

## Solvent Effects on Strong Charge Transfer Complexes.

### III. Trimethylamine and Sulphur Dioxide in Polar Solvents

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Recently we reported spectral and thermodynamic data for the strong charge transfer (*CT*) complex between trimethylamine (TMA) and sulphur dioxide in the gas phase and in heptane.<sup>1-3</sup> Internal energy and free energy changes were also determined for the solvation of the individual donor, acceptor and complex species. It was noted that both  $-\Delta G^\circ$  and  $-\Delta U^\circ$  for the complex formation reaction increase as the species are transferred from gas to heptane; this effect is opposite that normally observed in the formation of weak charge transfer complexes and hydrogen-bonded complexes.<sup>2,4</sup> In addition, data from the cycle indicate that the energy of transfer of TMA $\cdot$ SO<sub>2</sub> from gas to heptane ( $-10.5$  kcal/mole) is comparable to the energy of the charge transfer reaction itself. An interesting result of the spectral investigation is that the peak frequency of the *CT* absorption band is blue shifted as the medium is changed from gas to heptane to dichloromethane.

The present communication includes additional information about TMA $\cdot$ SO<sub>2</sub> in dichloromethane and chloroform, including complete thermodynamic cycles of the type described above. The results indicate that the complex is further stabilized in these polar solvents, as is indicated by the considerable increase in the equilibrium constant and  $-\Delta H^\circ$  for the complex formation reaction.

*Experimental.* The experimental procedure, including instrumental methods, determination and control of solute concentration and the numerical technique for calculating equilibrium constants and extinction coefficients from the ultraviolet absorbance data, have been described before.<sup>2</sup> The extinction coefficient for

SO<sub>2</sub> in the chlorinated solvents was determined by comparing the absorbance of a solution of SO<sub>2</sub> in each solvent with that of a solution of SO<sub>2</sub> in heptane of the same concentration; the value  $\epsilon_{\text{SO}_2}$  in heptane was taken to be  $339 \text{ l mole}^{-1} \text{ cm}^{-1}$ .<sup>2</sup> The values determined were  $\epsilon_{\text{SO}_2} = 407 \text{ l mole}^{-1} \text{ cm}^{-1}$  at the peak wavelength in dichloromethane (286  $\mu$ ) and  $365 \text{ l mole}^{-1} \text{ cm}^{-1}$  at the peak wavelength in chloroform (289  $\mu$ ). Silica cells of length 8 cm were used for the spectral measurements.

$\Delta H^\circ$  for the complex formation reaction in dichloromethane was calculated from the equilibrium constants at 11.0, 14.8, 20.0, and 29.5° by a least squares method. The concentration of SO<sub>2</sub> was kept constant at about  $3.0 \times 10^{-5} \text{ M}$ , and the concentration of TMA was varied so that between 25 and 75 % of the SO<sub>2</sub> molecules were in the complexed form in each solution. In alcohol-free chloroform the intensity of the *CT* band decreased slowly with time. Therefore, the values of  $K_c$  and  $\epsilon_c$  in chloroform were determined at one temperature (20°) using very fresh solutions, and the  $\Delta H^\circ$  value was inferred from the change in intensity of the *CT* band which occurred as the temperature was changed rapidly from 20 to 40° for a series of mixtures at different concentrations. In calculating  $K_c$  at the higher temperature, it was assumed that  $\epsilon_c$  varied with temperature by the same percentage as  $\epsilon_c$  in dichloromethane over a comparable temperature interval.

In order to determine the energies and free energies of solution of TMA in the chlorinated solvents, distribution experiments were performed. Aqueous solutions of the amine were shaken with heptane and with dichloromethane, and equilibrated at temperatures ranging from 13 to 27°. The equilibrium concentration of TMA in the aqueous phase was kept nearly constant in these experiments, so that it was possible to determine directly the distribution ratios for the amine between water-saturated heptane and dichloromethane. By utilizing previously reported solvation data for TMA in heptane<sup>2</sup> and values of the distribution ratios, corrected for the hydration of the amine in the two organic solvents,<sup>5</sup> both  $\Delta G^\circ$  and  $\Delta U^\circ$  for transfer of TMA from vapour to dilute solution in CH<sub>2</sub>Cl<sub>2</sub> could be calculated.  $\Delta G^\circ$  and  $\Delta U^\circ$  for transfer of SO<sub>2</sub> from heptane to CH<sub>2</sub>Cl<sub>2</sub> were estimated from literature values of Henry's law constants for aqueous solutions of SO<sub>2</sub>,<sup>6</sup> and distribution ratios for SO<sub>2</sub> between water and CH<sub>2</sub>Cl<sub>2</sub>.<sup>7</sup> It was assumed that SO<sub>2</sub> is not significantly hydrated in moist CH<sub>2</sub>Cl<sub>2</sub>. Solvation energies and free energies for TMA in chloroform were calculated from data similar to those obtained for TMA in CH<sub>2</sub>Cl<sub>2</sub>,

and the necessary solubility data for  $\text{SO}_2$  in chloroform were obtained from the literature.<sup>8</sup>

**Results and discussion.** Table 1 includes equilibrium constants and the thermodynamic functions  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  for the TMA- $\text{SO}_2$  complex formation reac-

Table 1. Thermodynamic and spectral data for the TMA- $\text{SO}_2$  complex in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ .

CH <sub>2</sub> Cl <sub>2</sub> system					
Temperature (°C)	$K_c$ (1 mole <sup>-1</sup> )	$\epsilon_c$ (1 mole <sup>-1</sup> cm <sup>-1</sup> )	$\Delta\bar{\nu}_{1/2}^a$ (cm <sup>-1</sup> )	$f^b$	
11.0	135 900 ± 4000	5350 ± 40	5960	0.215	
14.8	92 600 ± 3800	5350 ± 60			
20.0	63 500 ± 800	5270 ± 20	6180	0.220	
29.5	25 250 ± 490	5040 ± 35	6400	0.218	
CHCl <sub>3</sub> system					
20.0	36 100 ± 1750	5450 ± 100			
40.0	7 000 ± 500				

Summary of thermodynamic results for the reaction  $\text{TMA} + \text{SO}_2 = \text{TMA} \cdot \text{SO}_2$  at 20°, including data for heptane and gas phase<sup>c</sup>

Medium	$\Delta H^\circ$ , kcal/mole	$\Delta G^\circ$ , kcal/mole	$\Delta S^\circ$ , e.u.
CH <sub>2</sub> Cl <sub>2</sub>	-15.2 ± 0.6	-6.26 ± 0.04	-30.0 ± 2.1
CHCl <sub>3</sub>	-14.2 ± 1.2	-5.92 ± 0.04	-27.1 ± 4.0
heptane <sup>d</sup>	-11.0 ± 0.3	-4.65 ± 0.03	-21.4 ± 0.9
gas <sup>d</sup>	-9.7 ± 0.4	-3.45 ± 0.05	-21.0 ± 1.0

<sup>a</sup> Determined from the low frequency side of the *CT* band, assuming Symmetrical band.

<sup>b</sup> Oscillator strength, calculated as in Ref. 2.

<sup>c</sup> Standard states, ideal dilute solution, 1 mole/liter.

<sup>d</sup> Ref. 2.

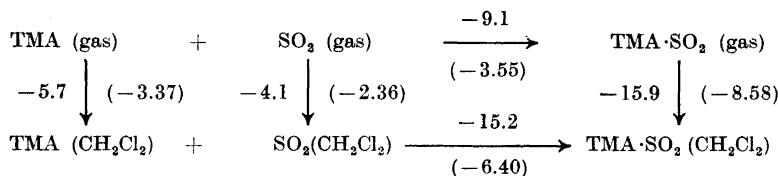
tion in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . The uncertainty in  $\Delta H^\circ$  in  $\text{CH}_2\text{Cl}_2$  is estimated to be 0.6 kcal/mole from the uncertainties in the formation constants. The corresponding error for the  $\text{CHCl}_3$  system is larger, but we feel that an uncertainty of 1.2 kcal/mole is a reasonable estimate. Table 1 also lists values of  $\epsilon_c$  at the various temperatures, together with the half band width,  $\Delta\bar{\nu}_{1/2}$ , deduced from the low frequency side of the band. These parameters correspond closely to values obtained for the heptane system, both with respect to absolute magnitudes and variation with temperature. It should be noted that the decrease in  $\epsilon_c$  parallels the increase in  $\Delta\bar{\nu}_{1/2}$ , so that the oscillator strength remains nearly constant as the temperature changes. The peak wavelength of the *CT* band, obtained by correcting the observed spectra for the absorbance of uncomplexed donor and acceptor, is 258  $m\mu$  in  $\text{CH}_2\text{Cl}_2$  and 259  $m\mu$  in  $\text{CHCl}_3$ . An explanation for the blue shift of the *CT* band in polar solvents, relative to heptane (peak wavelength 273  $m\mu$ ), has been given elsewhere.<sup>3</sup>

Data from the spectral and distribution studies may be combined to give thermodynamic constants for the cycle (at 20°) given in Table 2.

Numbers in parentheses represent Gibbs free energy values and the remaining numbers are internal energy changes in kcal/mole for the individual steps; the standard state for each species, in either vapour or condensed phase, is taken to be the ideal dilute solution at unit molarity. The effect noted previously — that the solvent stabilizes  $\text{TMA} \cdot \text{SO}_2$  relative to the unreacted components — is even more pronounced with dichloromethane than with heptane.

The complete cycle has also been obtained for the chloroform system, and analogous thermodynamic results are derived. The solvation energy and free energy for transfer of TMA from vapour to  $\text{CHCl}_3$  are -6.6 and -3.76 kcal/mole, respec-

Table 2.



tively. The corresponding values for  $\text{SO}_2$  in  $\text{CHCl}_3$  are  $-4.9$  and  $-2.02$  kcal/mole. Values of  $-16.4$  and  $-8.33$  kcal/mole are calculated for the energy and free energy of transfer of the complex from vapour to chloroform.

The results we have reported for the  $\text{TMA}-\text{SO}_2$  systems afford the first example of a  $CT$  complex for which the increase in  $K_c$  in polar solvents is accompanied by an increase in  $-\Delta H^\circ$  which definitely lies outside the experimental uncertainty in the enthalpy values. We believe, however, that when more accurate values of  $\Delta H^\circ$  become available for a number of strong  $CT$  complexes, it will be generally observed that  $-\Delta H^\circ$  and  $K_c$  vary in the same direction as the solvent is changed. The reasonable explanation for the increased value of the equilibrium constant in polar solvents, in terms of enhanced interaction between the dipole of the complex and the environment, implies that the magnitude of  $\Delta H^\circ$  for complex formation should also increase. In hydrogen-bonded systems, it has almost invariably been noted that  $\Delta H^\circ$  and  $\Delta G^\circ$  vary in the same direction as the medium is varied.<sup>9</sup>

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## Ion Pair Extraction in Preparative Organic Chemistry

### VI. Alkylation of Acetylacetone

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The alkylation of acetylacetone presents an interesting preparative problem. The anion of acetylacetone is a rather weak nucleophile and acetylacetone is alkylated much slower than ethyl acetoacetate and diethyl malonate. In a protic solvent the reaction is usually too slow to give an acceptable reaction time. In an aprotic solvent such as DMSO the rate is acceptable, but the main product is now the *O*-alkylated product.<sup>1</sup> In some recent publications it has been demonstrated that *O*-alkylation also occurs to some extent under other conditions.<sup>2</sup> The best compromise to date is to use acetone as a solvent and  $\text{K}_2\text{CO}_3$  as the base, although the reaction time is still very long (20 hours for methylation).<sup>3</sup> The time can be considerably decreased using  $\text{Rb}_2\text{CO}_3$  or  $\text{Cs}_2\text{CO}_3$  as the base,<sup>4</sup> but these are too expensive for routine use. The tetrabutylammonium ion behaves like a large alkali ion in many reactions. It can be expected therefore, that the tetrabutylammonium salt of acetylacetone is very rapidly alkylated.

We have recently demonstrated that tetrabutylammonium salts are readily prepared by ion pair extraction,<sup>5</sup> and that the salt of methyl cyanoacetate is rapidly alkylated in a chloroform solution.<sup>6</sup> We have now applied the same method to acetylacetone. Even in the present case the reaction is very rapid and the alkylations are quantitative in every case presented in Table 1. The percentage of the *O*-alkylated product is similar to that reported in the reference mentioned above.<sup>2</sup>

The identity of the alkylated products, with the exception of 3-butylacetylacetone, was ascertained by comparison with authentic samples by means of NMR and VPC. 3-Methyl- and 3-ethylacetylacetone were prepared by acetylation of the corresponding ketone with acetic an-