Solvent Effects on Strong Charge-Transfer Complexes. I. Trimethylamine and Sulfur Dioxide in Gas and in Heptane

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Abstract: Ultraviolet spectra and thermodynamic data have been obtained for the 1:1 donor-acceptor complex of trimethylamine and sulfur dioxide in the gas phase and in heptane solutions. The prominent spectral feature is the charge-transfer band of the complex, with maximum absorbance at 276 mμ in gas, 273 mμ in heptane, and 258 mμ in dichloromethane. Values are given for the equilibrium constant, enthalpy, and entropy of the formation reaction in gas and in heptane, and for individual energies and free energies of interaction of donor, acceptor, and complex with the solvent heptane. For the first time, the energy and free energy of sublimation of a charge-transfer complex (without dissociation) are reported. The complex is stabilized by transfer from gas to heptane to dichloromethane, as evidenced by increasing values of the equilibrium constant and $-\Delta H°$ for the formation reaction (K^{298} = 340 l. mole^{-1} in the gas and 2550 l. mole^{-1} in heptane; $-\Delta H°$ = 9.7 kcal/mole in gas and 11.0 kcal/mole in heptane). Explanations are offered for the unusual effects of solvent on the stability of the complex and the frequency of the ultraviolet absorption band. A general method is proposed for predicting the effect of variation in solvent properties on the thermodynamic functions for charge-transfer formation reactions.

Although there have been numerous reports of the properties of solid adducts of SO_2 with various donors,[1] relatively little is known about SO_2 charge-transfer complexes in solution, and no information is available on charge-transfer complexes of SO_2 in the gas phase. In only three previous publications have enthalpies of formation of charge-transfer complexes of SO_2 in solution been reported.[2-4]

We became interested in the complexes of SO_2 and aliphatic amines for several reasons: first, the information available about these adducts indicated that they are charge-transfer complexes with large formation constants;[5] second, SO_2 and the lower molecular weight amines are so volatile that it should be possible to obtain vapor-phase charge-transfer spectra for a number of these systems at moderate temperatures; and, finally, the strength and chemical stability of the amine–SO_2 complexes in a variety of media make it feasible to obtain accurate information about the effects of solvation on the thermodynamic and spectral properties of the complexes. Previous results from this laboratory have demonstrated that increasing solvent polarity stabilizes the strong triphenylarsine–I_2 complex, as indicated by increasing values of $-\Delta H$ and the equilibrium constant for the 1:1 complex formation reaction.[6] Since so little is known about the solvation of strong complexes, we thought it would be worthwhile to consider in detail the influence of solvent interaction on amine–SO_2 systems.

Recently we reported preliminary results of a spectral and thermodynamic study of the 1:1 charge-transfer complex between SO_2 and trimethylamine (TMA), in the gas phase and in heptane.[7] The present article includes detailed results of that study and additional thermodynamic data which are valuable in the elucidation of the effects of solvation on the complex formation equilibrium.

Experimental Section

Compounds and Solutions. Trimethylamine was liberated from 35% aqueous solution (Riedel-De Haën, A. G.) by two procedures: (a) distillation from sodium hydroxide pellets, and (b) extraction with heptane or hexane, in the presence of sodium hydroxide. Both the pure liquid (collected by condensing the distillate) and the organic amine solutions (collected by extraction) were stored over solid sodium hydroxide. Gas chromatographic analysis of the products revealed only a single peak corresponding to TMA. Amine concentrations in solution were determined by titration with aqueous HCl to the methyl red–brom cresol green mixed indicator end point.

Gaseous sulfur dioxide was bubbled into previously dried organic solvents to give solutions of approximately the desired concentration. Wet analysis of SO_2, where required, was accomplished by adding standard I_2 in CCl_4 to known volumes of SO_2 solutions and titrating with thiosulfate. A more convenient secondary analytical method, requiring knowledge of the extinction coefficient of SO_2 in heptane (see below), involved delivery of a known volume of SO_2 solution into 20.0 ml of pure heptane in an 8-cm spectral cell and measurement of the change in absorbance at 289 mμ. This method was used throughout in determining the concentration of SO_2 in the spectral studies.

The hydrocarbon solvents were Merck Uvasol spectral grade chemicals, dried over sodium wire prior to use.

Volumetric Additions. Because of the volatility of SO_2 (and to a lesser extent TMA), ordinary volumetric pipets are not adequate for the quantitative transfer of these compounds. In both the vapor and solution spectral studies. solutions of TMA or SO_2 were delivered with 0.200- and 2.00-ml micrometer burets manufactured by Roger Gilmont Industries (Catalog No. S-1101 and S-1201). Using these burets it was possible to attain an accuracy at least equal to that of standard volumetric methods for preparing solutions for complex–equilibrium studies; moreover, no significant loss of SO_2 or TMA from the burets occurred during periods of several hours. Thus, it was possible to fill a buret with a solution of SO_2 or TMA at the beginning of a series of spectral measurements, add increments of accurately known volume into solution or gas spectral cells, and analyze the solution remaining in the buret at the end of a set of experiments. No SO_2 appeared to be lost from solution cells when they were opened for the time required to add amine samples with the microburets (as controlled spectrally). We believe the volumetric techniques described here are capable of at least as great accuracy as the more complicated vacuum or pressure-transfer methods often used in the quantitative delivery of very volatile compounds into spectral cells.

