

## Short Communications

Non-spectroscopic Methods  
for Studying Gas Phase Charge  
Transfer Complexes. Diethyl Ether  
· I<sub>2</sub> and Trimethylamine · SO<sub>2</sub>

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Recent spectral studies of gas phase charge transfer (*CT*) complexes indicate that there is generally a drastic increase in the intensity of the *CT* absorption band when the medium is changed from vapour to a solvent.<sup>1-4</sup> An apparent exception to this rule has been reported in the case of the trimethylamine (TMA)·SO<sub>2</sub> complex.<sup>5</sup>

It is well known that spectrophotometric methods yield values of the product of the complex formation constant  $K_c$  and extinction coefficient  $\epsilon_c$ ; however, it is not possible to calculate reliable values for these two parameters separately unless ranges of concentration are attained in which a sizeable fraction of the least concentrated component is complexed.<sup>6</sup> Thus, attempts to obtain both  $K_c$  and  $\epsilon_c$  for complexes with small formation constants (such as benzene·I<sub>2</sub> and diethyl ether·I<sub>2</sub> in the gas phase) are questionable. In addition, relatively large random and systematic errors in absorbance must be expected in studies of vapour phase complexes. Hence, it is not surprising that even for the relatively strong complex diethyl sulfide·I<sub>2</sub>, reported values of  $\epsilon_c$  from two laboratories differ by

a factor of more than three.<sup>3,4</sup> Until accurate values of  $K_c$  and  $\epsilon_c$  become available for representative vapour phase *CT* complexes, it will be difficult to rationalize the effects of solvents on these parameters.<sup>7</sup>

Classical methods for determining formation constants in the gas phase (*e.g.*, from PVT or vapour density data) possess one important advantage over spectral techniques — there is only one unknown parameter to be inferred from a set of measurements made at varying concentrations of the reactants.<sup>8</sup> Thus, accurate values of  $K_c$  may be deduced for systems in which only a small percentage of either component is complexed. A program has been initiated in our laboratories for the determination of formation constants for charge transfer complexes by non-spectral methods. We report here preliminary results for the gas phase complexes of trimethylamine with sulfur dioxide and diethyl ether with iodine. The first system was chosen because the TMA·SO<sub>2</sub> complex spectrum has been reported to be virtually the same in the gas phase as in heptane.<sup>5</sup> Spectrophotometric data for the ether-iodine complex are available from two laboratories.<sup>1,9</sup>

A Burnett-type apparatus and numerical techniques similar to those described previously<sup>10</sup> were used to study the isothermal expansion of equimolar mixtures of TMA and SO<sub>2</sub>. Equilibrium constants at each temperature were inferred using a 1-dimensional non-linear least squares program, applied to 20–25 sets of values of (a) initial pressure in the large bulb, (b) initial pressure in the small bulb, and (c) final total pressure. Values of  $K_c$  and RMSD (the root mean square deviation between calculated and experimental final pressure) are given in Table 1.

Table 1.

<i>t</i> (°C)	35.0	40.0	44.0
$K_c$ (torr <sup>-1</sup> )	0.00946 ± 0.00057	0.00738 ± 0.00033	0.00550 ± 0.00031
$K_c$ (l mole <sup>-1</sup> )	182 ± 11	144 ± 6	109 ± 6
RMSD (torr)	0.0051	0.0063	0.0098

In a separate experiment, a fused silica buoyancy microbalance was used to determine vapour densities of equimolar mixtures of TMA and SO<sub>2</sub> at 35.00° and pressures less than 7 torr. The collection of 70 pairs of pressure-density measurements was treated by non-linear least squares analysis, yielding  $K=203 \pm 36$  l mole<sup>-1</sup> and an RMSD in pressure of 0.035 torr. Equilibrium constants determined here and those calculated from reported PVT data<sup>11</sup> are well correlated by the equation

$$\log K_c(\text{l mole}^{-1}) = -4.14 \pm 0.18 + \frac{9.07 \pm 0.27}{2.30 RT}$$

in which  $R=0.001987$  kcal mole<sup>-1</sup>deg<sup>-1</sup>. This relation gives values of  $K_c$  at 39.7° and  $-\Delta E^\circ(154$  l mole<sup>-1</sup> and  $9.07$  kcal mole<sup>-1</sup>) which fortuitously, are virtually identical with those inferred from the spectral results.<sup>5</sup> Therefore, since it is presumed that the product  $K_c \epsilon_c$  is accurately known from the previous study, it may be concluded that the reported values of  $\epsilon_c$  and the oscillator strength in the vapour phase are reliable and that these parameters do not change appreciably as the medium is changed from gas to heptane.

The association of Et<sub>2</sub>O with I<sub>2</sub> at 35.00° was investigated with a promising new vapour phase isopiestic technique,<sup>12</sup> which utilizes a sensitive fused silica torsion microbalance, supported inside an all-glass, thermostatted 3.4 l vacuum system fitted with teflon-plug stopcocks. The balance was loaded with about 100 mg of a mixture of the two solid polyiodides, (CH<sub>3</sub>)<sub>4</sub>NI<sub>5</sub> and (CH<sub>3</sub>)<sub>4</sub>NI<sub>3</sub>, which maintains an equilibrium pressure of iodine of 0.115 torr at 35.00°. Initially, the system was allowed to equilibrate with only the polyiodides and I<sub>2</sub> vapour present, and the mass of the solid was recorded. Then, a known volume of ether (1.0 to 4.6 ml) was vapourized into the system. After equilibration (approximately 24 h) the final mass of solid was noted. The difference in mass was equated to the amount of iodine present in the complexed form in the vapour phase; that is, all of the increase in iodine solubility in the vapour, at constant activity of iodine, was attributed to formation of Et<sub>2</sub>O·I<sub>2</sub>. Values of the mass of iodine extracted into the vapour phase ( $m$ ) corresponding to various pressures of ether ( $p$ ) were:

$m$ ( $\mu\text{g}$ )	55.2	58.0	69.0	73.8	102.9
$p$ (torr)	57.0	58.6	67.3	73.3	91.8
	121.4	159.0	168.1	181.0	205.7
	108.9	137.9	167.7	164.5	182.5
				211.0	198.2

These data yield a value of  $K_c$  equal to  $4.3 \pm 0.3$  l mole<sup>-1</sup> (allowing for a slight buoyancy correction). By combining the  $K_c$  value with values of  $K_c \epsilon_c$  extrapolated to 35° (from Refs. 1 and 9, respectively) the values  $\epsilon_c=2700$  l mole<sup>-1</sup>cm<sup>-1</sup> and  $\epsilon_c=2450$  l mole<sup>-1</sup> cm<sup>-1</sup> are calculated. These results confirm the previous conclusion that  $\epsilon_c$  is considerably lower in the vapour phase<sup>1</sup> than in solution.<sup>13</sup>

The unique experimental advantages of the classical methods for determining  $K_c$  should be exploited in further studies of gas phase  $CT$  complexes. Since it is relatively easy to determine the product  $K_c \epsilon_c$  for a given complex from spectral data, an independent accurate determination of  $K_c$  makes it possible to infer a reliable value of  $\epsilon_c$ . Such results will be essential in testing and developing theories of the effects of solvents on donor-acceptor interactions.

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