

Gas Phase Molecular Complexes. The Diethyl Ether–Iodine and Benzene–Iodine Charge-Transfer Complexes

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The diethyl ether–iodine and benzene–iodine systems have been investigated spectrophotometrically in the gas phase. In each case, a new band characteristic of neither component alone was observed in the ultraviolet region, which is attributed to charge-transfer absorption of the 1:1 molecular complex. The band maxima (2340 and 2680 Å. for the diethyl ether–iodine and benzene–iodine complexes, respectively) are at lower wave lengths than the comparable liquid phase complexes, indicating appreciable interaction between the complex excited state and solvent molecules in the liquid state. Although the standard enthalpies of complex formation are approximately the same in the gas and liquid phases for each system, the equilibrium constant (K_c) is appreciably larger in the gas phase. These results are discussed in terms of possible solvation effects.

Introduction

Since the spectrophotometric studies by Benesi and Hildebrand¹ of the ultraviolet absorption band that is characteristic of iodine dissolved in aromatic hydrocarbon solvents, many systems of this general type have been investigated. This band, which is characteristic of neither the aromatic nor the iodine molecule alone, is attributed² to a partial intermolecular transfer of charge between an electron-donor (solvent) and an electron-acceptor (iodine) species. Theoretical and experimental aspects of solution charge-transfer (CT) systems have been summarized in detail by Briegleb.³

Relatively few studies have been made of comparable complexes in the gas phase. Chatelet⁴ observed a new absorption band in the ultraviolet spectral region of iodine in benzene vapor at 90° which he attributed to a molecular complex involving approximately ten benzene molecules per iodine molecule. Atack and Rice⁵ investigated the *PVT* relationships for the gaseous benzene–iodine system above 427°K. and from these calculated the equilibrium constant and enthalpy of formation of the benzene–iodine complex; they concluded from these results that the interaction is of a nonspecific van der Waals type. The effect of other gases on the iodine absorption band in the visible region has been studied by Luck.⁶ From collision theory he was able to calculate the effective optical diameter of an iodine molecule–foreign molecule pair. The ratio of this diameter (σ_{opt}) to the gas kinetic diameter (σ_{gk}) was 1.43, 1.52, and 1.53 for gaseous

mixtures of iodine with benzene, diethyl ether, and pyridine, respectively, indicating intermolecular forces of the Mulliken type, while somewhat lower values were obtained for iodine mixed with carbon tetrachloride, cyclohexane, hydrogen, and the inert gases. The absorption by iodine vapor alone does not obey Beer's law in the region of 2670 Å., presumably owing to the formation of an I_4 association complex⁷; in this case I_2 serves both as a donor and as an acceptor.

The possible role of transient iodine atom–aromatic charge-transfer complexes in gas phase recombination processes has been discussed by Porter and Smith⁸ to explain abnormally high recombination rate constants; comparable complexes have been observed spectrophotometrically in the liquid phase, where the charge-transfer absorption band is in the visible region.^{9, 10}

In the present work the gaseous benzene–iodine and diethyl ether–iodine systems have been investigated spectrophotometrically, and the spectra, extinction coefficients, formation constants, and enthalpies of formation for the charge-transfer complexes have been determined. Attempts to investigate iodine complexes of diisopropyl ether, *n*-butylamine, diethylamine, or triethylamine were unsuccessful. Diisopropyl ether and iodine reacted irreversibly in the vapor phase as shown by a slow decrease in the iodine absorption at 5200 Å. and the concurrent appearance of an absorption band at 2620 Å. With the aliphatic amines, a white solid was formed very rapidly as the amine was vaporized in the presence of solid iodine. The product was soluble in water and probably is the same type of ionic compound formed more slowly in triethylamine–iodine liquid solutions.¹¹ There was no gaseous absorption for the amine–iodine systems at wave lengths greater than 2800 Å.