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(3) D. Booth, F. S. Dainton, and J. K. Ivin, *Trans. Faraday Soc.*, 1293 (1959).

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(6) E. Augdahl, J. Grundnes, and P. Klaboe, *Inorg. Chem.*, **4**, 1475 (1965).

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Instrument. All spectral measurements were made with a Beckman DK-1 recording spectrophotometer equipped with a thermostated cell holder. Temperatures could be maintained to within 0.1° over the range 10–60°.

Extinction Coefficient of SO_2. In order to obtain an accurate value of the extinction coefficient of SO_2 in heptane, it was necessary to titrate the entire contents of an 8-cm cell containing 20.0 cc of approximately 0.004 M SO_2. Loss of SO_2 by evaporation was prevented by use of the following procedure. After the ultraviolet spectrum of the solution had been recorded, 1.00 cc of standard 0.01 M iodine solution and about 2 cc of 0.1 M aqueous KI were added directly to the heptane solution in the cell; the contents were then thoroughly agitated, and the mixture in the cell was transferred to an erlenmeyer flask and titrated with aqueous thiosulfate solution. In this way the value $\epsilon_{SO_2} = 339 \pm 5$ l. mole^{-1} cm^{-1} at the peak wavelength, 289 mμ, was obtained. This value agrees well with that reported by Booth, *et al.*, for hexane (342 l. mole^{-1} cm^{-1} at 290 mμ).[3] They commented that most previously reported values of ϵ_{SO_2} appear to be too low, owing to loss of SO_2 by evaporation from nonvacuum apparatus.

Starting with the value for ϵ_{SO_2} in heptane, it was not difficult to determine extinction coefficients for SO_2 in a second solvent or in the gas phase. A micrometer buret was filled with a solution of SO_2 in hexane or heptane of approximately known concentration. A measured volume of the solution was delivered into a known volume of solvent in a spectrophotometer cell (or into the gas cell) and the absorbance was determined. Next, an equal volume of the same SO_2 solution was added to pure heptane contained in another cell. From the ratio of the observed absorbances, the extinction coefficient of SO_2 in any medium could be inferred. Since only small volumes of heptane or hexane were added to the second medium, no corrections were made for the effect of the increments on the absorbance of SO_2. Using this method, the value $\epsilon_{SO_2} = 230 \pm 5$ l. mole^{-1} cm^{-1} at 286 mμ was obtained for the vapor phase.

Spectral Cell for Gas Measurements. The gas cell employed was an ordinary 8-cm solution spectrophotometer cell. A mercury-covered sintered glass disk, connected to the cell with a standard taper, served as an inlet valve.[8] Gases or volatile liquids may be introduced through the disk using quantitative techniques developed previously.[9]

Gas Spectra. To obtain the gas spectrum of the complex, a sample of pure amine was first introduced by warming a small reservoir of TMA to about 0° and allowing the vapors of the compound to escape through a capillary tube into the cell. From the absorbance of the vapors at 260 mμ (in comparison with a standard curve of amine absorbance *vs.* vapor concentration), the initial TMA concentration could be calculated. Next, 0.01–0.02 ml of a solution of SO_2 in hexane of known concentration was added through the disk with the 0.200-ml microburet. Hexane, in quantities 0 to 0.03 ml at temperatures in the range 35–60°, did not appear to influence the gas spectra of either the complex or the pure components.

Solution Spectra. A small quantity of SO_2 solution was added volumetrically to dry heptane in an 8-cm solution cell to give an accurately known initial concentration in the range 2.3×10^{-5} to 4.6×10^{-5} M. Increments of TMA were added volumetrically to give concentrations varying from 3×10^{-5} to 1×10^{-3} M.

Vapor Pressure Measurements. Vapor pressures of the systems TMA–heptane and SO_2–heptane were determined for the temperature range 10–30°, using an apparatus described previously.[9] Solutions of SO_2 or TMA in heptane were delivered through the mercury disk into the manometric apparatus, the bulb of which contained a given volume of pure heptane. From the equilibrium vapor pressure, the known volume of the system, and the known total amount of amine introduced, it was possible to infer Henry's law constants for the volatile solute in heptane.

Results and Calculations

Ultraviolet Spectra. The prominent spectral feature of the TMA–SO_2 systems is the new, intense absorption band which appears in the 270–280-mμ region. This broad band is well suited for investigation of the complex formation equilibrium. Data in Table I are representative of the results obtained for the two phases. Included in the table are values of the measured absorbance, $E = \log I_0/I$; analytical concentrations of donor and acceptor, [D] and [A]; calculated values of the absorbance, E_{calcd}, obtained by nonlinear least-squares analysis; derived values of the complex extinction coefficient, the formation constant, and the entropy and enthalpy of the formation reaction, $\Delta S°$ and $\Delta H°$; the half-band width of the complex absorption band, $\Delta\bar{\nu}_{1/2}$; and the oscillator strength, f.[10] Standard states of 1 mole/l. are used for all components; errors given are standard errors.

