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Vapor-Phase Charge-Transfer Complexes. III. Iodine Complexes with Benzene, *p*-Xylene, and Mesitylene¹

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Abstract: The 1:1 complexes of benzene-iodine, *p*-xylene-iodine, and mesitylene-iodine were studied spectrophotometrically in the vapor phase. The charge-transfer bands of all three complexes in the vapor phase are blue-shifted relative to those in solution. Only for mesitylene-iodine was a band maximum observed (at $\sim 3010 \text{ \AA}$); the band maxima for the other two complexes were obscured by the absorption of the donor molecule. Values for the product of extinction coefficient times equilibrium constant (ϵK_c) are reported. However, meaningful separation into individual terms was not possible. The vapor-phase enthalpies of complex formation increase with increasing methyl substitution and are slightly larger than those measured in solution.

In contrast to the extensive studies of charge-transfer (CT) or donor-acceptor complexes in solution,² relatively little has been done on similar studies in the vapor phase.³⁻⁷ Since CT theory⁸ is based on the interaction of isolated molecules, vapor-phase studies offer the best opportunity for direct comparison with theory, being free from interference by a condensed medium.

The most extensively studied donor-acceptor systems in solution have been those in which iodine has been the acceptor.² Of these, the iodine complexes with benzene and its methyl-substituted derivatives are considered to be the *classical* series⁹ of CT complexes,

having served as the experimental basis for much of the theory.⁸

The only report of vapor-phase work on any member of the series has been that of Lang and Strong³ on the benzene-iodine complex. Their results show significant differences between vapor and solution. Considering the importance of this classical system, a reinvestigation of the benzene-iodine complex was undertaken along with two other members of the series, namely, *p*-xylene-iodine and mesitylene-iodine.

Experimental Section

Purification of Materials. Benzene (Analytical Reagent, Malinkrodt Chemical Works) was purified by a method described by Potts.¹⁰ A pure sample of *p*-xylene was generously provided by Mr. Marvin Kroll of the University of Chicago. Mesitylene (J. T. Baker Chemical Co.) was distilled and dried over calcium chloride. All three donors were redistilled immediately before use, and their purity was verified by vapor phase chromatography.

Baker Analyzed Reagent iodine was purified by twice subliming it from a finely pulverized mixture with potassium iodide.

Spectrophotometric Equipment. A special reflectance unit was built, utilizing a cell 25.0 cm long. Preliminary tests showed that mirrors coated with beral or silicon monoxide were not protected from attack by iodine. Consequently, the apparatus was designed with the mirrors outside the cells. Four passes were made through

(1) Taken in part from the Ph.D. thesis of W. K. Duerksen, University of Michigan, 1967.

(2) (a) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962); (c) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

(3) (a) F. T. Lang and R. L. Strong, *J. Am. Chem. Soc.*, **87**, 2345 (1965); (b) F. T. Lang, Ph.D. Dissertation, Rensselaer Polytechnic Institute, Troy, N. Y., 1964.

(4) (a) J. Prochrow and A. Tramer, *J. Chem. Phys.*, **44**, 4545 (1966); (b) J. Prochrow, *ibid.*, **43**, 3394 (1965).

(5) (a) M. Tamres and J. M. Goodenow, *J. Phys. Chem.*, **71**, 1982 (1967); (b) *J. Chem. Phys.*, **43**, 3393 (1965).

(6) M. Kroll and M. L. Ginter, *J. Phys. Chem.*, **69**, 3671 (1965).

(7) M. Tamres, W. K. Duerksen, and J. M. Goodenow, in press.

(8) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

(9) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(10) W. F. Potts, *J. Chem. Phys.*, **20**, 809 (1949).

