Communications

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

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RECENTLY a paper appeared by Lang and Strong\textsuperscript{1} 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 \((K_a)\) and a markedly smaller value for the molar absorbancy index \((a_e)\). The differences are greater for the iodine complex with benzene than with diethyl ether. The latter is a better electron donor, although a

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 \(K_a\) and of \(a_e\) 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,\textsuperscript{4} 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.\textsuperscript{6} But, unlike the amine\textsuperscript{1} (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\textdegree to 126\textdegree C, with the sulfide concentration varying from 2.8\times10\textsuperscript{-4} to 1.6\times10\textsuperscript{-5}M and iodine from 1.4\times10\textsuperscript{-4} to 5.8\times10\textsuperscript{-4}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 \(\mu\)m, which is a blue shift of 13 \(\mu\)m from that found when the complex is dissolved in \(n\)-heptane. This shift is only slightly smaller than that reported \((14 \mu m)\) for diethyl ether-iodine.\textsuperscript{4} The shape of the CT vapor band is not temperature dependent and, in fact, has the same shape

![Fig. 1. Charge-transfer spectral band for the diethyl sulfide-iodine complex: (1) in vapor phase, and (2) in \(n\)-heptane solution.](image-url)
as that in solution. This is shown in Fig. 1 where the relative molar absorbancy 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 $a_v$ with temperature. The average value of $a_v$ max for the vapor is $11\,400\pm850$ liter mole$^{-1}\cdot$cm$^{-1}$, which is about half that found in $n$-heptane solution. Comparison of vapor and solution data is made in Table I. The agreement between $K_s$ and $a_v$ for the two phases is much closer than for the complexes studied by Lang and Strong, and is in accord with prediction. The work was supported by grants from the Horace H. Rackham School of Graduate Studies at the University of Michigan and from the National Science Foundation.

CHARGE-transfer complexes in condensed phases have been extensively studied by spectroscopic methods. For gas-phase experiments, a strong electron acceptor with high vapor pressure is needed. We have used for this purpose carbonyl cyanide CO(CN)$_2$ ($\rho = 120$ mm Hg at 20°C), of which the spectra of charge-transfer complexes in solutions have been recently reported. The spectra of gaseous mixtures of CO(CN)$_2$ 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)$_2$. 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 $K_s$ is impossible. Values of $K_s$ were estimated by assuming that the molar extinction coefficients have the same values as in hexane solutions. $K_s$ found in this way must be treated as a very rough estimate. The differences in $K_s$ 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 $dK_s/dT$ give reasonable values of 4–6 kcal/mole. On the other hand, the contact charge-transfer absorption, found in the liquid CO(CN)$_2$–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

**Table I. Vapor and liquid spectral and thermodynamic properties of the diethyl sulfide–iodine complex.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Vapor</th>
<th>$n$-Heptane solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ max. (nm)</td>
<td>290</td>
<td>303</td>
</tr>
<tr>
<td>$a_v$ at $\lambda$ max. (liter mole$^{-1}\cdot$cm$^{-1}$)</td>
<td>$11,400\pm850^b$</td>
<td>$26,400\pm1050^b$</td>
</tr>
<tr>
<td>$K_{en}$ (liter mole$^{-1}$)</td>
<td>16.2</td>
<td>9.38$^c$, 12.5$^d$</td>
</tr>
<tr>
<td>$K_{en}$ (liter mole$^{-1}$)</td>
<td>226$^e$</td>
<td>200; 181$^f$</td>
</tr>
<tr>
<td>$-\Delta G_{en}$ (kcal/mole)</td>
<td>2.07</td>
<td>1.66$^e$, 1.75$^d$</td>
</tr>
<tr>
<td>$-\Delta G_{en}$ (kcal/mole)</td>
<td>3.21$^e$</td>
<td>3.14; 3.08$^e$</td>
</tr>
<tr>
<td>$-\Delta S^o$ (e.u.)</td>
<td>1153±1.1$^f$</td>
<td>19.4±2.0$^f$; 17.6±0.5$^f$</td>
</tr>
<tr>
<td>$-\Delta H^o$ (kcal/mole)</td>
<td>8.5±0.4$^f$</td>
<td>8.9±0.6$^f$, 8.3±0.2$^f$</td>
</tr>
</tbody>
</table>

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**Notes:**
- $^a$ Reference 4.
- $^b$ Average error.
- $^c$ Extrapolated from uv data.
- $^d$ Extrapolated from data in visible region.
- $^e$ From study of blue shift of $\lambda$ band in visible region.
- $^f$ Standard error.

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**Charge-Transfer Complexes in Gas Phase**

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**Charge-transfer complexes in condensed phases have been extensively studied by spectroscopic methods.** For gas-phase experiments, a strong electron acceptor with high vapor pressure is needed. We have used for this purpose carbonyl cyanide CO(CN)$_2$ ($\rho = 120$ mm Hg at 20°C), of which the spectra of charge-transfer complexes in solutions have been recently reported. The spectra of gaseous mixtures of CO(CN)$_2$ 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.)

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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)$_2$ complex; (A) $n$-hexane solution, (B) gas (intensity in arbitrary units).