Equilibrium constants for the reaction TMA (D) + SO_2 (A) = TMA·SO_2 (AD) were calculated by utilizing the "pit-mapping" technique of Sillén and co-workers for nonlinear least-squares analysis.[11] Since the method is well suited in general for analysis of spectral data to yield extinction coefficients and equilibrium constants, we will outline its application to the 1:1 complex equilibrium situation.[12] Assuming the validity of Beer's law and the laws of dilute solution, three equations may be considered in the analysis

$$[\mathrm{D}] = c_\mathrm{D} + Kc_\mathrm{A}c_\mathrm{D} \qquad (1)$$

$$[\mathrm{A}] = c_\mathrm{A} + Kc_\mathrm{A}c_\mathrm{D} \qquad (2)$$

$$E/l - \epsilon_\mathrm{A}c_\mathrm{A} - \epsilon_\mathrm{D}c_\mathrm{D} = \epsilon = \epsilon_\mathrm{AD}Kc_\mathrm{A}c_\mathrm{D} \qquad (3)$$

in which c_A and c_D represent concentrations of the species A and D (uncomplexed donor and acceptor), ϵ_A and ϵ_D are the known extinction coefficients of the species A and D, and l is the path length of the cell. Two unknown constants, K and ϵ_AD, are to be inferred from several sets of simultaneously measured values of E, [A], and [D].

Equations 1 and 2 may be solved simultaneously (using an assumed initial value of K) to yield trial values of c_A and c_D corresponding to each pair of [D], [A] values. Using these values of c_A and c_D, ϵ in eq 3 may be calculated for each set of measurements and by ordinary linear least-squares analysis the best value of ϵ_AD may be calculated corresponding to the assumed value of K. The quantity $\Delta = \Sigma_i(\epsilon_i - \epsilon_\mathrm{AD}Kc_{\mathrm{A}_i}c_{\mathrm{D}_i})^2$ is also computed for the entire collection of measurements, for the chosen value of K. By using an appropriate optimum-seeking method,[18] Δ can be minimized with respect to both K and ϵ_AD, to yield the least-squares

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(12) Recently Wentworth, *et al.*,[13] and Trotter and Hanna[14] have discussed methods for treating the 1:1 equilibrium problem and they list numerous references to the techniques which are available. Our procedure resembles the method utilized by Conrow, *et al.*,[15] but differs in the treatment of errors in the parameters. The present method gives values for the parameters which compare closely with those obtained using the Lang method[16] but is more readily generalized to cases where more than one complex species is present. Similar computer methods have been applied in treating vapor density, vapor pressure, partition, and activity data.[17]

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Table I. Spectral Data[a] for the Trimethylamine–Sulfur Dioxide System in Heptane and in the Gase Phase

[D] × 10^5 M	[A] × 10^5 M	273 mμ		290 mμ		296 mμ	
		E	E_{calcd}	E	E_{calcd}	E	E_{calcd}
Heptane, 12.9°							
3.53	2.309	0.150	0.152	0.092	0.094	0.063	0.064
7.06	2.309	0.266	0.266	0.165	0.165	0.113	0.112
14.11	2.308	0.422	0.423	0.263	0.263	0.179	0.180
21.16	2.307	0.528	0.525	0.328	0.327	0.225	0.224
35.23	2.304	0.650	0.649	0.404	0.404	0.278	0.278
49.28	2.302	0.719	0.721	0.449	0.449	0.308	0.309
K (l. mole^{-1})		5740 ± 75		5625 ± 70		5550 ± 80	
$\epsilon_{AD} - \epsilon_A$ (l. mole^{-1} cm^{-1})		5330 ± 30		3350 ± 20		2310 ± 15	
ϵ_{AD} (l. mole^{-1} cm^{-1})		5540 ± 30		3690 ± 20		2630 ± 15	
$\Delta\bar{\nu}_{1/2}$ (cm^{-1})[b]			5950				
f (oscillator strength)			0.222				
Heptane, 20.0°							
3.51	4.559	0.185	0.184	0.118	0.118	0.082	0.082
7.01	4.558	0.339	0.340	0.215	0.217	0.150	0.151
10.51	4.557	0.475	0.472	0.302	0.301	0.212	0.210
14.01	4.555	0.586	0.586	0.374	0.373	0.260	0.260
17.51	0.554	0.682	0.684	0.436	0.435	0.304	0.304
21.01	4.553	0.767	0.769	0.488	0.489	0.340	0.342
24.50	4.552	0.845	0.845	0.538	0.537	0.375	0.375
28.00	4.551	0.913	0.911	0.579	0.579	0.406	0.405
K (l. mole^{-1})		3415 ± 55		3465 ± 60		3390 ± 80	
$\epsilon_{AD} - \epsilon_A$ (l. mole^{-1} cm^{-1})		5330 ± 50		3365 ± 30		2380 ± 35	
ϵ_{AD} (l. mole^{-1} cm^{-1})		5540 ± 50		3705 ± 30		2700 ± 35	
$\Delta\bar{\nu}_{1/2}$ (cm^{-1})[c]			6050				
f (oscillator strength)			0.226				
Heptane, 30.0°							
3.47	3.369	0.080	0.082	0.056	0.055	0.041	0.039
6.94	3.368	0.152	0.155	0.103	0.104	0.073	0.074
13.88	3.367	0.276	0.279	0.187	0.188	0.132	0.133
20.80	3.365	0.382	0.382	0.256	0.256	0.182	0.182
34.64	3.362	0.544	0.540	0.361	0.361	0.256	0.257
48.44	3.358	0.656	0.655	0.439	0.437	0.312	0.311
69.10	3.353	0.781	0.780	0.522	0.519	0.371	0.369
89.69	3.349	0.867	0.869	0.573	0.576	0.408	0.410
K (l. mole^{-1})		1920 ± 30		1950 ± 35		1940 ± 40	
$\epsilon_{AD} - \epsilon_A$ (l. mole^{-1} cm^{-1})		5080 ± 40		3405 ± 30		2430 ± 20	
ϵ_{AD} (l. mole^{-1} cm^{-1})		5290 ± 40		3745 ± 30		2750 ± 20	
$\Delta\bar{\nu}_{1/2}$ (cm^{-1})[c]			6300				
f (oscillator strength)			0.225				
Heptane, 40.3°							
6.87	4.628	0.118	0.116	0.081	0.079	0.059	0.058
20.59	4.623	0.308	0.309	0.210	0.211	0.154	0.154
34.29	4.619	0.464	0.463	0.315	0.316	0.230	0.230
54.77	4.612	0.643	0.644	0.440	0.439	0.320	0.320
75.20	4.605	0.781	0.783	0.532	0.532	0.386	0.388
95.57	4.599	0.894	0.892	0.605	0.605	0.443	0.441
K (l. mole^{-1})		1035 ± 15		1040 ± 15		1030 ± 25	
$\epsilon_{AD} - \epsilon_A$ (l. mole^{-1} cm^{-1})		4790 ± 40		3340 ± 30		2445 ± 30	
ϵ_{AD} (l. mole^{-1} cm^{-1})		5000 ± 40		3680 ± 30		2765 ± 30	
$\Delta\bar{\nu}_{1/2}$ (cm^{-1})[c]			6550				
f (oscillator strength)			0.221				
For the formation reaction in heptane: $\Delta H° = -11.0 \pm 0.3$ kcal/mole; $\Delta S° = -21.4 \pm 0.9$ eu/mole; $K^{298} = 2550 \pm 50$ l./mole							