Experimental

Diethyl ether (Fisher Reagent), benzene (Fisher 99+ nole %), *n*-butylamine (Fisher Certified), and diisopropyl ether (Fisher Certified) were vacuum distilled through P_2O_5 , the outgassed middle portion being collected and stored on a high-vacuum Pyrex transfer apparatus in reservoirs isolated by Fischer–Porter greaseless Teflon-threaded valves using Viton-A O-rings. Triethylamine (Eastman) and diethylamine (Fisher Reagent) were fractionally distilled over phosphorus pentoxide, then vacuum distilled, and stored as above. Iodine (Fisher Certified, resublimed) was ground with potassium iodide prior to vacuum sublimation through phosphorus pentoxide.

(1) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(2) R. S. Mulliken, *ibid.*, **74**, 811 (1952), and subsequent papers in this series.

(3) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

(4) M. Chatelet, *Compt. rend.*, **190**, 927 (1930).

(5) D. Atack and O. K. Rice, *J. Phys. Chem.*, **58**, 1017 (1954).

(6) W. Luck, *Z. Naturforsch.*, **6a**, 313 (1951); **7a**, 823 (1952); *Z. Elektrochem.*, **56**, 870 (1952).

(7) G. Kortüm and G. Friedheim, *Z. Naturforsch.*, **2a**, 20 (1947).

(8) G. Porter and W. A. Smith, *Nature*, **184**, 446 (1959).

(9) S. J. Rand and R. L. Strong, *J. Am. Chem. Soc.*, **82**, 5 (1960).

(10) T. A. Gover and G. Porter, *Proc. Roy. Soc. (London)*, **A262** 476 (1961).

(11) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

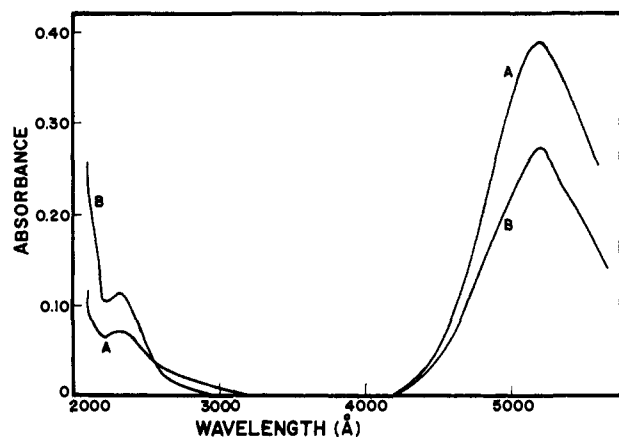


Figure 1. Absorption spectra of gas phase diethyl ether-iodine mixtures at 50°. Curve A: $[I_2] = 5.8 \times 10^{-5} M$, $[(C_2H_5)_2O] = 1.3 \times 10^{-2} M$; curve B: $[I_2] = 4.2 \times 10^{-5} M$, $[(C_2H_5)_2O] = 4.1 \times 10^{-2} M$.

Ether vapor was metered into a cylindrical quartz absorption cell (10-cm. light path, 26-mm. i.d.) by two different procedures. The first method involved the vaporization of ether from the liquid reservoir (thermostated below room temperature) into the previously evacuated and outgassed cell; the concentration of ether in the cell was calculated after liquid-vapor equilibrium was attained in the reservoir from the measured temperature and pressure in the cell assuming ideal gas behavior (corrected for the decrease in volume of the cell system when it was removed from the vacuum rack by sealing off). In the second technique, permitting gas concentrations at elevated temperatures corresponding to pressures greater than the vapor pressure of ether at room temperature, a small amount of ether was distilled under vacuum into a graduated capillary tube, excess liquid was distilled away until the desired amount was attained, and this aliquot (corrected for the relatively small amount of equilibrium vapor) was distilled and frozen out in the evacuated absorption cell. Benzene and the other donor species, with their relatively low vapor pressures at room temperature, were metered into the absorption cell using this second technique.

