$	31.3	$(CH_3)_2CO$	32.1	CF_3CO_2H	28.9
CH_3OH	31.4	$(n\text{-}C_3H_7)_2O$	30.9	$CH_3COC_2H_5$	31.2	$HCO_2C_2H_5$	29.4
C_2H_5OH	31.3	$(i\text{-}C_3H_7)_2O$	27.2	$(C_2H_5)_2O$	31.2	$CH_3CO_2C_2H_5$	30.1
$n\text{-}C_3H_7OH$	31.4		32.9				
$i\text{-}C_3H_7OH$	31.4[d]		31.4				
$n\text{-}C_4H_9OH$	31.3						
$sec\text{-}C_4H_9OH$	32.4[d]						
$t\text{-}C_4H_9OH$	29.4[d]						

[a] All values in kcal mol^{-1} obtained from this work as described in text, unless otherwise noted. [b] Reference 12, value used as reference standard. [c] Reference 16, value used as reference standard. [d] Reference 24.

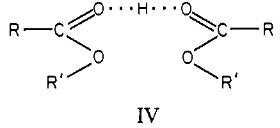
For the ethanol system our values of $\Delta G°$ of 2.4 kcal mol^{-1} using *n*-propyl alcohol as an intermediate equilibrium step and 2.5 kcal mol^{-1} using acetic acid as an intermediate are in excellent agreement with the value of 2.5 kcal mol^{-1} obtained by Bomse and Beauchamp[24] who generated proton-bound dimers via ion-molecule reaction sequences in isopropyl alcohol and *tert*-butyl alcohol.

Lau, Saluja, and Kebarle have examined clustering equilibria in acetone.[35] Their data for $\Delta G°_{12}$ and the difference in proton affinities of acetone and dimethyl ether may be used to calculate a value of $\Delta G°_{12}$ of −2.9 kcal mol^{-1}, with a *minimum* stated uncertainty of 1.2 kcal mol^{-1}. We thus believe our value of $\Delta G°_{12}$ of −4.9 ± 0.3 kcal mol^{-1} reported here to be the more accurate determination.

Hydrogen Bond Strengths in Symmetrical Dimers. The overall stability scale shown in Table II reveals that proton-bound dimer stability closely parallels the gas-phase basicity scale with stability of symmetric proton-bound dimers increasing with increasing proton affinity of the constituent base. There are, however, some noteworthy exceptions. For example, the proton-bound dimer of acetic acid is less stable than that of ethanol by 0.6 kcal mol^{-1} even though the proton affinity of acetic acid is 1.3 kcal mol^{-1} greater than that of ethanol. A similar reversal occurs upon comparison of other carboxylic acids and esters with appropriate reference compounds. Trifluoroacetic acid proton-bound dimer is found to be only 0.3 kcal mol^{-1} more stable than that of water while its basicity is 3.0 kcal mol^{-1} greater. The proton-bound dimer of ethyl formate is 1.6 kcal mol^{-1} less stable than that of dioxane even though their proton affinities are nearly equal. Methyl acetate proton-bound dimer is 0.5 kcal mol^{-1} less stable than that of acetone while the proton affinity of methyl acetate is 1.5 kcal mol^{-1} greater than acetone. In each of the above cases a protonated acid or ester appears to have a proton-bound dimer stability which is less than that expected on the basis of its proton affinity. In addition, from the data in Table III, it may be seen that each of these compounds has a hydrogen bond energy in the proton-bound dimer which is 1–2 kcal mol^{-1} less than that observed for the majority of alcohols, ethers, and ketones. This result may be understood in terms of the differences in resonance stabilization of positive charge in the protonated acids and esters and their corresponding proton-bound dimers. The protonated bases themselves may be stabilized by the valence bond structures I–III delocalizing positive charge significantly. However, in the proton-bound dimers, the positive charge may be delocalized away from the binding proton only at the expense of appreciably weakening the hydrogen bond. Hence the symmetric proton-bound dimer is probably best represented by the single valence bond structure IV. This may thus be regarded as an example of *inhibition of resonance by solvation* and provides concrete evidence that reversals in relative gas-phase and solution basicities are due to the masking of intrinsic electronic effects by coordination of solvent molecules with the ionic species of interest.



I II III



IV

Another interesting reversal of proton-bound dimer stability and gas-phase basicity arises in comparison with diethyl ether and tetrahydrofuran (THF). In the gas phase, diethyl ether is more basic than THF by 1.0 kcal mol^{-1};[2] however, solution-phase experiments indicate that THF is both a stronger base and better hydrogen bond acceptor than diethyl ether.[36,37] Taft et al.[2] have interpreted the reversal of gas-phase and solution relative basicities to be due to steric effects associated with the bulkier diethyl ether which weakens the solvation of $(C_2H_5)_2OH^+$ and the hydrogen bond acceptor ability of $(C_2H_5)_2O$ relative to THF. However, our results for proton-bound dimers of diethyl ether and THF indicate that this is clearly not the case. The proton-bound dimer of THF is shown in Table II to be more stable than that of diethyl ether by 0.8 kcal mol^{-1}. Moreover, the data of Table III reveal that the proton-bound dimer of diethyl ether has a hydrogen bond energy similar to the average of other oxygen n-donor bases, whereas in THF the hydrogen bond is the strongest of any of the compounds studied. This result would thus indicate that, rather than diethyl ether having a depressed solvating ability for steric reasons, THF has either an enhanced solvating ability or an enhanced hydrogen bond acceptor ability. One possible explanation of this observation may be that protonation of THF leads to an increase in ring strain energy which may be partially relieved in proton-bound dimer formation. This would then account for the lower gas-phase basicity of THF relative to diethyl ether and a greater tendency of protonated THF to form hydrogen bonds with n-donor molecules.

The substantially lower (~4 kcal mol^{-1}) hydrogen bond energy in the proton-bound dimer of diisopropyl ether relative to that for other oxygen bases is also of interest. In solution diisopropyl ether is found to be a weaker base than diethyl ether, whereas in the gas phase diisopropyl ether has a proton affinity 5.6 kcal mol^{-1} greater than that of diethyl ether. This solution–gas-phase basicity reversal and the very low proton-bound dimer hydrogen bond energy may be ascribed to significant steric repulsions which arise in the solvation of $(iC_3H_7)_2OH^+$. Construction of space-filling models of $[(iC_3H_7)_2O]_2H^+$ indicates that the isopropyl groups give rise to a great deal of steric hindrance and crowding of a magnitude not found for any other proton-bound dimer examined, including di-*n*-propyl ether. This steric hindrance to solvation of the $(i\text{-}C_3H_7)_2OH^+$ will thus also lead to a depressed solution basicity.

The similarity in the magnitudes of the hydrogen bond energies for the symmetric proton bound dimers is especially noteworthy. Kebarle[35] and Beauchamp[24] have previously noted that the binding energies in the proton-bound dimers of water, methanol, ethanol, isopropyl alcohol, *sec*-butyl alcohol, *tert*-butyl alcohol, dimethyl ether, and acetone are relatively constant at 31.5 ± 1.5 kcal mol^{-1}. From the data in Table III it may be seen that with the exception of isopropyl ether and carboxylic acids and esters, this constant hydrogen bond energy is maintained for a wide variety of compounds, including alcohols, ethers, ketones, and aldehydes. The fact that the hydrogen bond strengths in aldehydes and ketones are essentially the same as those in water, alcohols, and ethers indicates that the hybridization and functionality of the oxygen has essentially no effect on proton-bound dimer bond strength, even where the proton affinities of the compounds studied vary over a 30-kcal mol^{-1} range. Quantum chemical calculations on proton-bound dimers of water[30] and formaldehyde[33] have also been carried out, and these show an oxygen–oxygen distance in the symmetric proton-bound dimers of water and formaldehyde which differ by only 0.02 Å using 4-31G basis sets.

It is of some interest to note that the constant value for proton-bound dimer hydrogen bond strengths in gas-phase oxonium ions has an analogy in the solution chemistry of acids. For two given acids, A_1H and A_2H, if A_1H is the stronger acid it will be a better hydrogen bond donor than will A_2H. However, of the conjugate bases A_1^- and A_2^-, A_2^- will be the stronger base and hence the better hydrogen bond acceptor. These two factors have the effect of cancelling each other, leading to a near constant value for hydrogen bond strengths in bicarboxylate ions in solution.[38]

These data for symmetric proton-bound dimers lend a great deal of support to the concept that the potential energy surface

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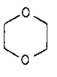
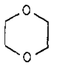
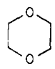
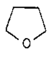
[35] Lau, Y. K.; Saluja, P. P. S.; Kebarle, P. *J. Am. Chem. Soc.* **1980**, *102*, 7429.

[36] Taft, R. W.; Gurka, D.; Joris, L.; v. R. Schleyer, P.; Rakskys, J. W. *J. Am. Chem. Soc.* **1969**, *91*, 4801.

[37] Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223.

[38] Speakman, J. C. *Struct. Bonding* (*Berlin*) **1972**, *12*, 141.

Table IV. Hydrogen Bond Strengths in Assymmetric Proton-Bound Dimers (All Values in kcal mol^{-1})

B	B*	D(BH$^+$-B*)	D(B-$^+$HB*)
H_2O	CF_3CH_2OH	33.0	31.1
H_2O	CF_3CO_2H	31.6	28.6
H_2O	CH_2O	32.2	27.9
HCO_2H	CH_3OH	31.8	29.7
CH_3OH	CH_3CHO	32.4	29.6
CH_3OH	C_2H_5OH	33.7	29.2
CH_3CHO	C_2H_5OH	32.2	30.5
CH_3CHO	CH_3CO_2H	32.1	29.1
C_2H_5OH	CH_3CO_2H	30.7	29.4
C_2H_5OH	n-C_3H_7OH	32.1	30.0
C_2H_5OH	n-C_4H_9OH	32.4	29.8
CH_3CO_2H	$(CH_3)_2O$	31.3	29.2
n-C_3H_7OH	n-C_4H_9OH	31.5	31.0
n-C_3H_7OH	$(CH_3)_2O$	31.7	30.4
$(CH_3)_2O$	$HCO_2C_2H_5$	31.2	30.1
$(CH_3)_2O$		31.7	30.5
$HCO_2C_2H_5$		30.3	30.2
	$(CH_3)_2CO$	33.1	30.5
$(CH_3)_2CO$	$CH_3CO_2CH_3$	32.0	30.5
$(CH_3)_2CO$		34.0	31.5
$(CH_3)_2CO$	$CH_3COC_2H_5$	33.3	30.2
$(CH_3)_2CO$		33.5	30.0
$(CH_3)_2CO$	$(C_2H_5)_2CO$	34.0	29.4
	$(C_2H_5)_2O$	32.3	31.3
	$(C_2H_5)_2CO$	33.0	30.9
$CH_3COC_2H_5$	$(C_2H_5)_2CO$	31.9	30.4
$(C_2H_5)_2O$	$(C_2H_5)_2CO$	31.8	30.7
$(C_2H_5)_2O$	$(n$-$C_3H_7)_2O$	32.4	30.5
$(C_2H_5)_2O$	$(i$-$C_3H_7)_2O$	32.3	26.7

for the hydrogen bond in such systems is a broad single minimum potential well.[24] The oxygen lone pairs of the participating bases all have relatively little bonding characater with respect to the base molecules themselves, giving rise to a nearly identical width and depth of the potential well.

Hydrogen Bond Strengths in Unsymmetrical Dimers. Hydrogen bond energies in unsymmetrical proton-bound dimers may be obtained from the experimentally determined equilibrium constants for eq 1 and 2, and the thermochemical data summarized in Table I. These data are summarized in Table IV.

Kebarle[39] has recently shown that for clustering equilibria involving water, eq 15, unsymmetrical proton-bound dimer, or

$$BH^+ + H_2O \rightleftharpoons B\cdots\overset{+}{H}\cdots OH_2 \qquad (15)$$

hydrate, formed is inversely related to the proton affinity difference, PA(B) − PA(H_2O), and over a 70-kcal mol^{-1} range of proton affinity differences, hydrogen bond energies have been shown to regularly decrease with increasing ΔPA. Conversely, these data may be rearranged to show that the hydrogen bond energy of H_3O^+ to solvents, B, eq 16, increases with increasing

$$H_3O^+ + B \rightarrow B\cdots\overset{+}{H}\cdots OH_2 \qquad (16)$$

proton affinity difference, PA(B) − PA(H_2O). In the results presented in Table IV there is no common ion such as H_3O^+ or common solvent such as H_2O to make exactly the same type of correlations as that shown by Kebarle. However, a meaningful understanding of the effect of proton affinity difference may be obtained by comparing the hydrogen bond energy in an unsymmetric proton-bound dimer with the hydrogen bond energy for the corresponding symmetric species. The quantity, $D(BH^+{-}B') - D(BH^+{-}B)$, may be plotted vs. proton affinity difference, PA(B′) − PA(B), as in Figure 2 for the data from Table I, to reveal that the hydrogen bond energy has a marked dependence on the basicity difference.

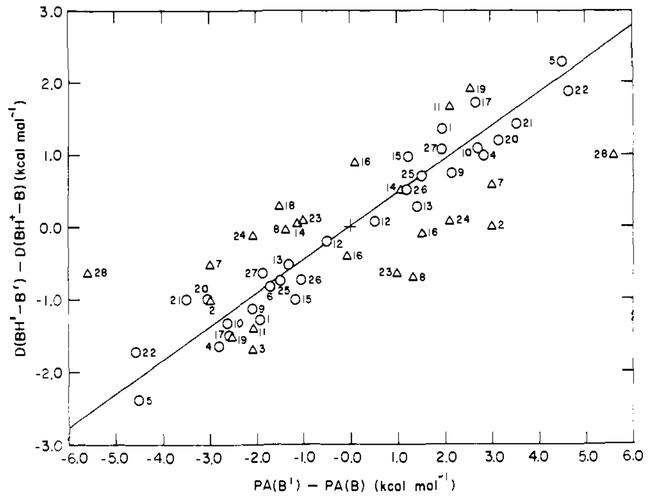


Figure 2. Dependence of the difference in hydrogen bond energies of symmetric and unsymmetric proton bound dimers on difference in proton affinity of bases involved. Points in the upper right quadrant are $-\Delta H°_1$ values from Table I; points in the lower left quadrant are $\Delta H°_2$ values from Table I. Numbers on all points correspond to numbers of reactions in Table I. Triangles correspond to equilibria involving carboxylic acids, esters, THF, and diisopropyl ether which are expected to give the poorest correlation. Circles correspond to all other equilibria.

Scheme II

$$\begin{tikzcd}
BHB^+ + B' \arrow[r, "{-[D(BH^+-B') - D(BH^+-B)]}"] \arrow[d, "{D(BH^+-B)}"] & B'HB^+ + B \\
BH^+ + B + B' \arrow[r, "{-[PA(B') - PA(B)]}"] & B'H^+ + 2B \arrow[u, "{-D(B'H^+-B)}"']
\end{tikzcd}$$

Linear regression analysis for this plot yields a straight line of slope 0.46 with an intercept of 0.01 kcal mol^{-1} and a good correlation coefficient of 0.92. The basis for the dependence of hydrogen bond energy differences in symmetric and unsymmetric dimers on proton affinity differences may be better understood from an examination of the thermochemical cycle in Scheme II which yields eq 17. This equation reveals that the difference in

$$D(BH^+{-}B') - D(BH^+{-}B) = PA(B') - PA(B) + [D(B'H^+{-}B) - D(BH^+{-}B)] \qquad (17)$$

hydrogen bond energies of B′ and B to BH^+ will be directly proportional to the proton affinity difference but also proportional to the difference in binding energies of B to $B'H^+$ and BH^+. As shown by the data of Kebarle this second term, $D(B'H^+{-}B) - D(BH^+{-}B)$, will also be dependent on PA(B′) − PA(B), but evidently, as revealed by the data in Figure 2, this dependence is roughly one-half that of the difference $D(BH^+{-}B') - D(BH^+{-}B)$. These data can thus be rearranged to show that for the coordination of two ions, $B'H^+$ and BH^+, to a given molecule, B, the binding energy is less for the conjugate acid of the base of greater proton affinity, and that the difference in binding energies is roughly 0.54 (PA(B′) − PA(B)). Thus, in general, the two empirical relationships

$$D(BH^+{-}B') - D(BH^+{-}B) = 0.46[PA(B') - PA(B)] \qquad (18)$$

$$D(B'H^+{-}B) - D(BH^+{-}B) = -0.54[PA(B') - PA(B)] \qquad (19)$$

may be concluded, which are in good qualitative agreement with the similar empirical relationships derived by Kebarle.[39] The

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[39] Davidson, W. R.; Sunner, J.; Kebarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1675.

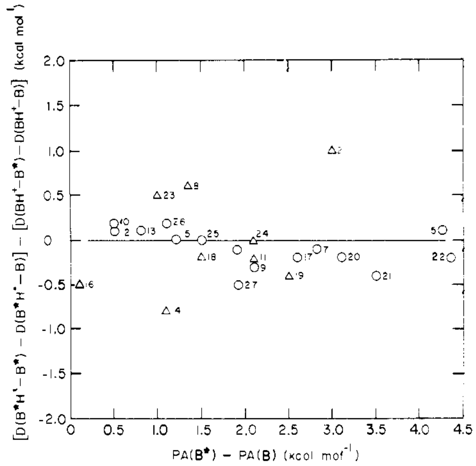

Figure 3. Dependence of the enthalpy change for the double replacement reaction, eq 20, on difference in proton affinity of the bases involved. Points are calculated from the data of Tables III and IV. Triangles correspond to equilibria involving carboxylic acids, esters, THF, and diisopropyl ether which are expected to give the poorest correlation. Circles correspond to all other equilibria.

Scheme III

$$\begin{tikzcd}
\mathrm{BHB^+ + B^*HB^{*+}} \arrow[rr, "\Delta H^\circ_{20}"] \arrow[dr, "D(\mathrm{BH^+{-}B}) + D(\mathrm{B^*H^+{-}B^*})"'] & & \mathrm{2B^*HB^+} \\
& \mathrm{BH^+ + B + B^*H^+ + B^*} \arrow[ur, "-[D(\mathrm{BH^+{-}B^*}) + D(\mathrm{B^*H^+{-}B})]"'] &
\end{tikzcd}$$

similarity of the coefficients in these two relationships and the fact that they are nearly equal to 0.5 lends strong support to the conjecture that in proton-bound dimers the proton is nearly equally shared by the two bases involved. The scatter in the data of Figure 2 may be largely ascribed to differences in steric effects in the different dimers.

A further interesting relationship is revealed from our examination of the enthalpy change for the double replacement reaction, eq 20. The thermochemistry for this process may be broken down

$$\mathrm{BHB^+ + B^*HB^{*+} \rightarrow 2B^*HB^+} \tag{20}$$

into the components shown in Scheme III and the overall enthalpy change given by eq 21. If the relationship derived from the data

$$\Delta H^\circ_{20} = D(\mathrm{B^*H^+{-}B^*}) - D(\mathrm{B^*H^+{-}B}) - [D(\mathrm{BH^+{-}B^*}) + D(\mathrm{B^*H^+{-}B})] \tag{21}$$

of Figure 2 is valid, then the difference in binding energies of $\mathrm{B^*H^+}$ to B* and B should be roughly equal to the difference in binding energies of $\mathrm{BH^+}$ to B* and B since the proton affinity difference is the same in each case and $D(\mathrm{B^*H^+{-}B^*})$ is on the average equal to $D(\mathrm{BH^+{-}B})$. Thus, as a result, ΔH°_{20} should show no dependence on PA(B*) – PA(B) and further should be roughly equal to zero. The validity of this hypothesis is supported by the data shown in Figure 3. Most of the values for ΔH°_{20} lie within ±0.2 kcal $\mathrm{mol^{-1}}$ of zero with the only exceptions being those involving either THF or a carboxylic acid or ester.

The above results indicate that the potential energy surface for asymmetric proton-bound dimers is qualitatively similar to that for symmetric proton-bound dimers, with the proton being almost equally shared in a broad minimum potential well.

Conclusion

We have presented a general method whereby proton-bound dimers of oxygen n-donor bases may be readily generated and solvent-exchange equilibria between dimers containing species of comparable base strength obtained. The results obtained for 20 symmetric proton-bound dimers and 30 asymmetric proton bound dimers indicate that there is a remarkable constancy in the hydrogen bond energetics. For symmetric proton-bound dimers a hydrogen bond energy of 30.8 ± 2 kcal $\mathrm{mol^{-1}}$ may be derived for all of the dimers studied virtually independent of gas-phase basicity and variation in functionality for water, alcohols, ethers, aldehydes, ketones, carboxylic acids, and esters. The upper limit of hydrogen bond energies is given by THF which is known from solution results to be a stronger base than other ethers and better solvating agent. The lower limits are occupied by carboxylic acids and esters, which may be interpreted as inhibition of resonance stabilization by solvation, and by diisopropyl ether which has a hydrogen bond weakened by steric crowding. In asymmetric proton-bound dimers a dependence of hydrogen bond energy on the *difference* in proton affinities of the bases involved is shown. In all cases hydrogen bond energies in excellent agreement with HPMS clustering experiments are obtained.

Work extending the above experiments to other bases involving heteroatoms other than oxygen is currently in progress.

Acknowledgment. Financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.