

## Letters to the Editor

**T**HE *Letters to the Editor* section is subdivided into four categories entitled *Communications, Notes, Comments, and Errata*. The textual material of each Letter is limited to 950 words minus the following: (a) 200 words for each average-sized figure; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. The publication charge for *Communications, Notes, and Comments* is \$50 per page with a minimum of \$50 per Letter. The publication charge, if honored by the author's institution, entitles the author to 100 reprints without covers at no extra charge. The publication charge for *Errata* is at the \$50-per-page rate with a minimum of \$10, and no free reprints are provided. On all Letters a charge of \$10 per Letter is made toward the support of abstracting and indexing in *Physics Abstracts*. See the issue of 1 January 1965 for a fuller description of *Letters to the Editor*.

### Communications

#### Vapor-Phase Charge-Transfer Complexes. Diethyl Sulfide-Iodine

JOHN M. GOODENOW AND MILTON TAMRES  
*Chemistry Department, University of Michigan  
Ann Arbor, Michigan*

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**R**ECENTLY a paper appeared by Lang and Strong<sup>1</sup> on the diethyl ether-iodine and benzene-iodine complexes in which direct comparison is made of the spectral and thermodynamic properties of these CT complexes in the vapor phase with those in solution. Their results show that, although the enthalpies of formation are about the same in the two phases, there are a number of significant differences: (1) There is a spectral shift of the CT band toward the red in going from vapor to solution, and (2) the vapor data give an appreciably larger value for the association constant ( $K_c$ ) and a markedly smaller value for the molar absorptivity index ( $a_c$ ). The differences are greater for the iodine complex with benzene than with diethyl ether. The latter is a better electron donor, although both complexes are considered weak.

For weak complexes, electron transition should give a highly polar excited state. According to Bayliss and McRae,<sup>2</sup> the dipole-polarization forces due to interaction of complex with solvent should result in greater solvation energy for the excited state than the ground state, thereby giving a red shift. Strong complexes have a more polar ground state, and the CT band shift in going from vapor to liquid might be expected to be diminished.

It has been pointed out very recently also<sup>3</sup> that solvation competes with complexation, and the effect of neglecting the former in treating the data is to

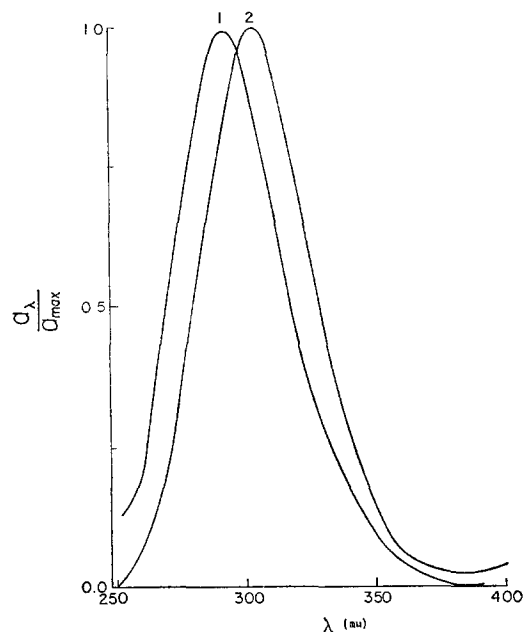


Fig. 1. Charge-transfer spectral band for the diethyl sulfide-iodine complex: (1) in vapor phase, and (2) in *n*-heptane solution.

decrease  $K_c$  and to increase  $a_c$ . The competition between solvation and complexation is particularly pronounced for weak complexes. It should be much less so for strong complexes, and closer agreement would be expected for the values of  $K_c$  and of  $a_c$  obtained between vapor phase and solution.

We should like to present a preliminary report of some vapor-phase studies on diethyl sulfide-iodine. This complex already has been studied in *n*-heptane solution,<sup>4</sup> and its properties have been characterized both from its CT band in the uv region and the blue shift of the  $I_2$  band in the visible region. Iodine forms a stronger complex with diethyl sulfide than with diethyl ether, although not quite as strong as that with an amine.<sup>5</sup> But, unlike the amine,<sup>6</sup> (and also diethyl ether) diethyl sulfide-iodine has the advantage of not undergoing secondary reaction at elevated temperatures.

The complex was studied spectrophotometrically in a 10-cm cell in the temperature range of 93° to 126°C, with the sulfide concentration varying from  $2.8 \times 10^{-3}$  to  $1.6 \times 10^{-2} M$  and iodine from  $1.4 \times 10^{-5}$  to  $5.8 \times 10^{-5} M$ . The absorbancy decreased with increase in temperature, and readings were reproducible in returning to any given temperature.

The characteristic CT band is observed in the near-uv region where neither the vapor of diethyl sulfide nor of iodine absorbs. A peak is observed at 290  $m\mu$ , which is a blue shift of 13  $m\mu$  from that found when the complex is dissolved in *n*-heptane. This shift is only slightly smaller than that reported (14  $m\mu$ ) for diethyl ether-iodine.<sup>1</sup> The shape of the CT vapor band is not temperature dependent and, in fact, has the same shape

TABLE I. Vapor and liquid spectral and thermodynamic properties of the diethyl sulfide-iodine complex.