[D] × 10^3 M	[A] × 10^5 M	276 mμ	
		E	E_{calcd}
Gas, 39.7°			
2.31	4.93	0.558	0.565
1.82	5.04	0.478	0.482
1.58	5.92	0.508	0.506
1.37	5.04	0.381	0.383
0.99	4.93	0.285	0.285
0.45	5.04	0.144	0.143
0.77	4.93	0.216	0.226
1.60	3.19	0.281	0.276
1.17	3.26	0.205	0.217
1.17	3.26	0.217	0.217
0.59	3.19	0.125	0.116
0.59	3.19	0.123	0.116
3.48	2.30	0.376	0.352
4.46	2.34	0.417	0.418
4.85	2.34	0.429	0.439
2.70	2.34	0.315	0.301
K (l. mole^{-1})	154 ± 12		
$\epsilon_{AD} - \epsilon_A$ (l. mole^{-1} cm^{-1})	5500 ± 350		
ϵ_{AD} (l. mole^{-1} cm^{-1})	5700 ± 350		
$\Delta\bar{\nu}_{1/2}$ (cm^{-1})[b]	5500		
f (oscillator strength)	0.212		
For the formation reaction in gas: $\Delta H° = -9.7 \pm 0.4$ kcal/mole; $\Delta S° = -21.0 \pm 1.0$ eu/mole; $K^{298} = 340 \pm 35$ l. mole^{-1}			

[a] E values represent differences between the absorbance of the mixture and the absorbance of SO_2 at the concentration [A] in the absence of amine. [b] Calculated from absorption curve. [c] Calculated from the long-wavelength side of the curve.

values of these parameters and the standard errors (σ_K and $\sigma_{\epsilon_{AD}}$).

During the early phases of the present study we were greatly aided by the availability of Burg's measurements of the dissociation pressure of the solid adduct TMA · SO_2.[19] Burg assumed that the vapor above the solid compound consists almost entirely of the dissociated components, SO_2 and TMA, and he calculated thermodynamic constants for the reaction TMA·SO_2(s) = TMA(g) + SO_2(g). At 44.2°, for example, the dissociation pressure of the compound is 20.1 mm; therefore, the product of the partial pressures of free SO_2 and free amine cannot exceed approximately 100 mm^2. From our preliminary results we estimated that the saturation partial pressure of the complex is about 0.5 mm at 44°. Thus, if equal concentrations of donor and acceptor are present in the vapor, no more than about 5% of either the donor or the acceptor can be converted into the complex. On the other hand, if the initial partial pressure of SO_2 is on the order 0.7 mm, and if the amine is added to give a total pressure of about 120 mm, approximately 40% of the SO_2 molecules will be in the complexed form—hence it is quite feasible to determine both K and ϵ_{AD} from the variation of E with c_D.[20] The gas phase absorbance values in Table I correspond to 5 to 45% complexation of acceptor molecules. Figure 1 shows calculated absorption spectra for the TMA·SO_2 complex in heptane and in the gas phase, together with the spectrum of pure SO_2 in heptane.