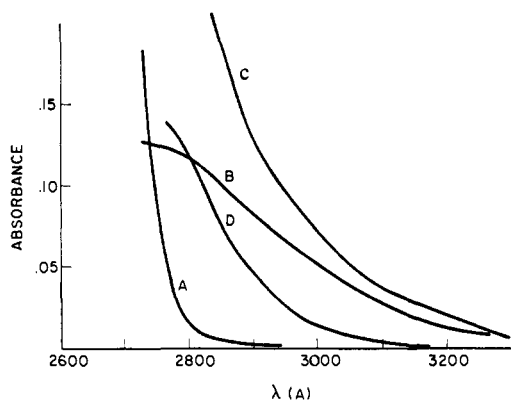


Figure 1. The benzene-iodine vapor-phase spectrum, 100.0-cm optical path, 70.0°: (A) [benzene] = $5.96 \times 10^{-3} M$; (B) [iodine] = $7.66 \times 10^{-5} M$; (C) mixture of A + B; (D) CT absorbance.

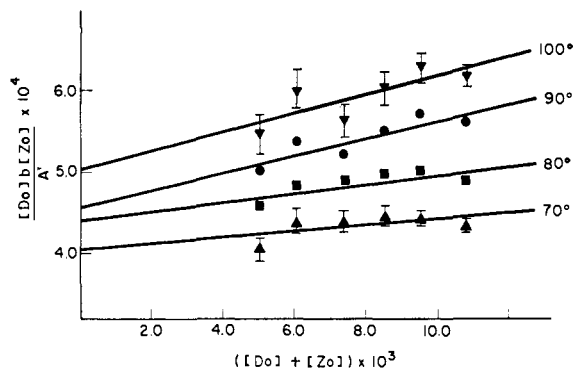


Figure 2. Scott-type plot for the benzene-iodine complex at $\lambda = 2820 \text{ \AA}$.

the cell, giving an effective path length of 100.0 cm. Loss of light at the cell windows necessitated using somewhat larger slit widths. A deuterium lamp was used for added light intensity. Measurements were taken with a Beckman UV spectrophotometer, Model 2400.

The sample and reference cells were thermostated by an aluminum oven heated electrically. The design of the oven and the cell housing is similar to that described for a smaller cell.^{6a,7,11}

Analytical Method. A vacuum line was used to transfer reagents from storage tubes. The amount of aromatic hydrocarbon transferred was determined by measuring with a cathetometer the height of the liquid before and after transfer from a calibrated capillary tube attached to the vacuum line.^{3,7} Tests showed that this method agreed to better than 1% with that of direct weighing of the compound in the cell.

The concentration of iodine was determined after the spectrophotometric measurements were completed. The aromatic hydrocarbon-iodine mixture was washed out of the cell with a known volume of *n*-heptane, and the absorbance of the solution was measured at the isosbestic point in the visible region.

The cell volume, ~240 ml, was determined by the weight of distilled water needed to fill the cell. The volume varied very little from one run to another, the change being due to the small variation in the position at which the tube connecting the cell was pulled off the vacuum line.

The range of donor-to-acceptor ratios was as follows: benzene-iodine, $(10.68-5.96) \times 10^{-3}$ and $(8.40-6.41) \times 10^{-5} M$; *p*-xylene-iodine, $(3.18-1.52) \times 10^{-3}$ and $(12.67-8.98) \times 10^{-5} M$; mesitylene-iodine, $(10.85-1.30) \times 10^{-4}$ and $(12.80-1.54) \times 10^{-5} M$.

Analysis of Data. The data were analyzed using the Scott-type¹² modification of the Benesi-Hildebrand⁹ equation, *i.e.*

$$\frac{[D_0]b[Z_0]}{A'} = \frac{[D_0] + [Z_0]}{\epsilon'} + \frac{1}{\epsilon'K_c} \quad (1)$$

(11) J. M. Goodenow, Ph.D. Thesis, University of Michigan, 1965.

(12) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956).

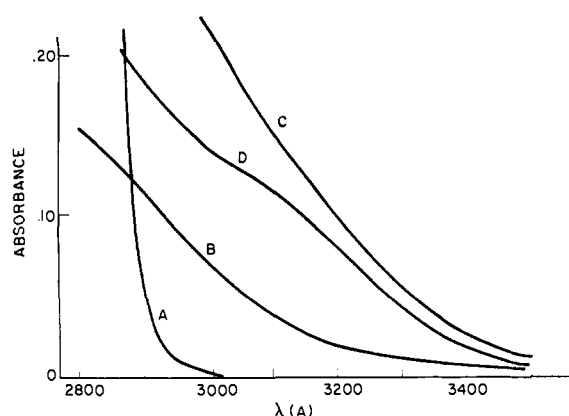


Figure 3. The *p*-xylene-iodine vapor-phase spectrum, 100.0-cm optical path, 87.0°: (A) [*p*-xylene] = $3.05 \times 10^{-3} M$; (B) [iodine] = $1.00 \times 10^{-4} M$; (C) mixture of A + B; (D) CT absorbance.