	Vapor	<i>n</i> -Heptane solution <sup>a</sup>
$\lambda$ max. (m $\mu$ )	290	303
$a_e$ at $\lambda$ max. (liter mole <sup>-1</sup> ·cm <sup>-1</sup> )	11 400 $\pm$ 850 <sup>b</sup>	26 400 $\pm$ 1050 <sup>b</sup>
$K_{c378}$ (liter mole <sup>-1</sup> )	16.2	9.38 <sup>c</sup> ; 12.5 <sup>d</sup>
$K_{c298}$ (liter mole <sup>-1</sup> )	226 <sup>e</sup>	200; 181 <sup>e</sup>
$-\Delta G^\circ_{378}$ (kcal/mole)	2.07	1.66 <sup>e</sup> ; 1.75 <sup>d</sup>
$-\Delta G^\circ_{298}$ (kcal/mole)	3.21 <sup>e</sup>	3.14; 3.08 <sup>e</sup>
$-\Delta S^\circ$ (e.u.)	15.3 $\pm$ 1.1 <sup>f</sup>	19.4 $\pm$ 2.0 <sup>f</sup> ; 17.6 $\pm$ 0.5 <sup>e,f</sup>
$-\Delta H^\circ$ (kcal/mole)	8.5 $\pm$ 0.4 <sup>f</sup>	8.9 $\pm$ 0.6 <sup>f</sup> ; 8.3 $\pm$ 0.2 <sup>e,f</sup>

<sup>a</sup> Reference 4.<sup>b</sup> Average error.<sup>c</sup> Extrapolated from uv data.<sup>d</sup> Extrapolated from data in visible region.<sup>e</sup> From study of blue shift of I<sub>2</sub> band in visible region.<sup>f</sup> Standard error.

as that in solution. This is shown in Fig. 1 where the relative molar absorptance indices are plotted against wavelength. Except for the shift, the two bands appear to be essentially superimposable.

Within experimental limits, there is no observable variation of  $a_e$  with temperature. The average value of  $a_{e \text{ max}}$  for the vapor is 11 400 $\pm$ 850 liter mole<sup>-1</sup>·cm<sup>-1</sup>, which is about half that found in *n*-heptane solution. Comparison of vapor and solution data is made in Table I. The agreement between  $K_c$  and  $a_e$  for the two phases is much closer than for the complexes studied by Lang and Strong, and is in accord with prediction.<sup>3</sup>

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<sup>1</sup> F. T. Lang and R. L. Strong, *J. Am. Chem. Soc.* **87**, 2345 (1965).<sup>2</sup> N. S. Bayliss and E. G. McRae, *J. Phys. Chem.* **58**, 1002 (1954).<sup>3</sup> S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.* **1965**, 2048.<sup>4</sup> M. Tamres and S. Searles, Jr., *J. Phys. Chem.* **66**, 1099 (1962).<sup>5</sup> S. Nagakura, *J. Am. Chem. Soc.* **80**, 520 (1958).<sup>6</sup> This laboratory (unpublished work).

## Charge-Transfer Complexes in Gas Phase

J. PROCHOROW

*Institute of Physics, Polish Academy of Sciences  
Hoża 69, Warsaw, Poland*

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CHARGE-transfer complexes in condensed phases have been extensively studied by spectroscopic methods.<sup>1</sup> For gas-phase experiments, a strong electron

acceptor with high vapor pressure is needed. We have used for this purpose carbonyl cyanide CO(CN)<sub>2</sub> ( $p$  = 120 mm Hg at 20°C), of which the spectra of charge-transfer complexes in solutions have been recently reported.<sup>2</sup> The spectra of gaseous mixtures of CO(CN)<sub>2</sub> with ethyl ether, dioxane, benzene, toluene, and *p*-xylene were studied by a photoelectric method, with partial pressures of components varying between 10 and 140 mm Hg, at different temperatures in the range of 20° to 130°C. (See Table I.)

All mixtures show an "extra" absorption in the near-ultraviolet region, partially superimposed on the weak absorption of the  $n \rightarrow \pi^*$  transition in CO(CN)<sub>2</sub>.<sup>3</sup> The intensity of the band decreases with temperature increase, the process being quite reversible. This effect is due to a temperature dependence of equilibrium constants and cannot be caused by thermal decomposition or substitution reactions. The error in intensity measurements is relatively important and direct determination of equilibrium constants  $K_c$  is impossible. Values of  $K_c$  were estimated by assuming that the molar extinction coefficients have the same values as in hexane solutions.<sup>2</sup>  $K_c$  found in this way must be treated as a very rough estimate. The differences in  $K_c$  values for gas and solution are, however, quite systematic and can be hardly explained by experimental errors and approximations involved. Such a change corresponds to a case, where the decrease in free energy, due to solvation effects, is stronger for free molecules than for the complex. The values of equilibrium constants and their temperature dependence show that in gaseous mixtures with  $\pi$  and  $n$  donors stable (not collisional) complexes are formed. Binding energies estimated in the usual way from  $dK_c/dT$  give reasonable values of 4–6 kcal/mole. On the other hand, the contact charge-transfer absorption, found in the liquid CO(CN)<sub>2</sub>-hexane mixtures, disappears in the gas phase, even at *n*-hexane pressures as high as 140 mm Hg.

The shape of charge-transfer bands in gas and in solutions is almost the same; the bands are broad and

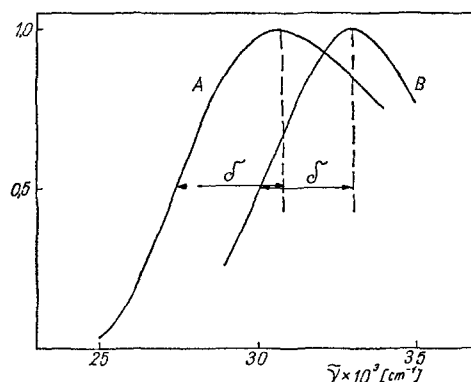


FIG. 1. Charge-transfer absorption bands of toluene-CO(CN)<sub>2</sub> complex; (A) *n*-hexane solution, (B) gas (intensity in arbitrary units).