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(20) W. B. Person, *ibid.*, **87**, 167 (1965).

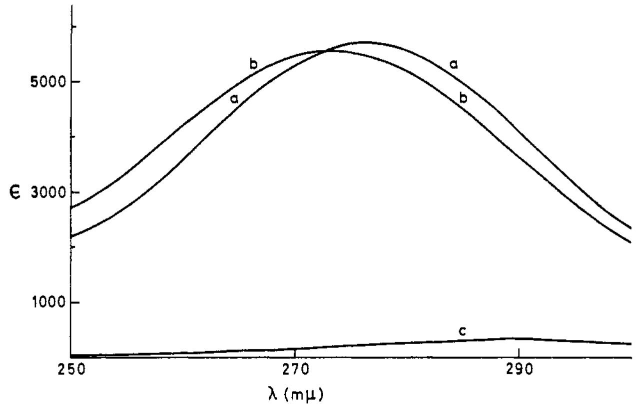

Figure 1. Calculated ultraviolet absorption spectra for the trimethylamine–sulfur dioxide complex in the gas (a) at 39.7° and in heptane (b) at 12.9°; (c) showing the absorption of SO_2 in heptane. The gas spectrum of SO_2 (ϵ_{max} 230 at 286 mμ) and the absorption curves for the amine are omitted.

The $\Delta H°$ value for the formation reaction in heptane (Table I) was obtained from the variation of K with temperature; however, values of $\Delta H°$ for the gas reaction were calculated from the variation of E with temperature for a constant composition of the gas mixture in the cell. This procedure was utilized because of the somewhat larger errors in K values determined for the gas phase as compared to heptane solution. As noted by Drago, *et al.*,[21] the direct enthalpy method is capable of high precision when it can be assumed that $\epsilon_{AD} - \epsilon_A$ is independent of temperature at a particular wavelength. Gas spectra were obtained for several SO_2–TMA mixtures at temperatures ranging from 39 to 60°. In view of the fact that the peak absorptivity decreases significantly with temperature in heptane, it was not assumed that $\epsilon_{AD} - \epsilon_A$ is constant at the peak wavelength in the vapor. However, in heptane, it appears that $\epsilon_{AD} - \epsilon_A$ is nearly constant at 290 mμ, 17 mμ away from the peak wavelength (see Table I); therefore, the assumption was made that $\epsilon_{AD} - \epsilon_A$ is temperature independent in the gas phase at 293 mμ (also 17 mμ away from the peak). Since the complex absorption band shape and change of half-band width with temperature are nearly the same in the two phases, this seems to be a reasonable premise. The data in Table I indicate that there is a definite tendency for the complex absorption band in heptane to broaden and decrease in peak intensity with increasing temperature, but the integrated intensity (proportional to the product of $\Delta\bar{\nu}_{1/2}$ and ϵ_{AD} at the peak wavelength) is practically constant. In the gas phase $\Delta\bar{\nu}_{1/2}$ also increases with temperature (about 4% per 10°, compared to 3.5% per 10° in heptane).

A variation of the technique used in studying the homogeneous gas phase reaction was applied in determining thermodynamic constants for the reaction $TMA \cdot SO_2(s) = TMA \cdot SO_2(g)$. A large concentration of amine (~0.01 M) was added to the gas cell initially, and SO_2 was added in sufficient quantities to precipitate a milligram or so of the solid complex in the neck of the cell. Spectra were recorded at temperatures varying from 15 to 37°; at least 30 min was allowed for equilibration at each temperature. To analyze these spectra, two wavelengths were selected at which the extinction coefficient of SO_2 vapor is the same (*e.g.*, 276 and 296 mμ). The saturation concentration of the complex is directly proportional to the difference between the absorbances at these two wavelengths, corrected slightly for the absorbance of amine at 276 mμ. From the assumed dependence of the complex extinction coefficient on temperature, it is possible to compute the concentration of the molecular complex in the vapor phase at saturation at each temperature. We believe this is the first example of the determination of the thermodynamic properties associated with the sublimation of a charge-transfer complex (without dissociation). The thermodynamic constants $\Delta H° = 17.7 \pm 1.0$ kcal/mole and $\Delta S° = 35.1 \pm 3.5$ eu/mole were calculated for the sublimation reaction, using standard states of pure solid complex and complex vapor at 1 mole/l. An alternate way of calculating these values is to combine the results of Burg[19] for the reaction $TMA \cdot SO_2(s) = TMA(g) + SO_2(g)$ with the thermodynamic data obtained here for the reaction $TMA(g) + SO_2(g) = TMA \cdot SO_2(g)$. This yields $\Delta H° = 19.2$ kcal/mole and $\Delta S° = 40.6$ eu/mole for the sublimation, in reasonable agreement with the values obtained directly from the measurement of the spectra of the saturated vapors.

Vapor Pressures. The Henry's law constants, K_h = partial pressure of a species divided by its molar concentration in solution, were determined for TMA and SO_2 in heptane at 10°, 20°, and 30°, corresponding to solute partial pressures in the range 2 to 40 mm. The values are summarized in Table II, along with values of the Henry's law constants for TMA in heptane calculated from the results of Wheeler and Levy.[22] We were unable to find literature values of K_h for SO_2 in heptane.

Table II. Henry's Law Constants for Trimethylamine and for Sulfur Dioxide in Heptane

Solute	t, °C	K_h, mm mole^{-1} l.
TMA	-40^a	20
	0^a	124
	10	155 ± 5
	20	228 ± 10
	30	292 ± 13
SO_2	10	1270 ± 40
	20	1650 ± 50
	30	2050 ± 100

[a] Calculated from data in ref 22.

Summary of Thermodynamic Results. A major goal of the present research was to obtain energy and free energy values for all the interaction and solvation steps relating to the formation of the complex in the gas phase, in heptane solution, and in the solid state. The data reported here make it possible to calculate these constants, which are summarized in the following cycle.

$$\begin{tikzcd}
 & & & \text{TMA}\cdot\text{SO}_2\text{(s)} \arrow[d, "17.1"', "(7.40)"] \\
\text{TMA(g)} \arrow[d, "-4.8"', "(-2.57)"] & + & \text{SO}_2\text{(g)} \arrow[d, "-3.8"', "(-1.40)"] \arrow[r, "-9.1", "(-3.55)"'] & \text{TMA}\cdot\text{SO}_2\text{(g)} \arrow[d, "-10.5"', "(-5.15)"] \\
\text{TMA (heptane)} & + & \text{SO}_2\text{ (heptane)} \arrow[r, "-11.0", "(-4.73)"'] & \text{TMA}\cdot\text{SO}_2\text{ (heptane)}
\end{tikzcd}$$

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(21) R. S. Drago, R. L. Carlson, N. J. Rose, and D. A. Wenz, *J. Am. Chem. Soc.*, **83**, 3572 (1961).

(22) O. H. Wheeler and E. M. Levy, *Can. J. Chem.*, **37**, 1727 (1959).

The numbers in parentheses represent Gibbs free energy values (ΔG°) and the remaining numbers are internal energy changes (ΔU°) for the various steps. All values are given in kcal/mole, and standard states for components in solution and in the gas phase are 1 mole/l. ideal dilute solution. Internal energy changes were considered in the cycle, rather than ΔH° values, because of the irrelevance of pV terms to a discussion of molecular interactions and solvation effects. For the condensed phases it is assumed that enthalpy and internal energy may be used interchangeably. Uncertainties in ΔU° values for gas and heptane are approximately 0.5 kcal/mole, whereas the ΔG° values have standard errors of about 0.03 kcal/mole.

Discussion

Thermodynamic Data. The thermodynamic cycle and the constants ΔG° and ΔU° reported in the previous section are of considerable interest in a discussion of solvation effects. The large magnitudes of the contributions of solvation to the thermodynamic properties of the three species should caution one against concluding that equilibrium constants and energies of association will not vary much from gas to inert solvent, or from one inert solvent to another.

It is generally expected that the equilibrium constant and $-\Delta H^\circ$ for a molecular complex formation reaction will decrease or remain nearly the same as the medium is changed from gas to a nonpolar solvent or from a nonpolar solvent to a polar solvent. Such a situation prevails in the few charge-transfer systems for which both gas phase and solution data are available.[23-28] However, the data reported in the previous section show that the TMA–SO_2 complex interacts more strongly with heptane than do the two separated components. The solvent effect probably reflects the large dipole moment of the complex, which leads to strong dipole-induced dipole interactions in solution. Moede and Curran[5] have previously reported dielectric data for mixtures of TMA and SO_2 in benzene, from which they calculate a dipole moment of 4.95 D for the 1:1 complex, compared to moments of 1.6 D for SO_2 and 0.86 D for TMA. The effect of solvent-dipole interactions is further exhibited by the thermodynamic data for the complex in polar solvents; preliminary results indicate that the equilibrium constant for the reaction TMA + SO_2 = TMA·SO_2 in dichloromethane is approximately a factor of ten greater than K in heptane, and the value of ΔU° is 2 or 3 kcal/mole more negative.[29]

We know of only two previously reported types of charge-transfer systems for which increasing solvent polarity apparently favors the formation of the complex. The strong aliphatic amine–iodine complexes studied by Nagakura and co-workers[30] appear to be stabilized by polar solvents, as indicated by increasing K values and dipole moments. However, no direct information is available about the change of $-\Delta H^\circ$ with solvent polarity. The only complex for which both $-\Delta H^\circ$ and K have been reported to increase with increasing polarity of the solvent is the triphenylarsine–iodine complex.[6]

In attempting to explain the role of the solvent in charge-transfer equilibria, previous investigators have considered both specific interactions of the solvent (*via* competing chemical equilibria) and non-specific solvation effects. Recently Trotter and Hanna[14] and Drago, *et al.*,[31] have discussed some of these approaches and listed several references to publications in which both types of interaction are considered. Drago and co-workers consider specific and nonspecific solvent effects in relation to the thermodynamic properties of the reaction dimethylacetamide + I_2 = dimethylacetamide·I_2 in CCl_4, benzene, and dichloromethane. They attempt to infer the various contributions to the enthalpy of the formation reaction by utilizing cycles similar to the one presented in the previous section. Apparently the concept of specific interaction of the solvent benzene with iodine is adequate to explain differences in ΔH and K for the dimethylacetamide–I_2 complex formation reaction in CCl_4 and benzene. On the other hand, Drago, *et al.*, conclude that in CH_2Cl_2 both specific and nonspecific solvation effects are important in altering the values of thermodyanmic constants for the formation reaction from those obtained using the more nearly inert solvents. Sufficient data were not available to allow a separation of the effects of solvation on the enthalpies and free energies (or activity coefficients) of the three individual solute species (donor, acceptor, and complex). Several years ago Kortüm and Vogel[32] reported results of a thorough study of activity coefficients of the species involved in a charge-transfer reaction. They emphasized the importance of considering solvation effects on values of the thermodynamic parameters characteristic of association reactions, even when dealing exclusively with solvents which are frequently characterized as inert.

In treating the influence of solvation we will use a method proposed by Christian, *et al.*,[33] to correlate solvent effects on hydrogen-bonding equilibria. They related equilibrium constants for the reaction pyridine + H_2O = pyridine·H_2O in several organic solvents to the free energy changes for the following equilibria, which involve only the individual components

$$H_2O\text{ (solvent A)} = H_2O\text{ (solvent B)} \qquad \text{(I)}$$

and

$$\text{pyridine (solvent A)} = \text{pyridine (solvent B)} \qquad \text{(II)}$$

It was assumed that the thermodynamic parameters ΔH° and ΔG° for the reaction

$$H_2O\cdot\text{pyridine (solvent A)} = H_2O\cdot\text{pyridine (solvent B)} \qquad \text{(III)}$$

can be calculated from those for reactions I and II by the expressions

$$\Delta H^\circ_{III} = \alpha(\Delta H^\circ_I + \Delta H^\circ_{II}) \text{ and } \Delta G^\circ_{III} = \alpha(\Delta G^\circ_I + \Delta G^\circ_{II})$$

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where α is an empirical constant, unaffected by temperature or choice of solvent (at least in the absence of strong specific interactions between the solvent and any of the three species involved in the association equilibrium). The single fitting parameter $\alpha = 0.71$ was adequate for correlating the effects of the solvents cyclohexane, carbon tetrachloride, toluene, benzene, and 1,2-dichloroethane on the $\Delta G°$ values for the 1:1 association reaction; however, no $\Delta H°$ data were available for testing the temperature dependence of α. To the extent that the method of correlation proves to be reliable, it makes possible the prediction of variation in K and $\Delta H°$ for a complex formation reaction in a range of solvents from thermodynamic constants for the individual donor and acceptor molecules in these solvents.

The data in the thermodynamic cycle given above correspond to a bonding situation very different from that for the hydrogen-bonding reaction of water with pyridine. For the TMA·SO_2 complex, α may be calculated from the $\Delta G°$ values to be $-5.15/(-2.57 - 1.40) = 1.30 \pm 0.02$ and from the $\Delta U°$ values to be $-10.5/(-4.8 - 3.8) = 1.22 \pm 0.11$, in reasonable agreement. The purpose of examining the premise that solvent effects can be correlated with a single value of the parameter α is illustrated by the following calculation: using only the $\Delta G°$ values in the cycle, one would have obtained the value $\alpha = 1.30$. Starting with this number, and the known $\Delta U°$ for the gas phase association reaction (−9.1 kcal/mole), it would have been possible to predict in advance the value of $\Delta U°$ for the complex formation reaction in heptane. This calculation would yield the result

$$\Delta U° = -9.1 + 1.30(-3.8 - 4.8) - (-3.8 - 4.8) = -11.7 \text{ kcal/mole}$$

in fair agreement with the observed value for the formation energy, $\Delta U° = -11.0$ kcal/mole.

An advantage of the solvation correlation considered here is that it may be used to classify complexes into those that are favored by reactive solvents and those that are not. The complexes for which $\alpha > 1$, such as TMA·SO_2 and triphenylarsine·I_2, may be concluded to be much more polar than the reactant molecules, so that interaction between the solvent and the dipole of the complex more than compensates for the loss of direct contact between the reacting groups of the uncombined species and the solvent. In the case of complexes for which $\alpha < 1$, the primary effect of formation of a bond between donor and acceptor is to "squeeze out" solvent molecules. This class of complexes apparently includes most charge-transfer complexes and to our knowledge all the hydrogen-bonded complexes for which adequate solvation data are available.

Ultraviolet Spectra. The spectral and thermodynamic data presented here may be interpreted as evidence for the formation of a charge-transfer complex of the Mulliken type,[34] stabilized by the partial transfer of an electron from the lone-pair orbital of the amine to a vacant acceptor orbital. Recent studies of the TMA·SO_2 complex in the infrared,[35] moreover, show that the S–O stretching vibrations are considerably shifted to lower wave numbers compared with the free SO_2 molecule, in accordance with this interpretation.[1]

According to Dunitz[36] the lowest unoccupied orbital in SO_2 is a hybridized $p\pi$–$d\pi$ antibonding orbital, mainly localized on the sulfur. From the principle of maximum overlap, the SO_2 would then act virtually as a σ acceptor, and the complex would be stabilized by a bond between nitrogen and sulfur. Recent MO LCAO calculations show, however, that 1.16 electrons in the lowest unoccupied acceptor orbital are connected with the oxygens.[37] Hence, it is at present not possible to characterize SO_2 as a particular type of acceptor, particularly in the absence of crystallographic data on the structure of donor–SO_2 complexes. Since the acceptor orbital apparently has π-type symmetry, the threefold axis of the amine molecule probably makes a nonzero angle with the plane of the SO_2 molecule; Moede and Curran[5] in fact assumed an angle of 55° between the N–S and SO_2 moment vectors.

