viewed in two ways: ligand selectivity for cations of a certain size, or cation selectivity for ligands of a certain size. This would suggest that, for example, 15-crown-5 is selective for Na^+ over K^+. This is not the case (see Table I). On the other hand, according to this principle, Na^+ should select "appropriately sized" 15-crown-5 over the larger 18-crown-6. This is not the case either, suggesting that the hole-size correlation, while not without some foundation, is not true in general.

As mentioned above, the most important point to note about the binding constant data is that the hole-size relationship is simply not obeyed for this group of unsubstituted, flexible crown ethers. Instead, the two rules that can be formulated are the following: (1) For this series of crowns and cations, K^+ is bound more strongly than Na^+, Ca^+, or NH_4^+ by all of the crowns irrespective of hole size. (2) For this series of crowns and cations, the strongest binding is observed with 18-crown-6, irrespective of cation size or geometry (i.e., spherical for metals and tetrahedral for ammonium).

It has been reported previously that the K^+·18-crown-6 complex is intrinsically less stable than the corresponding Na^+ complex, and that the K^+ selectivity in this case is due to solvation and conformation differences between these two complexes.[6,14,15] In this group of crowns, the special stability of the K^+·18-crown-6 complex may be due to a combination of a high complexation enthalpy for K^+[6,8] and the ligand's symmetry,[14] planarity, and absence of eclipsing interactions in the backbone.[15]

There are at least four factors that make significant contributions to the binding of cations by crowns. These are the following: (1) the cation-diameter–hole-size relationship, (2) the solvation enthalpies and entropies of the cation and ligand, (3) the number of donor atoms participating in binding, and related to the latter, (4) the conformation of the bound and unbound macrorings. Of these factors, the hole-size relationship probably plays its greatest role when the ligands are relatively inflexible (not the case here) or when cation–crown affinity is determined by the picrate extraction technique. In this experiment, the ligand draws a cation across an organic–aqueous phase boundary and the colored anion that accompanies the cation is detected colorimetrically.[2,13] In this two-phase system, it is obviously more difficult to sort out the question of hole size vs. solvation enthalpy and entropy contributions. The key point, however, is that while both picrate extraction and homogeneous binding constant determinations provide useful information, they do not provide the same information.

Summary

The new, competitive ISE-based method we present here allows Ca^{2+}–cation equilibrium stability constants to be determined in solvents outside water or the usual aqueous solvent mixtures. Although we have applied the method only to anhydrous methanol, it should be applicable in any solvent system compatible with the Na^+-selective glass electrode.

We have used this new technique to complete the series of Na^+, K^+, NH_4^+, and Ca^{2+} binding constants (in anhydrous MeOH) for the 12- through 24-membered homologues of 18-crown-6. The binding constants do not obey the much publicized "hole-size relationship". Instead, for this group of crowns and cation, the strongest binding for each cation is observed with 18-crown-6 irrespective of diameter or charge. Further, it is found that K^+ is bound more strongly by all of the crowns than is any other cation in this group.

Acknowledgment. We thank the National Institutes of Health for grants (GM 29150, GM 29706, and GM 31846) that supported this work.

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Identification of the Gas-Phase Trimer $(CH_3)_2S{\cdot}(HF)_2$ by Photoelectron Spectroscopy

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Received March 31, 1983

Abstract: Analysis of the He I photoelectron spectrum measured for the binary intermolecular complex $(CH_3)_2S{\cdot}HF$ indicates the presence of another gas-phase species that is assigned as the trimeric system $(CH_3)_2S{\cdot}(HF)_2$. The first ionization energy of $(CH_3)_2{\cdot}(HF)_2$, measured at 10.3 eV, is higher than that for $(CH_3)_2S{\cdot}HF$, which is 9.5 eV. Molecular orbital calculations that suggest that $(CH_3)_2S{\cdot}HF$ has a nonplanar equilibrium geometry of C_s symmetry indicate that the addition of the second hydrogen-bonded HF moiety is achieved with little change in the structure of the dimer.

In a recent paper[1] we described how, on the basis of the He I photoelectron spectra measured for the dimeric complexes $(CH_3)_2O{\cdot}HF$ and $(CH_3)_2O{\cdot}HCl$, we were able to identify the weaker gas-phase complex $(CH_3)_2S{\cdot}HF$ from its He I spectrum. The measurements involved the use of a pinhole inlet system with high-pressure equilibrium mixtures of the respective monomer gases. A spectrum-stripping procedure that subtracts the appropriate monomer spectra is used to reveal the spectrum of the intermolecular complex.