Iodine vapor was metered into the cell by means of a calibrated bulb isolated by two greaseless valves. The vapor in this bulb, after equilibration with the solid iodine in the storage reservoir, was frozen into the absorption cell containing the metered and outgassed donor species. After the desired number of iodine meterings (of approximately 5×10^{-7} mole/transfer), the cell was removed from the vacuum transfer apparatus by sealing off. The iodine concentration was determined spectrophotometrically at 4800 Å.; the apparent gas phase extinction coefficient at this wave length (the region of continuous absorption) was determined from known liquid phase extinction coefficients^{1,7} by adding a weighed amount of liquid donor solvent to the frozen cell contents after the series of gas phase absorbance measurements was completed.

The absorption spectra of the samples were measured in the ultraviolet and visible regions with a Beckman DU spectrophotometer using a hydrogen lamp light source, photomultiplier detector, and an evacuated

quartz matched (or calibrated) reference cell. Slit widths varied from 0.1 mm. at 2100 Å. to 0.025 mm. in the visible region. A standard 10-cm. Beckman cell compartment was modified to hold the 26-mm. i.d. absorption cells and to permit temperatures in excess of 100° to be used. Suprasil quartz windows in the light path were used to enclose the compartment. Two heating tapes (Powerstat-controlled) lined the inside of the compartment, and a small circulating fan projected through the cover. Thermostated silicone oil was circulated through the inner pair of Beckman "thermospacers," and cold water was passed through the outer pair (adjacent to the monochromator and photomultiplier housings). The temperature was controlled by the two heating tape settings and the temperature of the silicone oil and was monitored by five thermocouples in the cell compartment; maximum temperature variations over the compartment ranged from $\pm 0.8^\circ$ at 50° to $\pm 2.8^\circ$ at 100°.

Results

The Diethyl Ether-Iodine System. The gas phase absorption spectra of two diethyl ether-iodine mixtures are shown in Figure 1. The maximum at 2340 Å., absent in the spectra of the pure components, is attributed to the CT absorption of a complex between the diethyl ether donor and iodine acceptor; below this band are the overlapping tails from the diethyl ether and iodine ultraviolet bands.

The location of the iodine band in the visible region (5200 Å.) is the same as for iodine vapor in the presence of inert gases¹²; no new band was detected in the visible region as contrasted to the appearance of a band at 4600 Å. in diethyl ether-iodine liquid solutions,¹³ and the apparent extinction coefficient at 4800 Å., $\epsilon_{1,2}^0$ (340 l. mole⁻¹ cm.⁻¹), is independent of diethyl ether pressure. However, at the pressures used in this work, a maximum of 20% of the iodine is complexed (as calculated with eq. 2 below) so that it would be difficult to detect a small shift in the maximum or the appearance of a new band owing to complexed iodine, and 4800 Å. may in fact be quite close to an isosbestic point for free and complexed iodine. Bayliss and co-workers¹⁴ attribute the observed blue shift of the iodine visible peak in various solvents to the packing strains which the solute molecule (iodine) undergoes on enlargement during electronic excitation when surrounded by a solvent cage; a shift for this reason would of course be absent in the gas phase.

The ultraviolet absorption spectrum from 2000 to 2800 Å. on an expanded absorbance scale is shown in Figure 2; also shown are the spectra for pure ether (curve B), pure iodine (curve C), and the resultant curve owing to absorption by the complex (curve D). The temperature dependence of curve D is given in Figure 3; the decrease in absorbance with increasing temperature (which was completely reversible between 50 and 80°) is indicative of a complex in equilibrium with the free donor and acceptor species. At 90° and above, an irreversible reaction occurred, as indicated by a slow decrease in absorption at 4800 Å.

(12) E. Rabinowich and W. C. Wood, *Trans. Faraday Soc.*, **32**, 540 (1936).

(13) P. A. D. De Maine, *J. Chem. Phys.*, **26**, 1192 (1957).