From the measured dipole moment of the complex (4.95 D) and the assumed geometry of the complex, a bond moment 2.7 ± 0.4 D was calculated for the donor–acceptor coordinate bond.[5] The dipole moment of the pure dative structure (for assumed donor–acceptor distances of 2 to 3 Å) would be in the range 10 to 14 D. Thus, the contribution of the dative structure to the ground state of the complex should be on the order of 20 to 30%, although for several reasons this estimate must be considered very approximate.

The observed blue shift of the complex absorption band (from 276 mμ in gas to 273 mμ in heptane to 258 mμ[29] in dichloromethane) is opposite that commonly observed on transfer of a charge-transfer complex from a less reactive to a more reactive medium. A similar trend was observed previously[6] for the strong triphenylarsine–I_2 complex, and it was suggested that the unexpected blue shift might indicate that the ground state was more than 50% dative, corresponding to a larger dipole moment in the ground state than in the excited state. Considering the results in the previous paragraph, we doubt that this explanation is satisfactory for the TMA–SO_2 system.

Recently, Offen and Abidi have surveyed some of the theories which have been proposed to explain both observed blue shifts and observed red shifts induced by solvation.[38] We believe that the blue shifts for TMA·SO_2 can be rationalized by considering only two competing solvent effects; the interaction between the ground and excited state dipoles and the solvent, as discussed by Bayliss and McRae,[39] and the influence of solvent on the per cent dative contribution to the wave function of the ground state of the complex, as proposed by Offen and Abidi. Kobinata and Nagakura[30] have given experimental evidence that the dipole moments of aliphatic amine–iodine complexes increase with increasing solvent dielectric constant, indicating that the dative contribution to the ground state increases, as is expected theoretically.[38] In our discussion we will assume that the dipole moment of the complex is somewhat larger in the excited state than in the ground

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state, and that the per cent dative character of the ground state (hence, its polarity) increases significantly as the complex is transferred from gas to heptane to dichloromethane.

Let us imagine that the solvation of the complex occurs in two steps: (a) transfer of the complex from gas to solvent *without change in per cent dative character of* the complex; followed by (b) an increase in the contribution of the dative structure to the ground state wave function. The hypothetical step a would by itself lead to a red shift for a complex that is more polar in the excited state than in the ground state. On the other hand, step b should produce an opposite effect because the energies of the ground and excited states will separate as the per cent dative character of the ground state wave function increases. Effect b should be operative in all complexes, weak or strong, but it is probably relatively more important in the case of strong complexes. It is not likely that the mechanism proposed by Emslie and Foster[40] to explain blue shifts for some $\pi-\pi$ complexes in strongly ionizing solvents is important in the present system where the dipole moments of both the ground and excited states include a large contribution from the dative structure.

Several authors have proposed mechanisms to explain observed differences in extinction coefficients for weak charge-transfer complexes in the gas phase as compared to solution.[41] Carter, *et al.*, consider that a large part of the apparent increase in extinction coefficient on transfer of a weak complex from gas to solvent can be explained by considering chemical equilibria between the solute molecules and a well-defined solvation shell. Trotter prefers to explain intensity enhancements by considering the effect of internal mechanical pressures on the equilibrium distance between the donor and acceptor in the complex, which significantly affects the ground–excited-state orbital overlap. The close similarity of the spectra of TMA·SO_2 in gas and heptane should not be used as an argument in favor of either point of view, but only demonstrates that the mechanisms responsible for the effect of the medium on the experimental extinction coefficients are not important for strong complexes of this type.

The variation of the extinction coefficient and half-band width with temperature may also be noted (see Table I). Theoretically it should be expected that the extinction coefficient will decrease and the half-band width will increase with increasing temperature, as is observed; however, there are many examples in the literature of apparent changes in charge-transfer absorption bands with temperature that do not conform to the expected behavior. Undoubtedly in many reported systems, experimental errors in extinction and interference by donor or acceptor bands have made it difficult to determine values of ϵ and $\Delta\bar{\nu}_{1/2}$ that are accurate enough to permit any conclusion to be drawn relative to the variation of these parameters with temperature. We believe that in many change-transfer systems, particularly where strong interaction occurs between donor and acceptor, it may be justifiable to assume in advance that the per cent increase in half-band width with temperature will equal the per cent decrease in ϵ at the peak wavelength. This approach may be useful in attempts to infer ΔH from studies of the changes in absorbance with temperature of a single solution (the so-called direct enthalpy method[21]), since it is usually simpler to determine the change in half-band width with temperature than the change in extinction coefficient of the complex.

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