An important aspect of this analysis concerns the effect of the intermolecular hydrogen bond in stabilizing the nonbonding n_s electrons of $(CH_3)_2S$ as indicated by a 0.8-eV increase in their vertical ionization energy (IE) on complexation. The appearance of this first ionization band of $(CH_3)_2S{\cdot}HF$ between the first and second bands of $(CH_3)_2S$ assisted in its identification. Molecular

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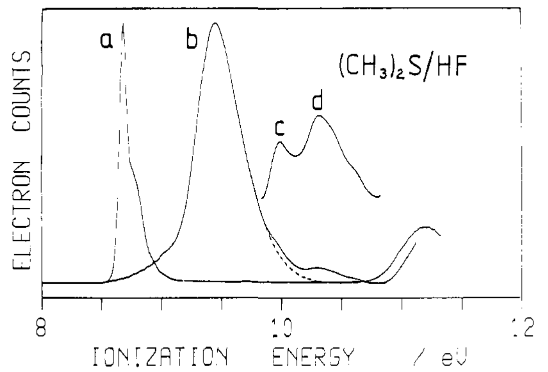

Figure 1. He I photoelectron spectra of (a) $(CH_3)_2S$ and (b) $(CH_3)_2S{\cdot}HF$. Bands c and d are low-intensity peaks extracted from spectrum b.

orbital calculations[2] simulate this effect and indicate that it arises mainly from the electrostatic effect of the polar HF moiety. Calculations[1] also suggested that while the $(CH_3)_2O{\cdot}HF$ complex is essentially planar in geometry, the $(CH_3)_2S{\cdot}HF$ complex has an energy minimum for a structure of C_s symmetry with an out-of-plane angle of 67° made by the S--H–F line with the C–S–C plane. This trend is in line with the experimental geometries determined for $H_2O{\cdot}HF$[3] and $H_2S{\cdot}HF$[4] (though $(CH_2)_2O{\cdot}HF$[5] shows an out-of-plane angle of 72°).

However, the He I spectrum of $(CH_3)_2S{\cdot}HF$ presented as Figure 3c in our earlier paper[1] includes some weaker bands not assigned to the dimeric species. Our further analysis of this structure allows the identification of the symmetric trimeric species $(CH_3)_2S{\cdot}(HF)_2$ incorporating two equivalent S--H hydrogen bonds, and suggests that the isomeric species $(CH_3)_2S{\cdot}HF{\cdot}HF$ incorporating one S--H hydrogen bond and one F--H hydrogen bond may also be present.

Spectra

The relevant He I photoelectron spectra covering the 10–12-eV IE range are shown in Figure 1. Spectrum a is of the $(CH_3)_2S$ monomer and shows the narrow first band at a vertical IE of 8.7 eV associated with the nonbonding sulfur 3p orbital, n_s. Spectrum b is the stripped spectrum assigned as that of the dimer $(CH_3)_2S{\cdot}HF$ and described in our earlier paper.[1] The main band centered at 9.5 eV is of the n_s orbital in the complex increased by 0.8 eV from that of the monomer. On the high IE side of this band, between 10 and 11 eV, there is additional structure. The dashed curve that represents a Gaussian function fitted to the major band b allows the extraction of this structure which is given in an upscaled form as bands c and d. If bands c and d are each assumed to be reasonably symmetric then c can be regarded as considerably weaker than d. Then the relative areas of the four bands in the measured spectrum of the $(CH_3)_2S/HF$ mixture are estimated as a:b:c:d = 100:7.7:0.1:0.3.

It is possible that peaks c and d arise from impurity species in the gas mixture or from impurity lines in the helium discharge. A careful analysis of the monomer $(CH_3)_2S$ spectrum in the 10–11-eV range revealed no additional bands, and a consideration of the possible stable reaction products of $(CH_3)_2S$ and HF showed that no bands, with one exception, would be expected in this region. So a small amount of H_2S, identified by its narrow first band at 10.48 eV, was easily stripped from the measured spectrum. Bands arising from He Iβ radiation were also eliminated as possible explanations for the weak bands c and d.

The fwhm of band d is around 0.4 eV similar to that of band b. It corresponds to a vertical IE of 10.3 eV, which represents an increase of 0.8 eV over band b and an increase of 1.6 eV over band a. These shifts suggest that the addition of a second HF monomer to $(CH_3)_2S{\cdot}HF$ via a second S--H hydrogen bond producing the $(CH_3)_2S{\cdot}(HF)_2$ trimer is occurring in the gas mixture. The electrostatic effect of two HFs on the IE of the n_s orbital is double that of one HF.

Table I. Comparison of Experimental and Calculated First Ionization Energy Shifts (in eV) for $(CH_3)_2S/HF$ Complexes

		calcd	
	exptl ΔI^a	STO-3G $\Delta(-\epsilon)^b$	4-31G $\Delta(-0.92\epsilon)^c$
$(CH_3)_2S{\cdot}HF^d$	0.8	0.61	0.88
$(CH_3)_2S{\cdot}(HF)_2{}^e$	1.6	1.15	1.69
$(CH_3)_2S{\cdot}HF{\cdot}HF^f$	1.3	0.88	1.24

[a] Experimental value of the difference of vertical IEs, $I_1(\text{complex}) - I_1((CH_3)_2S)$. [b] Theoretical value based on calculated eigenvalues. [c] Theoretical value based on scaled eigenvalues. [d] For the partly optimized geometry with $R_{S--H} = 2.26$ Å and θ(out-of-plane) = 67°, C_s symmetry. [e] For $R_{S--H} = 2.29$ Å and $\theta_1 = \theta_2 = 67°$, C_{2v} symmetry. [f] For $R_{S--H} = 2.18$ Å and $\theta = 67°$ with linear $(HF)_2$, C_s symmetry.

Calculations

Molecular orbital calculations on these complexes agree with this interpretation. Earlier calculations[6] on the $(CH_3)_2O{\cdot}HF$ dimer showed that the n_0 IE shift on complexation is dominated by the electrostatic influence of the HF and that Koopmans' approximation used with the closed-shell neutral molecular ground states adequately simulates this observation. Open-shell calculations of the ion states indicated that electronic relaxation effects contribute minimally to the calculated IE shifts. The results of the calculations on $(CH_3)_2S{\cdot}(HF)_2$ are summarized in Table I. With both the STO-3G and 4-31G bases the IE shifts are approximately doubled for the trimer in comparison with the dimer. A partial geometry optimization at the STO-3G level carried out for the trimer was based on the experimental monomer geometries. This gave a structure of C_{2v} symmetry with HF monomers placed symmetrically out of the C–S–C plane at equal angles of 67°, this angle being the same as that obtained for the dimer. However, a hydrogen bond length of 2.29 Å for $R_{S..H}$ was obtained for the trimer, slightly larger than the 2.26 Å determined for the dimer.

Discussion

While geometry optimization using small basis sets cannot be regarded as reliable, the calculated IE shifts can be considered to be more accurate as they involve energy differences that are not very sensitive to changes in geometry. Within these limitations the calculations suggest that the trimeric species can be formed in observable quantities by HF addition to the $(CH_3)_2S{\cdot}HF$ dimer without appreciable geometric perturbation of the dimer structure. This observation agrees with the recently determined structure of the $H_2S{\cdot}HF$ dimer[4] where an out-of-plane angle close to 90° was obtained. A $H_2S{\cdot}(HF)_2$ trimer consisting of approximately colinear hydrogen bonds might hence be expected.

The weaker band c shown in Figure 1 might arise from the isomeric trimer species $(CH_3)_2S{\cdot}HF{\cdot}HF$ which in thermodynamic terms is expected to be more stable than $(CH_3)_2S{\cdot}(HF)_2$. Our STO-3G calculations based on the experimental geometries of $(CH_3)_2S$ and $(HF)_2$ give a hydrogen bond length, $R_{S..H}$, of 2.18 Å which is considerably smaller than that in both $(CH_3)_2S{\cdot}HF$ and $(CH_3)_2S{\cdot}(HF)_2$. At these geometries calculations at the 4-31G level give stabilization energies of 55 kJ/mol for $(CH_3)_2S{\cdot}(HF)_2$ and 72 kJ/mol for $(CH_3)_2S{\cdot}HF{\cdot}HF$. The calculated IE shifts given in Table I show reasonable agreement with the observed shift for band c.

This indication of the presence of $(CH_3)_2S{\cdot}HF{\cdot}HF$ is rather tentative, and it is possible that higher clusters are involved. However, a recent experimental result suggests that the trimer and higher clusters of HF are cyclic,[7] which might preclude their complexation with $(CH_3)_2S$.

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Conclusion

An analysis of the UV photoelectron spectra of gaseous mixtures of $(CH_3)_2S$ and HF has indicated the presence of the trimeric intermolecular complex $(CH_3)_2S\cdot(HF)_2$. This is identified by its first PE band, associated with the localized nonbonding sulfur 3p electrons, which is 0.8 eV higher than that of the dimer $(CH_3)_2S\cdot HF$ and 1.6 eV above that of the $(CH_3)_2S$ monomer. A comparison of these IE shifts with typical hydrogen bond energies suggests that the complex ions produced by UV ionization are quite unstable.

Acknowledgment. This work was supported by the Australian Research Grants Scheme.

Registry No. $(CH_3)_2\cdot HF$, 87261-56-1; $(CH_3)_2S\cdot(HF)_2$, 87261-57-2.

EPR and ODMR Studies of the Lowest Excited Triplet States of Two Tautomers of Indazole in a Benzoic Acid Host Crystal

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Received February 1, 1983

Abstract: It is shown that, in a benzoic acid host, indazole in the T_1 state exists in two tautomeric forms (abbreviated as 1H and 2H). The properties of the T_1 states of both tautomers are investigated by means of EPR and zero-field ODMR techniques. The T_1 state of 1H is located 23 590 cm^{-1} above the ground state while that of 2H is 20 903 cm^{-1}. Zero-field splittings of two tautomers are $D = 0.1077$ cm^{-1} and $|E| = 0.0293$ cm^{-1} for 1H and $D = 0.0983$ cm^{-1} and $|E| = 0.0120$ cm^{-1} for 2H, respectively. The phosphorescence decay takes place predominantly from the middle sublevel in both tautomers, but the decay rate constant of 2H is about 5 times larger than that of 1H, which is likely due to the larger nonradiative decay rate constant. From the angular dependence of the EPR signals, the orientations of the two tautomers in benzoic acid are determined. Spin distributions of the two tautomers are estimated from the analysis of the hyperfine splittings and are compared with the result of π-electron UHF calculations. Good agreement was obtained in the case of 2H. The low-field EPR signals exhibit hyperfine anomalies due to forbidden transitions.

The lowest excited triplet (T_1) states of purine, benzimidazole, and indole have received considerable attention because of their possible importance in photobiological processes.[1-11] Indazole is interesting as a member of this series of molecules but also from viewpoints of tautomerism and photochemistry.

Indazole has two tautomeric forms (*1H*- and *2H*-indazole are hereafter abbreviated as 1H and 2H, respectively), as shown in Figure 1. The question whether indazole can exist in two different forms in nature has attracted much interest. Rousseau and Lindwall[12] compared the UV absorption spectrum of indazole with those of 1-methyl- and 2-methylindazole and concluded that 2H does not exist in water. Buu-Hoi et al.[13] and Black et al.[14] studied the NMR spectra in acetone and chloroform and also concluded that the 1H form is predominant. An ^{14}N NMR investigation by Witanowski et al.[15] showed that only the 1H form exists in acetone. An X-ray study of the indazole crystal[16] shows that indazole exists in the 1H form in the crystal. Therefore, so far there has been no experimental evidence that indazole exists in the 2H form. It seems interesting to examine the possibility that both forms of tautomers might exist in the T_1 state in a favorable environment.

The photochemistry of indazole has been investigated by several workers.[17-20] The transposition of the nitrogen atom to produce benzimidazole and the isomerization into *o*-aminobenzonitrile are known to take place photochemically. The T_1 state may play an important role in these reactions.

In the present work we have studied the T_1 state of indazole in the mixed single crystal of benzoic acid (abbreviated as BAC) by means of EPR and zero-field ODMR techniques at liquid helium temperatures. The BAC host is particularly suited to the present study because indazole dissolves into BAC by forming hydrogen bonds with BAC. We have found that in the T_1 states both 1H and 2H exist in the BAC host and studied the properties of the T_1 states of both tautomers in detail. Interestingly, the magnetic and decay properties of these tautomers are rather

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