(14) N. S. Bayliss and A. L. G. Rees, *ibid.*, **8**, 377 (1940); N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

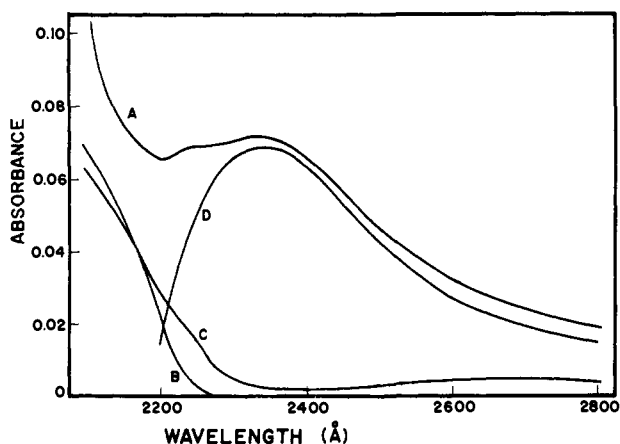


Figure 2. A: ultraviolet portion of absorption curve A in Figure 1; B: absorbance of pure diethyl ether; C: absorbance of pure iodine; D: absorption spectrum of the diethyl ether-iodine complex (calculated by difference).

and a concurrent increase at 2600 Å., and therefore these data are not included in the thermodynamic calculations. Absorbance measurements at 2380 Å., rather than at the maximum of 2340 Å., were used in order to minimize possible errors resulting from free diethyl ether absorption (Figure 2).

The data were plotted according to the Scott modification¹⁵ of the Benesi-Hildebrand equation

$$\frac{[I_2]^0[D]}{A} = \frac{[D]}{\epsilon_c} + \frac{1}{\epsilon_c K_c} \quad (1)$$

where A is the absorbance at 2380 Å., ϵ_c is the molar extinction coefficient of the complex at 2380 Å., $[D]$ is the donor (diethyl ether) concentration, $[I_2]^0$ is the total iodine concentration (free and complexed) as determined by the absorbance at 4800 Å., and K_c is the formation constant of the complex in concentration units.

$$K_c = \frac{[c]}{[I_2][D]} = \frac{[c]}{([I_2]^0 - [c])[D]} \quad (2)$$

where $[c]$ is the concentration of the complex. Diethyl ether concentrations from 1.3 to $5.3 \times 10^{-2} M$ were used at a constant ($5 \times 10^{-5} M$) iodine concentration. From these plots ϵ_c and K_c were calculated from the slopes and intercepts using the method of least squares. The standard enthalpy of formation, ΔH_f° , assumed constant, was calculated from the plot of the integrated van't Hoff equation.

The results are given in Table I, and are compared with those obtained on the diethyl ether-iodine liquid system^{7,13,16-19} (converted to units of concentration in moles/liter and 25° where necessary).

The Benzene-Iodine System. Figure 4 shows a portion of the ultraviolet spectrum at 70° of gaseous benzene, iodine, and a mixture of the two under the condition of relatively low benzene pressure such that the maximum of the charge-transfer band is not completely masked by the attendant ${}^1B_{2u} \rightarrow {}^1A_{1g}$ band of benzene, at least to 2630 Å.

(15) R. L. Scott, *Rec. trav. chim.*, **75**, 787 (1956).

(16) J. Ham, *J. Am. Chem. Soc.*, **76**, 3875 (1954).

(17) M. Brandon, M. Tamres, and S. Searles, *ibid.*, **82**, 2129 (1960).

(18) J. Ham, *J. Chem. Phys.*, **20**, 1170 (1952).

(19) H. Yamada and K. Kozima, *J. Am. Chem. Soc.*, **82**, 1543 (1960).

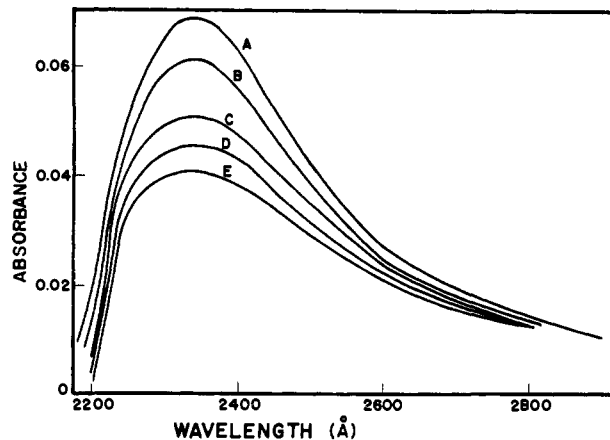


Figure 3. Effect of temperature on the diethyl ether-iodine complex ultraviolet absorption spectrum (curve D of Figure 2): A, 50°; B, 60°; C, 70°; D, 80°; E, 90°.

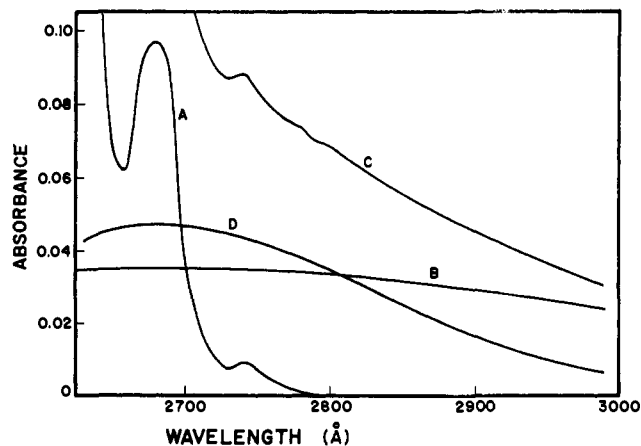


Figure 4. Ultraviolet absorption spectra of gas phase benzene, iodine, and benzene-iodine mixtures. Curve A: absorbance of pure benzene ($2.1 \times 10^{-3} M$); curve B: absorbance of pure iodine ($3.1 \times 10^{-4} M$); curve C: absorbance of benzene-iodine mixture (same concentrations as for curves A and B, respectively); curve D: absorption spectrum of the benzene-iodine complex (calculated by difference).

In contrast to the diethyl ether-iodine system, no permanent reaction occurred, and absorbance changes were completely reversible over the temperature range covered (70 to 100°). Absorbance data for the com-

Table I. Spectral and Thermodynamic Results of the Diethyl Ether-Iodine Complex

	Gas phase	Liquid phase
λ_{\max} (Å.)	2340	2480 ^a 2490 ^b 2500 ^c 2520 ^d 4700 ^b 5650 ^d
ϵ_c at λ_{\max} (l. mole ⁻¹ cm. ⁻¹)	2100 ± 400	
$K_{c,298}$ (l. mole ⁻¹)	6.4 ± 1.2	0.97 ^d 0.81 ^b 0.66 ^e 0.32 ^f
ΔH_f° (kcal./mole)	-3.2 ± 0.1	-4.2 ^d -4.3 ^b -4.4 ^a

^a See ref. 7. ^b See ref. 13. ^c See ref. 16. ^d See ref. 17. ^e See ref. 18. ^f See ref. 19.

plex were analyzed at 2825 Å. rather than at the wave length of maximum absorption (*ca.* 2680 Å.) so that absorbance owing to the donor benzene alone is negligible (Figure 4). Thus, at 2825 Å.

$$A = \epsilon_{I_2}[I_2]d + \epsilon_c[c]d \quad (3)$$

where A is the absorbance, ϵ_{I_2} , ϵ_c , $[I_2]$, and $[c]$ are the extinction coefficients and concentrations of the free iodine and complex, respectively, and d is the optical light path (10 cm.). As with diethyl ether, the iodine band at 4800 Å. is independent of benzene pressure, and absorbance data at 4800 Å. were used to calculate the total iodine concentration ($[I_2]^0$). Thus, the absorbance at 4800 Å. is

$$A^0 = \epsilon_{I_2}^0[I_2]^0d \quad (4)$$

Combining eq. 2, 3, and 4 leads to

$$\frac{A^0S}{A} = \frac{\epsilon_{I_2}^0}{\epsilon_c}S + \frac{1}{\epsilon_cK_c} \quad (5)$$

where

$$S \equiv \frac{A[D]}{A\epsilon_{I_2}^0 - A^0\epsilon_{I_2}} \quad (6)$$

Values of A^0S/A were plotted as a function of S for benzene concentrations from 1.6 to $3.6 \times 10^{-2} M$ ($[I_2]^0 = 5 \times 10^{-5} M$) from 70 to 100°, ϵ_c and K_c were obtained from the least-squares slopes and intercepts, and the standard enthalpy of formation was determined as above from the van't Hoff relationship. The results are summarized and compared with those for the liquid phase complex^{1,5,16,20-26} in Table II.

Table II. Spectral and Thermodynamic Results of the Benzene-Iodine Complex

	Gas phase	Liquid phase
λ_{\max} (Å.)	2680	2,970 ^a 2,960 ^b 2,950 ^c 2,920 ^d 2,900 ^e 2,880 ^f 2,870 ^g
ϵ_c at λ_{\max} (l. mole ⁻¹ cm. ⁻¹)	1650 ± 100	14,700 ^c 15,400 ^e 16,400 ^d 16,700 ^b
$K_{c,298}$ (l. mole ⁻¹)	4.5 ± 0.6 3.4 ^h	0.157 ^a 0.158 ^b 0.145 ⁱ 0.15 ^d 0.149 ^e 0.338 ^j
ΔH_f° (kcal./mole)	-2.0 ± 0.1 -2.44 ^h	1.3 ^b

^a See ref. 1. ^b See ref. 20. ^c See ref. 21. ^d See ref. 22. ^e See ref. 23. ^f See ref. 16. ^g See ref. 24. ^h See ref. 5. ⁱ See ref. 25. ^j See ref. 26.

(20) J. A. Ketelaar, *J. Phys. Radium*, **15**, 197 (1954).

(21) M. Tamres, D. R. Virzi, and S. Searles, *J. Am. Chem. Soc.*, **75**, 4358 (1953).

(22) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).

(23) J. S. Ham, J. R. Platt, and H. McConnell, *J. Chem. Phys.*, **19**, 1301 (1951).

(24) S. H. Hastings, J. L. Franklin, J. C. Schiller, and F. A. Matsen, *J. Am. Chem. Soc.*, **75**, 2900 (1953).

(25) R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955).

(26) G. Kortüm and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953).

Discussion

Spectrophotometric studies of relatively weak molecular complexes in the gas phase (and hence low donor concentrations) inherently involve measuring small changes in absorbance, frequently less than 0.1 (as seen in Figures 1 and 4), and hence rather large errors in ϵ_c and K_c determined from the usual plots of the Benesi-Hildebrand equation (or modifications), which are particularly sensitive to absorbance errors.²⁷ The errors indicated in Tables I and II for these quantities were estimated from the degree of reproducibility of successive measurements on a given sample and from the scatter of points about the least-squares linear plots expected from the equations used. Even assuming appreciably larger experimental errors, it is difficult to rationalize the differences between the gas and liquid phase extinction coefficients (which would be expected to be relatively independent of solvent or phase) for the diethyl ether systems or (particularly) the benzene system where the two differ by approximately a factor of 10.

Orgel and Mulliken²⁸ have discussed the apparent anomaly of decreasing ϵ_c with increasing stability of the complex for weak complexes in terms of absorption due in part to charge transfer during random contacts in which no actual complex is formed, this effect being roughly inversely proportional to the formation constant of the complex. For the benzene-iodine complex, for example, it was shown²⁸ that, by assuming at least four or five possible contact sites for the benzene molecule around the iodine molecule, the complex extinction coefficient is equal to *ca.* 4000 l. mole⁻¹ cm.⁻¹ and increases as predicted² in going to the methylated benzenes as donor species. These "contact" effects are not expected to be significant in the gas phase where the cage effect is negligible at reasonably low pressures.²⁹

Another explanation for this anomalous behavior in terms of competition between complexing and solvation has recently been presented,³⁰ which suggests that for weak complexes the Benesi-Hildebrand treatment underestimates K_c and overestimates ϵ_c . The best correlation between K_c and ϵ_c is obtained³⁰ for the benzene-iodine complex in carbon tetrachloride when it is assumed that a benzene molecule is solvated with four or five solvent molecules and that two solvent molecules are expelled when the solvated donor and acceptor species combine to form the solvated complex; ϵ_c is then 2400 l. mole⁻¹ cm.⁻¹, in reasonably good agreement with the gas phase extinction coefficient obtained in this work.

The gas phase formation constants for the two complexes are greater by at least a factor of 10 than those for the corresponding liquid phase complexes. This is also true for charge-transfer complexes involving iodine atoms as acceptors¹⁰ and for dimerization processes involving hydrogen bonding³¹ and is to be expected if solvation and competing solvent-acceptor complexes are important. However, the standard

(27) P. R. Hammond, *J. Chem. Soc.*, 479 (1964).

(28) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

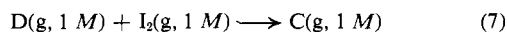
(29) R. K. Lyon, *ibid.*, **86**, 1907 (1964).

(30) S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.*, in press.

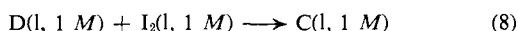
(31) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., New York, N. Y., 1960, Appendix C.

enthalpies of formation are of the same order of magnitude and do not reflect a solvent effect.

Even though the formation constants are expressed in concentration units (moles/liter), the standard states for the different phases are not strictly the same; the standard change in free energy calculated from $(K_c)_{\text{gas}}$ applies to the process



whereas $(K_c)_{\text{liquid}}$ leads to a standard free energy change for the reaction

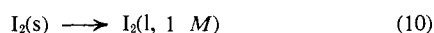


If it is assumed that the solution is sufficiently dilute so that Henry's law is applicable and that the vapors above the solution behave ideally, then

$$(K_c)_{\text{gas}} = RT(K_c)_{\text{liq}} \left(\frac{1000\rho_s k_c}{M_s k_D k_{I_2}} \right) \quad (9)$$

where ρ_s and M_s are the density and molecular weight of the solvent, k_c , k_D , and k_{I_2} are the Henry's law constants (in atm.), and R is in l. atm. mole⁻¹ deg.⁻¹. If it is further assumed that the donor forms an ideal solution with the solvent, then $k_D = P_D^0$, the vapor pressure of the pure donor.

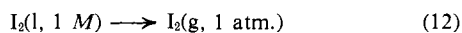
The molar chemical potential change for the process



in a binary mixture forming a regular solution is given by the relation³²

$$\Delta\mu_{I_2}^0 = RT \ln X_{I_2} + V_{I_2} \phi_s^2 (\delta_{I_2} - \delta_s)^2 \quad (11)$$

in which X_{I_2} is the mole fraction of I_2 in a 1 M solution, V_{I_2} is the molal volume of I_2 , ϕ_s is the volume fraction of the solvent, and δ_{I_2} and δ_s are the solubility parameters³² of iodine and solvent, respectively. The standard free energy of sublimation of iodine ($I_2(s) \rightarrow I_2(g, 1 \text{ atm.})$) at 25° is 4.63 kcal./mole, so that the change in chemical potential for the reaction



is

$$\Delta\mu_{I_2}^{0v} = 4630 - \Delta\mu_{I_2}^0 = -RT \ln \frac{k_{I_2} M_s}{1000\rho_s} \quad (13)$$

For iodine solutions in carbon tetrachloride at 25°, for which eq. 11 has been shown to be valid,³³ $X_{I_2} = 0.092$, $V_{I_2} = 59 \text{ cc.}$, $\phi_{\text{CCl}_4} = 0.90$, and δ_{I_2} and δ_{CCl_4} equal 14.1 and 8.6 (cal./cc.)^{1/2}, respectively³²; thus, $\Delta\mu_{I_2}^0 = 200 \text{ cal./mole}$ and $k_{I_2} M_s / 1000\rho_s = 5.6 \times 10^{-4} \text{ l. atm./mole}$. It follows, then, that for diethyl ether as donor ($P^0 = 535 \text{ torr}$, average $(K_c)_{\text{liq}}$ values from Table I) $k_c = 1.5 \times 10^{-4} \text{ atm.}$, and for benzene ($P^0 = 98 \text{ torr}$, average $(K_c)_{\text{liq}}$ values from Table II) $k_c = 0.9 \times 10^{-4} \text{ atm.}$ The similarity and order of magnitude of these Henry's law constants for the different complexes (considering the rather large

deviations for the gas phase values and the scattering of liquid phase constants reported in the literature) indicate a relatively high degree of solvation of the complex molecule.

The formation constant at 25° and standard enthalpy of formation of the benzene-iodine complex obtained in this work are compared in Table II with those determined by Atack and Rice⁵ from pressure-volume-temperature relations of mixtures of iodine and benzene above 150°. (In both cases ΔH_f^0 is assumed to be independent of temperature.) Agreement is quite satisfactory in view of the extrapolations and experimental errors involved and indicates that the same type of complex is studied by the two very different experimental techniques. This is in contrast to the conclusion reached by Atack and Rice,⁵ based on a comparison involving the thermodynamic properties of the liquid phase benzene-iodine complex, that the gas phase complex is adequately explained by van der Waals forces and that charge-transfer interactions are negligible in the gas phase.

The effect that various solvents should have on the position of the charge-transfer band is not clear, as in fact there appears to be very little solvent effect and no correlation between the band maximum position and the electrical properties of the solvent.³⁴ For weak complexes of the type reported in this work, the ground state has predominantly no-bond structure; hence, the structure of the excited state is primarily dative.² One would expect, therefore, appreciable solvent stabilization of the excited state leading to a red shift of the absorption band in going to more polar solvents (case III or IV of Bayliss and McRae¹⁴). The lack of an appreciable shift has been discussed in detail by De Maine³⁴ in terms of the formation of a "liquid-lattice penetration complex," whereby the charge-transfer complex is formed within a cage or aggregate of donor molecules that neutralizes the effect of the solvent. This penetration complex will not exist in the gas phase, and therefore an appreciable red shift is to be expected in going from the vapor to the liquid phase, the magnitude of the shift decreasing with increasing ionic character of the complex ground state. This behavior is indicated at least in a qualitative manner in the work reported here, the shifts being approximately 3100 and 2600 cm.⁻¹ for the benzene-iodine and diethyl ether-iodine complexes, respectively. The attempts to measure the absorption curves of the strong complexes between iodine and various aliphatic amines were unsuccessful (as discussed above); other systems are being investigated to verify quantitatively this apparent trend of wave length shift with complex stability in terms of the polar properties of the complex ground and excited states.

Acknowledgment. This research was supported in part by the National Aeronautics and Space Administration, Grant No. Nsg-100-60.

(32) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., New York, N. Y., 1962, p. 102.

(33) J. H. Hildebrand, *J. chim. phys.*, **61**, 53 (1964).

(34) P. A. D. De Maine, *J. Chem. Phys.*, **26**, 1199 (1957), and subsequent papers.