where $[D_0]$ and $[Z_0]$ are the initial concentrations of donor and acceptor, respectively; b is the cell length; K_c is the equilibrium constant (in l./mole); the extinction coefficient $\epsilon' = \epsilon_C - \epsilon_D - \epsilon_Z$, where the subscripts pertain to complex, donor, and acceptor; and the corrected absorbance $A' = A - \epsilon_C b[D_0] - \epsilon_Z b[Z_0]$. As expected,¹³ no error was introduced by using this approximate equation rather than the full one (which includes the term $-A'/b\epsilon'^2$). Measurements were made on six concentrations at between eight and ten wavelengths at four temperatures, and each set of data was analyzed using a Liptay¹⁴ treatment of eq 1. For each of the complexes, excellent agreement within the columns of the Liptay $[{}^0D_{i,k}]$ matrix was found, indicating that there is no appreciable interference from higher order complexes. The slopes and intercepts corresponding to eq 1 were determined using the method of least squares. All calculations were made on an IBM 7090 computer.

Results

Benzene-Iodine. Figure 1 shows the spectrum of the benzene-iodine system in the vapor phase. Unlike the solution spectrum which shows a band maximum, the maximum here is hidden by the absorption due to the benzene. Lang and Strong³ did observe a maximum at $\sim 2680 \text{ \AA}$ which appears to be reasonable from an extrapolation of curve D in Figure 1. It should be noted that the iodine concentration used by Lang and Strong was similar to that used in this study, and their benzene concentration was, at most, a factor of 3 larger. However, since they used a 10.0-cm path length as compared to the 100.0-cm path length used here, their absorption readings were smaller, which permitted them to extend measurements further into the uv region.

The Scott-type plot (eq 1) is shown in Figure 2. To illustrate the difficulty in obtaining a well-defined line, the error ranges that would be observed if the absorbances were in error by only ± 0.003 absorbance unit are shown for the points at 70 and 100°. The slopes and intercepts are reported in Table I. The error limits of the slope are much larger than those for the intercepts.

***p*-Xylene-Iodine.** Vapor-phase spectra for this system are shown in Figure 3. Again, the band maximum is hidden by the absorption due to the donor. The band shape for *p*-xylene-iodine is much more broad than that for benzene-iodine, although two distinct peaks do not appear as is the case for the *p*-xylene-TCNE complex.⁶ This has been explained as being

(13) M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).

(14) W. Liptay, *Z. Elektrochem.*, **65**, 375 (1961).

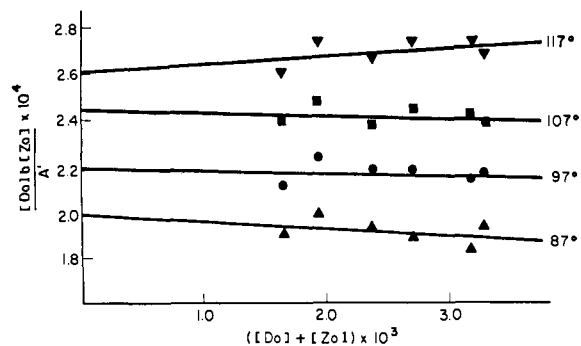


Figure 4. Scott-type plot for the *p*-xylene-iodine complex at $\lambda = 2940 \text{ \AA}$.

due to removal of π -orbital degeneracy upon substitution in the benzene ring,^{15,16} the effect being most pronounced for substituents in the *para* position.

A Scott plot of the data is shown in Figure 4, and the slopes and intercepts are compiled in Table I. Here, negative slopes were obtained at three of the four temperatures.

Table I. Liptay Analysis of Scott-Type Plot

System	Temp, °C	$(10^3/\epsilon')$ ^a	$(10^4/\epsilon'K_0)$ ^a
1. Benzene-iodine at $\lambda = 2820 \text{ \AA}$	70	4.2 ± 2.2	4.01 ± 0.17
	80	5.8 ± 1.6	4.40 ± 0.13
	90	10.6 ± 2.4	4.56 ± 0.20
	100	11.8 ± 3.4	5.00 ± 0.28
2. <i>p</i> -Xylene-iodine at $\lambda = 2940 \text{ \AA}$	87	-3.30 ± 2.45	1.99 ± 0.07
	97	-1.49 ± 2.65	2.20 ± 0.07
	107	-1.51 ± 2.25	2.45 ± 0.06
3. Mesitylene-iodine at $\lambda = 3000 \text{ \AA}$	117	$+3.43 \pm 2.45$	2.60 ± 0.06
	97	-0.29 ± 0.95	8.46 ± 0.09
	104	$+0.78 \pm 2.60$	9.10 ± 0.27
	111	2.47 ± 2.61	9.66 ± 0.27
	118	4.01 ± 4.28	10.66 ± 0.45

^a Probable errors at the 50% confidence level.

Mesitylene-Iodine. This complex was more difficult to investigate than the other two because of the lower volatility of the mesitylene. Even by reducing the donor-to-acceptor concentration ratios to only about 10:1, the temperature at which vapor-phase measurements could be begun was higher than those for the other complexes. In addition, a chemical reaction was noted above 118°, as evidenced by the time dependence of the absorbance. Consequently the measurements were confined to a smaller temperature range.

The mesitylene-iodine vapor spectrum is shown in Figure 5. Here, the band maximum of the complex is observed. The Scott plot in Figure 6 and the data in Table I summarize the results for this complex. A negative slope is obtained at one of the temperatures.

Discussion

The three complexes, the three donors, and iodine all absorb in the uv region. For iodine, there are two overlapping bands,¹⁷ one of low intensity for iodine

(15) L. E. Orgel, *J. Chem. Phys.*, **23**, 1352 (1955).
 (16) (a) E. M. Voigt, *J. Am. Chem. Soc.*, **86**, 3611 (1964); (b) E. M. Voigt and C. Reid, *ibid.*, **86**, 3930 (1964).
 (17) (a) V. G. Kortum and G. Friedhelm, *Z. Naturforsch.*, **2a**, 20 (1947); (b) P. A. D. De Maine, *J. Chem. Phys.*, **24**, 1091 (1956); (c) M.

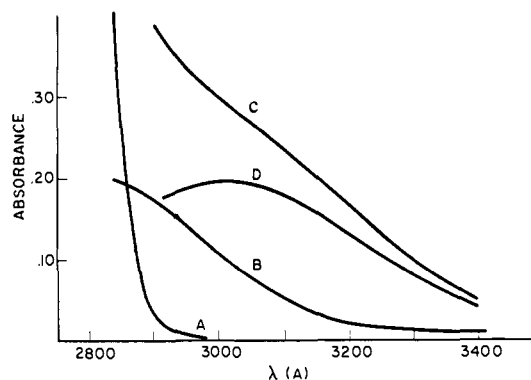


Figure 5. The mesitylene-iodine vapor-phase spectrum, 100.0-cm optical path, 97.0°: (A) [mesitylene] = $1.085 \times 10^{-3} M$; (B) [iodine] = $1.55 \times 10^{-4} M$; (C) mixture of A + B; (D) CT absorbance.

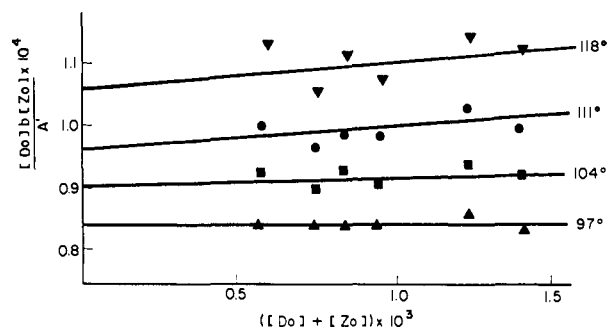


Figure 6. Scott-type plot for the mesitylene-iodine complex at $\lambda = 3000 \text{ \AA}$.

monomer and the other of high intensity for the dimer. In the present study, the concentration of iodine was kept low, the highest concentration being $1.28 \times 10^{-4} M$. For these conditions, there is no contribution in the uv due to I_2 ; it was shown recently that iodine vapor below $\sim 10^{-4} M$ can be considered to be entirely monomeric⁷ and obeys Beer's law.¹⁸ Each of the donors also obeys Beer's law at any single temperature, but with increase in temperature the tail of the band shows an absorption due to band broadening.

Comparison is made in Figure 7 of the vapor phase solution bands of the complexes. In solution, the band peak of each complex is distinct. In the vapor phase, however, each peak undergoes a large blue shift and, for the conditions of this study, only for mesitylene-iodine was the donor absorption sufficiently removed to permit observation of a band maximum. The shift, from $\sim 3320 \text{ \AA}$ in solution¹⁹ to $\sim 3010 \text{ \AA}$ in the vapor, is $\sim 3100 \text{ cm}^{-1}$. The solvent shift could be attributed to several factors, e.g., a dielectric effect,²⁰ solvent polarity²¹ and polarizability,²² and solvent pressure.^{4,23}

M. De Maine, P. A. D. De Maine, and G. E. McAlonie, *J. Mol. Spectry.*, **4**, 271 (1960); (d) R. M. Keefer and T. L. Allen, *J. Chem. Phys.*, **25**, 1059 (1956).

(18) M. Kroll, private communication.

(19) In this work (Figure 7); in CCl_4 solution: (a) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952); (b) M. Tamres, D. R. Virzi, and S. Searles, *ibid.*, **75**, 4358 (1953); (c) 3300 \AA in pure mesitylene, ref 9; and (d) in *n*-hexane, J. A. A. Ketelaar, *J. Phys. Radium*, **15**, 197 (1954).

(20) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

(21) (a) P. H. Emslie and R. Foster, *Rec. Trav. Chim.*, **84**, 255 (1965); (b) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

(22) (a) H. M. Rosenberg and D. Hale, *J. Phys. Chem.*, **69**, 2490 (1965); (b) E. M. Voigt, *ibid.*, **70**, 598 (1966).

(23) P. J. Trotter, *J. Am. Chem. Soc.*, **88**, 5721 (1966).

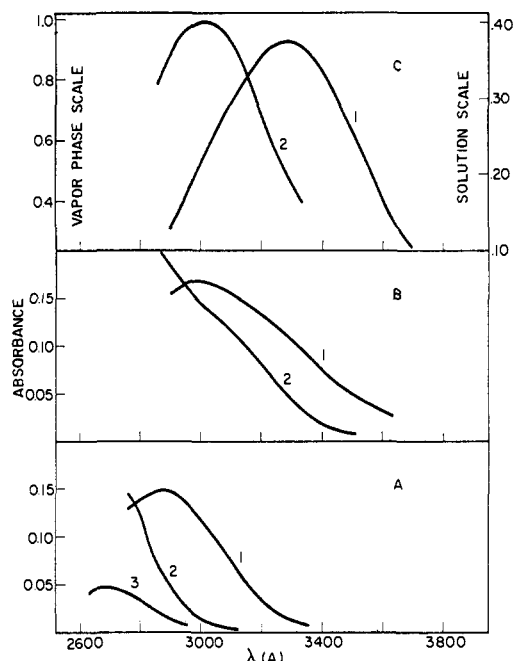


Figure 7. Solution and vapor-phase CT bands of aromatic hydrocarbon-iodine complexes. (A) Benzene-iodine: (1) *n*-heptane solvent, 1.00-cm cell, 25.0°, [benzene] = 0.1033 *M*, [iodine] = 4.73×10^{-4} *M*; (2) vapor phase from Figure 1; (3) vapor phase from ref 3a. (B) *p*-Xylene-iodine: (1) *n*-heptane solvent, 1.00-cm cell, 25.0°, [xylene] = 9.60×10^{-2} *M*, [iodine] = 4.73×10^{-4} *M*; (2) vapor phase from Figure 3. (C) Mesitylene-iodine: (1) *n*-heptane solvent, 1.00-cm cell, 25.0°, [mesitylene] = 1.095×10^{-3} *M*, [iodine] = 4.73×10^{-4} *M*; (2) vapor phase, 100.0-cm cell, 97.0°, [mesitylene] = 8.63×10^{-4} *M*, [iodine] = 9.53×10^{-5} *M*.

In general, the prediction is that the shift in band maximum between the two phases should be large for weak complexes, as is found here.

In the absence of the full vapor curve, the quantity $\nu_{\max} - \nu_L$ was used to compare band shapes. The difference, 2840 and 2960 cm^{-1} in the vapor phase and in solution, respectively, is small. Larger differences were observed for a number of complexes with carbonyl cyanide, again being broader in solution than in the vapor.⁴ For the stronger diethyl sulfide-iodine, the half-widths of the relative bands in the two phases were essentially the same.⁵

Iodine complexes with pentamethylbenzene and hexamethylbenzene should exhibit clearly observable vapor band maxima. However, their study would require temperatures higher than that for mesitylene-iodine, and chemical reaction is likely to occur. Reaction at 210° between toluene and iodine has been studied kinetically.²⁴

Meaningful separation of the extinction coefficient and equilibrium constant in the product $\epsilon'K_c$ cannot be made, as is apparent from the sometimes negative result in ϵ' and its erratic variation with temperature (Table I). Person²⁵ has proposed criteria, for the experimental condition when $[D_0] \gg [Z_0]$, to determine whether a reliable K_c can be found, namely, the boundary conditions $0.1/K_c < [D_0] < 9.0/K_c$. In the present study on benzene-iodine, the maximum $[D_0]$ was of the order 10^{-2} *M*, which would set a lower limit of detectability of K_c of 10 l./mole. From the manometric

(24) R. Walsh, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 650 (1966).

(25) W. B. Person, *ibid.*, **87**, 167 (1965).

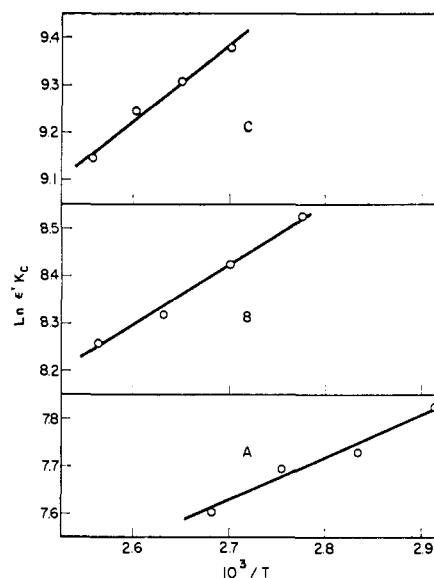


Figure 8. $\ln \epsilon'K_c$ vs. $1/T$ for vapor-phase iodine complexes with (A) benzene; (B) *p*-xylene; (C) mesitylene.

data of Atack and Rice,²⁶ the value of K_c is calculated to be 2.0 l./mole. Thus the system fails to fulfill the boundary condition. The Lang and Strong³ data fall just around the boundary limit.

Another way to examine the system is to use the Atack and Rice data for K_c together with the $\epsilon'K_c$ data in Table I to get an average value for ϵ' . This comes out to be 1080 l./mole. Thus, in eq 1 for benzene-iodine, the slope = $1/\epsilon' \approx 10^{-3} = \Delta Y/\Delta X = \Delta Y/[10.7 - 6.0] \times 10^{-3}$; from which $\Delta Y \approx 4.7 \times 10^{-6}$. Since the values of Y at 90° were of the order 5×10^{-4} , this means that $\Delta Y/Y$ is of the order of 1%. Therefore, to determine K_c with any certainty, it would be necessary to detect with precision a change in Y of about 1% over the concentration range studies, and this is not feasible with the spectrophotometric method. Similar remarks apply to the *p*-xylene-iodine and mesitylene-iodine complexes.

The $\epsilon'K_c$ product exhibits a systematic temperature dependence, as shown in the $\ln \epsilon'K_c$ vs. $1/T$ plot in Figure 8, from which ΔE can be calculated. The results are given in Table II. Comparison is made to the solu-

Table II. Vapor Phase and Solution Energies of Complexation from Spectrophotometric Studies

Class	Complex	$-\Delta E^\circ$ (soln)	$-\Delta E^\circ$ (vapor)	$\Delta(\Delta E^\circ)$
I	<i>p</i> -Xylene-TCNE	3.37 ^a	7.35 ^b	3.98
II	Benzene-I ₂	1.3 ^{c,d}	2.0, ^e 1.77 ^f	0.7, 0.5
	<i>p</i> -Xylene-I ₂	2.27 ^c	2.54 ^f	0.27
	Mesitylene-I ₂	2.86 ^c	3.14 ^f	0.28
III	Diethyl ether-I ₂	4.2 ^g	3.2 ^g	-1.0
	Diethyl sulfide-I ₂	8.6 ^{h,i}	7.7 ^{j,k}	-0.9

^a CH₂Cl₂ solvent: ref 34. ^b Reference 6. ^c CCl₄ solvent: L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 2164 (1955). ^d *n*-Hexane solvent: ref 19d. ^e Reference 3. ^f This work. ^g *n*-Heptane solvent: M. Brandon, M. Tamres, and S. Searles, *J. Am. Chem. Soc.*, **82**, 2129, 2134 (1960). ^h *n*-Heptane solvent, average of vapor and solution values: M. Tamres and S. Searles, Jr., *J. Phys. Chem.*, **66**, 1099 (1962). ⁱ H. Tsubomura and R. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961), found $\Delta E^\circ = -7.8$ kcal/mole. ^j Reference 5. ^k This value has been obtained independently by M. Kroll, private communication.

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

tion values and to available data on several other complexes. The vapor phase ΔE° result for benzene-iodine in the present study agrees well with that of Lang and Strong³ and, in fact, the $\epsilon_c K_c$ products are similar; e.g., at 70°, Lang and Strong obtain $2.8 \times 10^3 \text{ l.}^2/(\text{mole}^2 \text{ cm})$ at $\lambda = 2825 \text{ \AA}$, and in this study it is $2.5 \times 10^3 \text{ l.}^2/(\text{mole}^2 \text{ cm})$ at $\lambda = 2820 \text{ \AA}$. There is agreement with the manometric data of Attack and Rice,²⁶ who, for the temperature range 155–192°, reported $\Delta H^\circ = -2.44 \text{ kcal/mole}$, as compared with -2.37 kcal/mole found in this work. Further, there is internal consistency in the results for the aromatic hydrocarbon-iodine series; a similar trend in ΔE° is observed both in the vapor phase and in solution.

From the plot of Figure 8, it is possible to extrapolate to room temperature the value of $\epsilon' K_c$ at the band maximum of mesitylene-iodine for comparison with solution data. Since ϵ_D and ϵ_Z are small, $\epsilon' \simeq \epsilon_c$, and $\epsilon_c K_c$ for the vapor phase at 25° is $33,300 \text{ l.}^2/(\text{mole}^2 \text{ cm})$. The value in CCl_4 solution^{19a,b} at this temperature has been reported to be 7300 and 5900 $\text{l.}^2/(\text{mole}^2 \text{ cm})$.

Carter, Murrell, and Rosch²⁷ have suggested that for the aromatic hydrocarbon-iodine complexes a correction for solvation can be made to give a corrected ϵ_c and K_c which, in effect, should compare well to the vapor-phase results. Their analysis requires that the $\epsilon_c K_c$ product be the same before and after correction. For mesitylene-iodine, this product is very different in the two phases. For the aromatic hydrocarbon-TCNE complexes the differences in $\epsilon_c K_c$, and also in ΔE° , are even more pronounced.^{6,28}

For a thermodynamic property, X , the difference between vapor and solution values is^{5a} $\Delta X^\circ(\text{vap}) = \Delta X^\circ(\text{soln}) - [\Delta X^\circ_{DZ}(\text{soln}) - \Delta X^\circ_D(\text{soln}) - \Delta X^\circ_Z(\text{soln})]$, where the term in brackets is the difference in the thermodynamic property due to solvation of complex, donor, and acceptor. Comparison of the $\Delta(\Delta E^\circ)$ values in Table II shows that the differences due to solvation can be large in some cases and small in others, and at times may be positive or negative. The data seem to fall into three groups, with those within a group corresponding to similar type complexes.

It is apparent, both from the variation in thermodynamic properties of complexes in different solvents²⁹ and the variation between vapor phase and solution (Table II), that a model to explain the differences must be based on specific solute-solvent interaction. Although the data in Table II are too few for generalization, the groupings suggest a possible partial explanation based on the structures of the complexes. The presently accepted structures for the three groups of complexes are shown in Figure 9. Much of the evidence for these structures comes from studies of the crystalline state, and it is assumed that the geometries are similar in the vapor phase and in solution. Aromatic hydrocarbons have been shown to form a sandwich structure with π acceptors, such as TCNE,³⁰ in which the two molecular planes are parallel, and to form an axial structure of

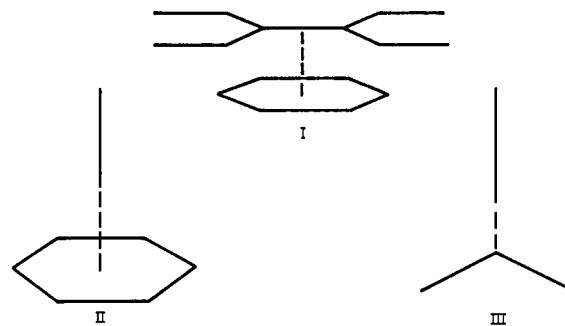


Figure 9. Assumed geometrics of isolated CT complexes: (I) aromatic hydrocarbon-TCNE; (II) aromatic hydrocarbon- I_2 ; (III) $\text{R}_2\text{X}-\text{I}_2$.

C_{6v} symmetry with iodine.³¹ In solution, the process of complex formation requires that solvent molecules be squeezed out from between donor and acceptor. This would involve a loss in solvation energy, although part of the energy is regained when the displaced solvent molecules enter the bulk solvent. The magnitude of the difference would depend not only on the number of solvent molecules displaced but also on the strength of the solute-solvent local interactions.

From the crystal structure data for TCNE,^{16a,32} the area within the four nitrogen centers of the planar molecule is very nearly 18 \AA^2 . If an allowance of $\sim 1.5 \text{ \AA}$ is made for the van der Waals radius of nitrogen,³³ the area attributed to the molecule would be $\sim 50 \text{ \AA}^2$. By contrast, the area of iodine, using 2.15 \AA for the van der Waals radius of the iodine atom,³³ is less than one-third of that. Thus more solvent molecules would be displaced when the solvated donor forms a complex with solvated TCNE than with solvated I_2 . However, the total number of solvent molecules involved would not be large, since the dimensions of the solvent molecules are not much different from those of some of the reactants. The treatment of Carter, Murrell, and Rosch²⁷ for the benzene-iodine complex leads to a displacement of about two or three solvent molecules. Further, the orientation of solvent around TCNE, which has several local dipoles, should be more of a factor than it is for the nonpolar iodine molecule. The aromatic hydrocarbon-TCNE complexes have been studied in methylene chloride.³⁴ This H-bonding solvent would interact both with the π -electron-rich cloud of the benzene ring and with the π -electron-deficient cloud of the TCNE, so that displacement of solvent on complex formation would result in a greater loss in solvation energy. The fact that TCNE is more soluble in methylene chloride than in *n*-heptane or CCl_4 would indicate greater solvent interaction.

For the above reasons, it would be expected that structure I would show larger solvation effects than structure II (Figure 9). The solvation trend might be expected to continue from structure II to III³⁵ because of the change from a complex with a rigid aromatic

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ring to that with a more flexible donor molecule which can better accommodate the solvent. The limited data in Table II are in accord with these assumptions.

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Association of Indole and Phenol with Diethyl Chalcogenides

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Abstract: The ir spectra of indole in solutions containing diethyl ether, diethyl sulfide, selenide, and telluride as well as those of phenol in solutions containing the first three chalcogenide compounds were obtained at 40°. The chemical shifts of the phenol hydroxyl proton were obtained for the latter three systems, at -20, 10, and 40° as a function of ether concentration. