appearance of a typical metal–metal π bond. For comparison, the maximum in-plane amplitude is 0.442 au. Thus the presence of the S_2 bridge has enhanced the π component of the metal–metal bond and moreover has significantly stabilized the level. Since π bonding is typically stronger than δ bonding it appears that the S_2 unit not only serves as a bridge so that Fe–S–Fe binding may occur but in fact also allows an increase in the *direct* (through space) Fe–Fe interaction. The stabilization of the b_1 level is one of the leading factors for the increased HOMO–LUMO gap in the bridged complex and its consequent stability. In summary, rather than a single metal–metal bonding orbital, $S_2Fe_2(CO)_6$ possesses, according to the Xα calculations, some multiple Fe–Fe bond character arising from bent, nearly σ bonding in the HOMO and a significant direct π component in the b_1 orbital at −12.5 eV. It is interesting to note in this regard that SCF-Xα-SW calculations on $Fe_2S_2(SH)_4^{2-}$ show that the major Fe–Fe bonding interaction occurs via the bridging sulfurs.[9]

It may be of some interest to note that the orbital ordering in $Fe_2(CO)_6$ is reminiscent of what Hoffmann and collaborators[31] have termed counterintuitive orbital mixing, (COM), that is the two Fe–Fe bonding levels, b_1 and a_1, are less stable than the group of nonbonding levels owing to appropriate small admixtures of CO character into the wave functions. The addition of the S_2 bridge removes one of the cases of COM by stabilizing the b_1 level so that in $S_2Fe_2(CO)_6$ it is below the nonbonding orbitals. The a_1 level, however, remains "counterintuitive".

The CO levels are also influenced by the addition of the S_2 bridge, the major effect being a further stabilization of the $\widetilde{5\sigma}$ levels by about 0.7 eV compared to their position relative to $\widetilde{1\pi}$ in the $Fe_2(CO)_6$ fragment; so once again, all other things being equal, one might expect a stronger Fe–CO bond in $S_2Fe_2(CO)_6$ than in $Fe_2(CO)_6$. Again, the reason is likely that the addition of the bridging S_2 unit causes a migration of electrons away from the Fe nuclei allowing further σ donation from the carbonyls. It is our hope that once calculations are at hand for a sufficient number of transition-metal carbonyls and for cluster models of CO adsorbed on different transition metals one might be able to correlate the position of the $\widetilde{5\sigma}$ levels with the catalytic activity of the different systems for reactions involving CO (e.g., the Fischer–Tropsch synthesis of hydrocarbons). Work in this direction is in progress.

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The Proton in Dimethyl Sulfoxide and Acetone. Results from Gas-Phase Ion Equilibria Involving $(Me_2SO)_nH^+$ and $(Me_2CO)_nH^+$

Y. K. Lau, P. P. S. Saluja, and P. Kebarle*

Contribution from the Chemistry Department, University of Alberta, Edmonton, Canada T6G 2G2. *Received May 13, 1980*

Abstract: The gas-phase equilibria $(Sl)_{n-1}H^+ + Sl = (Sl)_nH^+$, where Sl are the solvent molecules dimethyl sulfoxide and acetone, were measured with a pulsed electron beam high ion source pressure mass spectrometer. $\Delta H_{n-1,n}°$ and $\Delta S_{n-1,n}°$ were obtained for $n = 1$ to $n = 3$. These results are compared with previously determined values for Sl = H_2O, Me_2O, and MeCN and literature data for the transfer of the proton from the gas phase to the liquid solvent $\Delta H_{tr}(H^+)^{g\rightarrow Sl}$. The highly exothermic transfer enthalpy for Me_2SO is a result of the strong interactions from $n = 1$ to $n = 3$, particularly $n = 1$, i.e., the high proton affinity of Me_2SO. Interactions for $(Me_2SO)_nH^+$ for higher n must be considerably weaker than those for $(H_2O)_nH^+$.

Introduction

The present work is part of a continuing effort from this laboratory to provide additional insights on ion solvation by means of measured binding energies between the ion and a limited number of solvent molecules.[1-3] The energies are obtained by determining gas-phase ion equilibria $(n - 1,n)$ involving a given positive or negative ion $M^{\pm}$ and solvent molecules Sl.

$$(n - 1,n) \qquad M^{\pm}(Sl)_{n-1} + Sl = M^{\pm}(Sl)_n$$

Dimethyl sulfoxide, Me_2SO, is probably the most important dipolar aprotic solvent.[4] Following earlier measurements involving another dipolar aprotic solvent, acetonitrile, a program of measurements was undertaken involving Me_2SO with the alkali positive ions and halide negative ions,[5] large delocalized organic anions,[6] and the proton (present work). Regarding the proton, it was thought of interest to compare the Me_2SO results with those for some other dipolar aprotic solvents. Fortunately Meot-Ner[7] has published recently a study involving acetonitrile. We chose to do also acetone, which bears some structural similarity to dimethyl sulfoxide but is a much weaker dipolar solvent. This makes a comparison of these three solvents possible.

Experimental Section

The equilibrium constant $K_{n-1,n}$ for the reaction

$$H^+(Me_2SO)_{n-1} + Me_2SO = H^+(Me_2SO)_n$$

was obtained from the expression

$$K_{n-1,n} = \frac{I_n}{I_{n-1}} \frac{1}{P_{Me_2SO}}$$

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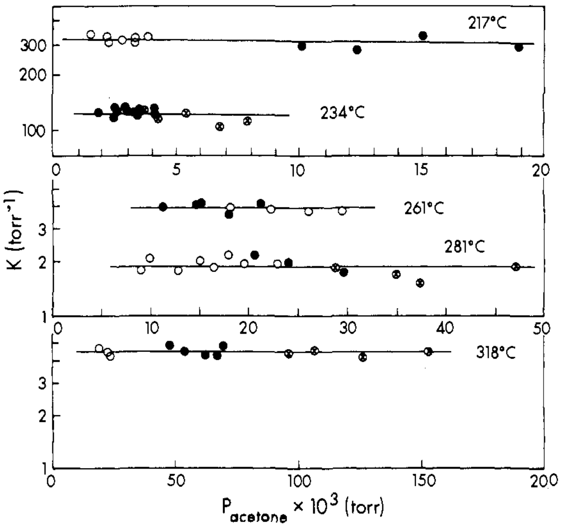

Figure 1. Equilibrium constants for reaction: $Me_2SOH^+ + Me_2CO = (Me_2SO)(Me_2CO)H^+$. Plots show independence of equilibrium constant with changing pressure of acetone. Pressures of carrier gas methane have also been changed in some runs. Thus results at 234 °C include results obtained at two different acetone to methane ratios: (●) 0.96×10^{-3}, (⊗) 1.9×10^{-3}. Results for 318 °C include the acetone to methane ratios (○) 9.6×10^{-3}, (●) 14.3×10^{-3}, (⊕) 28.2×10^{-3}.

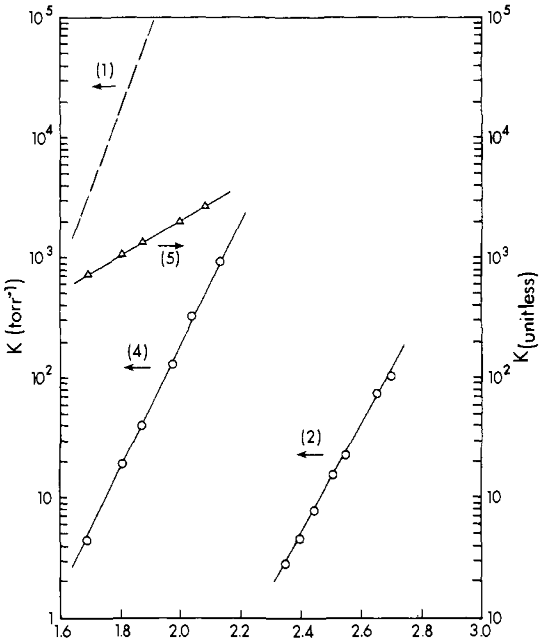

Figure 2. van't Hoff plots of equilibrium constants K, obtained from equilibrium constant plots like that in Figure 1. Calling A = actone and D = dimethyl sulfoxide, reactions correspond to (1) $DH^+ + D = D_2H^+$, (2) $D_2H^+ + D = D_3H^+$, (4) $DH^+ + A = DAH^+$, (5) $DAH^+ + D = D_2H^+ + A$. Reaction 1 was not measured directly. Since (1) = (4) + (5), the plot for (1) was obtained from $K_1 = K_4K_5$. The ΔH and ΔS data obtained from the plots are summarized in Table I.

where I_n/I_{n-1} is the equilibrium ion intensity ratio of protonated Me_2SO clusters and P_{Me_2SO} is the pressure of Me_2SO in the ion source. The measurements of I_n/I_{n-1} were made in a high-pressure mass spectrometer with a pulsed electron beam. Pulsing permits one to follow the kinetics of the approach to equilibrium. The apparatus was the same as that used in earlier work.[8] It is in all respects similar to that described earlier[9] but uses a quadrupole instead of a magnetic sector for mass analysis. A gas sample of 2–5 torr methane carrier gas containing a known pressure (1–150 mtorr) of Me_2SO was passed in slow flow through the ion source. The equilibrium constant, $K_{n-1,n}$, was evaluated from the time constant ion intensity ratio I_n/I_{n-1} observed over a 2000 μs time interval some 100–200 μs after the ionizing electron pulse.

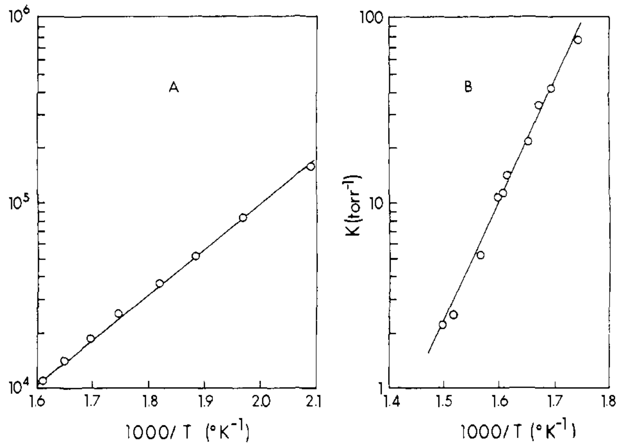

Figure 3. vant' Hoff plots for equilibria: $A_2H^+ + D = ADH^+ + A$ shown in A and $AH^+ + A = A_2H^+$ shown in B. ΔH and ΔS data obtained from van't Hoff plots are given in Table I.

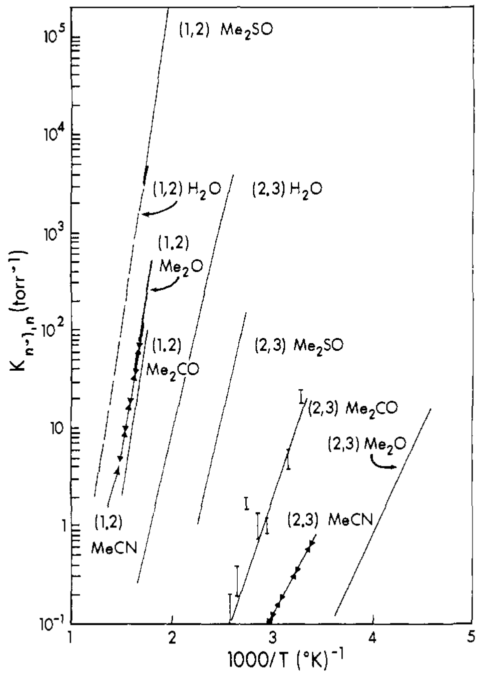

Figure 4. Comparison of van't Hoff plots involving proton and different solvent molecules Sl (Me_2SO, Me_2CO, H_2O, MeCN). The equilibria are $(Sl)_{n-1}H^+ + Sl = (Sl)_nH^+$, numbers besides plots give value for $(n-1,n)$. The (1,2) plots indicate binding free energies in the order $Me_2SO \approx H_2O > Me_2SO \approx MeCN \approx Me_2CO$ but they are all rather close. This similarity disappears completely for the dissociation $(Sl)_3H^+ \rightarrow (Sl)_2H^+ + Sl$. For this process the energies are $H_2O > Me_2SO > Me_2CO > MeCN > Me_2O$ with rather large differences between some pairs.

In all measurements, temperature and concentration conditions were so adjusted as to keep the I_n/I_{n-1} ratio less than ~0.2. The use of a major gas (CH_4), which is not the solvent vapor, permits measurements of clustering equilibria to be executed at very low (mtorr) solvent gas pressures. This leads to measurement of the $K_{n-1,n}$ at the lowest possible temperatures and wards off problems with unimolecular decomposition of the ion I_n in the vacuum of the mass analysis and detection region.[10] The use of $I_n/I_{n-1} < 0.2$ helps reduce problems[11] with collision induced preferential dissociation of I_n relative to I_{n-1} in the vacuum region immediately outside the ion exit slit.

The measurements involving acetone were done under similar conditions to those described above for Me_2SO.

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Table I. Summary of Thermodynamic Data for Protonated Clusters Involving D = Dimethyl Sulfoxide and A = Acetone

	$-\Delta H^{\circ a}$	$-\Delta G^{\circ}{}_{298}{}^{a}$	$-\Delta S^{\circ a}$
Association Reactions			
(1) $DH^+ + D = D_2H^+$	30.8 ± 0.3^b	24.0 ± 0.3^b	22.9 ± 0.5^b
(2) $D_2H^+ + D = D_3H^+$	21.3 ± 0.4	10.9 ± 0.5	34.9 ± 1.1
(3) $AH^+ + A = A_2H^+$	30.1 ± 1.0	21.0 ± 1.2	30.4 ± 1.7
(4) $DH^+ + A = DAH^+$	24.1 ± 0.3	16.8 ± 0.32	24.5 ± 0.5
Exchange Reactions			
(5) $DAH^+ + D = D_2H^+ + A$	6.76 ± 0.07	7.25 ± 0.08	1.66 ± 0.13
(6) $A_2H^+ + D = DAH^+ + A$	11.0 ± 0.2	11.3 ± 0.3	-0.80 ± 0.44

[a] ΔH° and ΔG° values are in kcal/mol and ΔS° is in cal/(K mol), standard state 1 atm. Errors given based on standard deviation of van't Hoff plots. Actual errors probably considerably larger, i.e., ±2 kcal/mol for ΔH° and ±5 cal/(K mol) for ΔS°. [b] Values calculated from those for reactions 4 and 5. All others are from directly measured equilibria as shown.

Results

The results of the experiments described in the previous section are shown in Figures 1–4. The reactions (1)–(6), whose equilibria were determined, are given in Table I.

Figure 1 illustrates that the equilibrium constants were independent of the pressure of the solvent gas, over a range of pressures. While Figure 1 gives results only for reaction 4, similarly wide pressure changes were used also in the other equilibria measurements.[12] Figures 2 and 3 give the van't Hoff plots for the equilibria (1)–(6).

Because of the very strong bonding in the $(Me_2SO)_2H^+$, the equilibrium (1) could not be measured at temperatures below 600

$$Me_2SOH^+ + Me_2SO = (Me_2SO)_2H^+ \qquad (1)$$

K. In order to avoid problems with pyrolysis of the Me_2SO which occur at higher temperatures, equilibrium 1 was not measured directly but via the two steps (4) and (5). Since (1) = (4) + (5), $K_1 = K_4K_5$. The equilibria (4) and (5) were determined separately.

$$Me_2SOH^+ + Me_2CO = (Me_2SO)(Me_2CO)H^+ \qquad (4)$$

Since Me_2SO interacts with the proton much more strongly than

$$(Me_2SO)(Me_2CO)H^+ + Me_2SO = (Me_2SO)_2H^+ + Me_2CO \qquad (5)$$

Me_2CO, equilibrium 5 could be measured only by using a very large ratio of Me_2CO/Me_2SO. This necessitated use of acetone as the carrier gas at pressures in the torr range, for these experiments.

The ΔH°, $\Delta G^\circ{}_{298}$, and ΔS° values for reactions 1–6 obtained from the van't Hoff plots in Figures 2 and 3 are given in Table I. Figure 4 and Table II were prepared in order to facilitate comparisons with other pertinent data from the literature. Figure 4 shows van't Hoff plots for previously determined equilibria from this laboratory involving the proton and water,[9] the proton and dimethyl ether[13] and Meot-Ner's determinations of the proton and acetonitrile.[7] The corresponding ΔH°, ΔG°, and ΔS° values are given in Table II. Values for the (2,3) equilibria involving acetone are not given in Tables I and II although a van't Hoff plot is shown in Figure 4. Actually, it was found that the equilibrium "constants" were not independent of pressure but decreased when the pressure of the third gas and of acetone were increased. In this temperature range there was also a side reaction leading to formation of an ion corresponding to $A_2H^+–H_2O$. This ion is probably protonated mesityl oxide formed by the acid-catalyzed aldol condensation of two acetone molecules. It appears that this side reaction affected the (2,3) equilibrium. Therefore the (2,3) van't Hoff plot for acetone in Figure 4 should be only taken as a rough guide to the values of the equilibrium constants for that reaction.

Scheme I

$$\begin{array}{rc r}
(3) & AH^+ + A = A_2H^+ & \\
(6) & A_2H^+ + D = ADH^+ + A & \\
-(4) & ADH^+ = DH^+ + A & \\
\hline
 & AH^+ + D = A + DH^+ & (7)
\end{array}$$

Also given in Table II are $-\Delta H_{0,1}$, which correspond to the proton affinities of the solvent molecules. The proton affinities for H_2O, MeCN, Me_2CO, and Me_2O are from an earlier compilation[1] but are adjusted to the new standard value of Houle and Beauchamp[14] for the PA of isobutene. The proton affinity for Me_2SO is based on a new ladder of equilibria by Lau et al.[15] This value is very close to a result given eariler by Taft.[16]

The experimental determinations of the present work can be checked by means of the thermodynamic cycle shown in Scheme I, where A stands for acetone and D for Me_2SO.

Reactions 3 + 6 − 4 add up to the proton transfer from actone to Me_2SO. This means that $\Delta H_3 + \Delta H_6 - \Delta H_4 = \Delta H_7 = PA(A) - PA(D)$. An identical relationship holds also for the entropy changes. The results obtained from the thermodynamic cycle above are $\Delta H_7 = -17.0 \pm 1.1$ kcal/mol and $\Delta S_7{}^\circ = -5.1 \pm 1.8$ cal/(deg mol) (see Table I). The proton-transfer equilibria ladder[15] gives $\Delta H_7 = -15.8 \pm 0.4$ kcal/mol (see Table II). This value is based on a $\Delta G_7{}^\circ$ measured[15] at 600 K and an estimated $\Delta S_7{}^\circ = -1.4$ cal/(deg mol) based solely on rotational symmetry numbers changes. The ΔH_7 from cycle and ladder agree within the estimated error of the measurements. The $\Delta S_7{}^\circ$ results are not in as good agreement. The cycle above may lead to cumulative errors; on the other hand the estimate of $\Delta S_7{}^\circ$ for the proton transfer is also not very reliable. The true $\Delta S_7{}^\circ$ may be somewhere between the two results.

Discussion

The present results for the proton and Me_2SO provide some interesting insights when compared to results for other solvent molecules like water, dimethyl ether, acetonitrite, and acetone. Such a comparison is possible on the basis of Figure 4 and Table II. The proton affinities of the compounds listed in Table II are very different. Particularly noticeable is the high proton affinity of Me_2SO and the large difference of 42.7 kcal/mol between $PA(Me_2SO)$ and $PA(H_2O)$. The binding free energies of the proton-held dimers $(Sl)_2H^+$ are given by the order of the van't Hoff plots (1,2) in Figure 4. An inspection of the figure shows that the interactions for all the molecules are rather similar; i.e., all the (1,2) plots are close together and have similar slope. The observed binding energy order is $Me_2SO \approx H_2O > Me_2O \approx MeCN \approx Me_2CO$. The $-\Delta H_{1,2}$ enthalpy changes (see Table II) are all between 31.6 and 30.2 kcal/mol. In contrast to this, the binding energies in the trimers $(Sl)_3H^+$ as reflected by the positions of the (2,3) van's Hoff plots and the $-\Delta H_{2,3}$ values are very different. The order observed is $H_2O > Me_2SO > Me_2CO > MeCN > Me_2O$; the $-\Delta H_{2,3}$ (kcal/mol) changes are 21.3 for Me_2SO and 19.5 for H_2O but only 10.1 for Me_2O and 9.3 for MeCN.

In earlier work dealing with proton-held dimers AHB^+ where A and B were oxygen and nitrogen *n*-donor bases, we had observed[17–19] that for a series in which B was held constant but AH^+

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[12] Details on all experimental results are available in: Lau, Y. K., Ph.D. Dissertation, "Studies of Thermal Ion-Molecule Equilibria—Determinations of Gas-Phase Basicities and Proton Affinities by High Pressure Mass Spectrometry", Department of Chemistry, University of Alberta, Edmonton, 1979.

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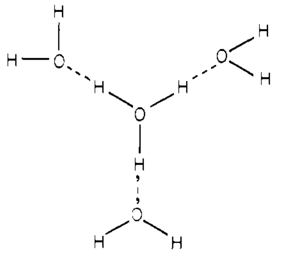
Table II. Data for Reactions: $\text{Ion(Sl)}_{n-1} + \text{Sl} = \text{Ion(Sl)}_n$[a]

$n-1,n$/Sl	H_2O[b]			$(CH_3)_2O$[c]			$(CH_3)_2SO$			CH_3CN[d]			$(CH_3)_2CO$		
	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$
0,1[e]	171.7			192.3			214.4			191.5			198.6		
1,2	31.6	24.3	24.3	30.7	21.9	29.6	30.8	24.0	22.9	30.2	21.6	29	30.1	21.0	30.4
2,3	19.5	13.0	21.9	10.1	1.9	27.6	21.3	10.9	34.9	9.3	3.6	19			
3,4	17.5	9.3	27.3												
							Ion = K^+								
0,1	17.4[f]	16.9[h]		20.8[f]			33.6[g]	30.2[h]		24.4[f]	22.4[h]		24.4[g]	19.8[h]	

[a] All values in kcal/mol except ΔS which is in cal/(K mol), standard state 1 atm. $\Delta G°$ values at 298 K. [b] Cunningham.[9] [c] Grimsrud.[13] [d] Meot-Ner.[7] [e] Proton affinities from ref 11 and 15 based on standard by Houle and Beauchamp.[14] [f] From Kebarle.[1] [g] From Magnera.[5] [h] Binding energies $\Delta E_{0,1}$ obtained from electrostatic calculations: Davidson[24] and Magnera.[5]

was changed, the binding energy increased with the acidity of AH^+ (i.e., decreased with increasing proton affinity of A). When AH^+ was kept constant and B changed, the binding energy increased with the basicity of B. The binding energy in AH^+B could thus be considered as a partial proton transfer in which the strength of the interaction increases with the acidity of AH^+ and the basicity of B. A qualitative theoretical justification for the above rule was given recently.[19] Allen and co-workers,[20] have made calculations for the binding energies of a series of proton-held dimers AH^+B consisting of the hydrides of elements in the first two rows of the periodic system and were able to validate the rule also for these systems. Unfortunately, when it comes to symmetric dimers A_2H^+, the rule cannot be applied since a high proton affinity of A decreases the acidity of AH^+ as it increases the basicity of the proton acceptor A′, i.e., the effects are opposed. Previously measured[18] binding energies of alkylamine dimers A_2H^+ were found rather similar and could not be related to the proton affinities of A or any other simple factor. The present results present the same picture. The proton affinities of the solvent molecules are very different, but the binding energies of the dimers A_2H^+ are found to be quite similar.

Previous work involving a comparison of protonated water, methanol, and dimethyl ether showed[13] that the binding energy of the third molecule in the trimer A_3H^+ is drastically lower if the bases A are so substituted that they do not provide hydrogen-bonding positions. For example, since with water hydrogen bonding is possible, the binding energy in the trimer I is relatively large. On the other hand in dimethyl ether the hydrogen bonding positions are blocked by methyl groups (see structure II), and the third ether molecule is bonded weakly.[13] Meot-Ner[7] has invoked the same argument for the weak bonding in the acetonitrile trimer. Comparing the $-\Delta H_{2,3}$ for Me_2O, MeCN, and Me_2SO which are 10.1, 9.3, and 21.3 kcal/mol, one is struck by the very high binding energy for the Me_2SO trimer, yet Me_2SO like Me_2O and MeCN does not have hydrogen bonding positions. The large dipole moment[21] of Me_2SO (3.96 D) cannot in itself be the reason, since the dipole[21] of MeCN (3.92 D) is of nearly the same magnitude. Also, one expects that for both compounds the dipole will be mostly concentrated in the functional group, i.e., SO and CN. On the basis of these considerations alone one is tempted to attribute the difference between Me_2SO and MeCN on structural factors. While MeCN is linear, Me_2SO has a pyramidal structure.[22] It may be that this pyramidal structure permits two Me_2SO molecules to align their dipoles as shown in structure III. The alignment III is analogous to the chain-like SO dipole alignments which have been suggested to occur in liquid Me_2SO by Parker[23] and others.[4] However, a somewhat more detailed examination shows that the dipole alignment as in III need not be the cause for the relatively strong bonding of the third molecule in $(Me_2SO)_3H^+$. The bonding in a structure like II, where the third molecule goes in a farther position, should bear some resemblance to the bonding of a first molecule to a large ion like Cs^+ or K^+. Fortunately $\Delta H_{0,1}$ for K^+ and all solvent molecules under consideration have been determined previously in this laboratory.[1,5] These data are included in Table II. Water has the lowest binding enthalpy ($-\Delta H_{0,1}$ = 17.4 kcal/mol); the very high $-\Delta H_{2,3}$ for the proton and water is thus clearly a consequence of hydrogen bonding, as concluded above. The $-\Delta H_{0,1}(K^+)$ in kcal/mol then increase in the order Me_2O (20.8), MeCN (24.4), Me_2CO (24.4), and Me_2SO (33.6). This is the same order as observed for the $-\Delta H_{2,3}(H^+)$ in the van't Hoff plots of Figure 4 and Table II. In particular the $-\Delta H_{0,1}(K^+)$ for Me_2SO is much larger than the rest just as $-\Delta H_{2,3}(H^+)$ for Me_2SO is much larger than the rest. Improved electrostatic calculations for the binding energy in $K^+(Sl)$, $\Delta E_{0,1}$ have been performed[5,24] for most of the molecules in Table II. These calculations[24] take into account the net atomic charge distribution whose vector addition leads to the dipole moment of the molecule. The net atomic charges were based on Mulliken electron populations[25-27] from STO-3G calculations. The molecular polarizabilities were also split up into bond polarizabilities.[5,24] The calculated $\Delta E_{0,1}(K^+)$ are given in Table II. It can be seen that these values are fairly close to the measured $\Delta H_{0,1}$. The difference in $\Delta E_{0,1}(K^+)$ between Me_2SO and MeCN is found to be largely due to a much stronger ion–permanent dipole in-



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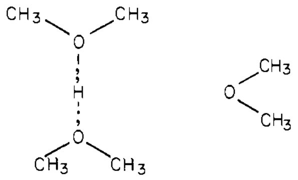

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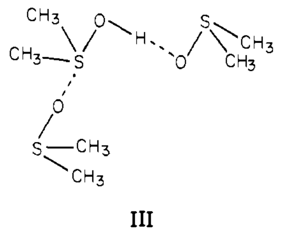

III

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(25) Unfortunately Mulliken electron populations are strongly dependent on the basis sets used and quantitatively unreliable. However since we are only considering relative values and all Mulliken populations were obtained[26,27] with STO-3G, one may assume that the $\Delta E_{0,1}$ results are significant.

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teraction for Me_2SO. Thus, while the magnitudes of the dipoles is the same for MeCN and Me_2SO, the actual distribution of the net atomic charges produces stronger interactions for Me_2SO. This is qualitatively revealed by the net atomic charges on the "electron donor" end of the molecules; the N atom in MeCN has only 0.185 negative charges, while the O atom of Me_2SO has 0.441 negative charges.[27]

Domain, Rinfret, and Benoit[28] on the basis of calorimetric measurements of the enthalpy of the reaction, in which gaseous HCl is dissolved in the given liquid solvent, have estimated the transfer enthalpies of the proton from the gas phase to the liquid solvent, $\Delta H_{tr}^{g\rightarrow Sl}$ (H^+). Their results are as follows: H_2O, –270.0; Me_2SO, –276.1; MeCN, –256.6 (all in kcal/mol). We have pointed out earlier[29] that the stepwise solvation enthalpies (n – 1,n) can on principle also be used for estimates of $\Delta H_{tr}^{g\rightarrow Sl}$ (ion). This can be done with eq 8, where $\Delta H_{n-1,n}(\mathrm{Ion(Sl)}_n)$ are the

$$\mathrm{H}_{tr}^{g\rightarrow Sl}(\mathrm{Ion}) = \sum_{n=1}^{n=n} \Delta H_{n-1,n}(\mathrm{Ion(Sl)}_n) - \sum_{n=2}^{n=n} \Delta H_{n-1,n}(\mathrm{Sl})_n \quad (8)$$

stepwise enthalpies for the ion solvent cluster while $\Delta H_{n-1,n}(\mathrm{Sl})_n$ are stepwise enthalpies for the neutral solvent cluster. Since for n large ("large" may mean less than 10 or 20) $\Delta H_{n-1,n}(\mathrm{Ion(Sl)}_n) \approx \Delta H_{n-1,n}(\mathrm{Sl})_n$, one needs to know only the first several stepwise enthalpies for the ion and the neutral cluster to obtain an insight into the ion solvation energy. Unfortunately data for the neutral Me_2SO clusters are completely absent. More information is available for water from calculations.[30] As a rough approximation,[30] for n = 1 to n = 3, one can replace $\Delta H_{n-1,n}(\mathrm{Sl})_n$ with $-^1/_2\Delta H_{evap}(\mathrm{Sl})$, bearing in mind that for small n, $\Delta H_{n-1,n}(\mathrm{Sl})_n$ is much smaller than $-\Delta H_{evap}(\mathrm{Sl})$. With use of the available three $\Delta H_{n-1,n}$ in Table II for H_2O and Me_2SO and $\Delta H_{evap}(H_2O)$ = 10.5 kcal/mol and $\Delta H_{evap}(Me_2SO)$ = 13.7 cal/mol one obtains

$$\Delta H_{0,3}(\mathrm{H^+(H_2O)}_n) + {}^2\!/_2\Delta H_{evap}(\mathrm{H_2O}) = -212.4 \text{ kcal/mol}$$

$$\Delta H_{0,3}(\mathrm{H^+(Me_2SO)}_n) + {}^2\!/_2\Delta H_{evap}(\mathrm{Me_2SO}) = -252.9 \text{ kcal/mol}$$

Comparing this result with Benoit's values $\Delta H^{g\rightarrow H_2O}(H^+) = -270$ kcal/mol and $\Delta H^{g\rightarrow Me_2SO}(H^+) = -276.1$ kcal/mol, one finds that the first three solvent molecules account for ~80% of the total solvation of H^+ in water and for 92% of the same quantity for Me_2SO. As expected, the interactions with the first few solvent molecules make a preponderant contribution. Furthermore, for water where only 80% of the total is accounted, interactions with the ion will be contributing to much higher n than for Me_2SO. This difference of behavior is easily understood. Three-dimensional hydrogen bonding and the smallness of the water molecules contribute to strong net interactions of the ion with solvent molecules even at large n. On the other hand for Me_2SO, even if linear dipole chains like that in structure III do occur for ion clusters with large n, the large bulk of the Me_2SO molecules will prevent efficient stacking near the ion and thus lead to a relatively rapid fall off for the net binding energies to the ion. Comparing the large proton affinity difference of –42.7 kcal/mol between Me_2SO and H_2O with the modest difference of –6 kcal/mol for the transfer enthalpies of the proton of liquid Me_2SO and H_2O, one comes to the conclusion, that the greater solvation of the proton in liquid Me_2SO is completely due to the very much higher proton affinity of Me_2SO. While the initial two interactions $\Delta H_{1,2}$ and $\Delta H_{2,3}$ for Me_2SO and H_2O are of comparable magnitude, the net effect of all the higher n interactions is one of much poorer solvation by Me_2SO as compared to water.

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The Solution Conformational Preferences of the Sugar and Sugar Phosphate Constituents of RNA and DNA

John A. Gerlt*[1] **and A. Virginia Youngblood**

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511.

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Abstract: The analysis of the proton NMR spectra of stereospecifically deuterated (*S*)-tetrahydrofuranmethanol, methyl β-D-ribofuranoside, methyl β-D-2-deoxyribofuranoside, and the 5-phosphates of the sugar acetals leads to several important and previously unrecognized observations about the determinants of the solution conformations of nucleosides and nucleotides: (1) in the unsubstituted sugars and their phosphates, the preferred furanoside ring conformation is the 3′-endo pucker and not the 2′-endo pucker observed in most nucleosides and nucleotides; (2) in the unsubstituted sugars and their phosphates, the gauche–gauche rotamer about the C_4–C_5 bond does not predominate as is found in the nucleosides and nucleotides but rather the two rotamers in which the vicinal C–O bonds are gauche to one another (gauche–gauche and gauche–trans) are about equally favored; (3) the observed predominant occurrence of the gauche–gauche rotamer about the $C_{4'}$–$C_{5'}$ bond in nucleosides and nucleotides is presumably the result of an interaction between the substituent on $C_{5'}$ and the heterocyclic base, which is made more favorable by a shift in the furanoside ring conformation; and (4) the rotameric distribution about the C_5–O_5 bonds in the sugar acetal phosphates is the same as that observed in nucleosides and nucleotides. These observations suggest that the nature of the furanoside ring conformation and the rotameric distributions about the $C_{4'}$–$C_{5'}$ and $C_{5'}$–$O_{5'}$ bonds may not be as intimately interdependent as previously believed.

NMR spectroscopy has permitted the determination of the conformational preferences of a large number of nucleosides, mononucleotides, and oligonucleotides in aqueous solution.[2] The most widely used experimental method has been to measure the vicinal coupling constants (J_{HCCH} and J_{POCH}) and relate these to the values of the intervening dihedral angle by application of the appropriate Karplus equation. Although there has been some disagreement as to the precise values of the parameters to be used in the Karplus equation, the results obtained by a large number of investigators are in qualitative agreement. In almost all nucleosides and mononucleotides, the furanoside ring has been observed to prefer the 2′-endo puckered conformation and the rotameric distribution about both the $C_{4'}$–$C_{5'}$ and $C_{5'}$–$O_{5'}$ bonds favors the gauche–gauche conformations. Determination of the

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[2] For an excellent recent review of the voluminous literature, see D. B. Davies, *Prog. Nucl. Magn. Reson. Spectrosc.*, **12**, 135 (1978).

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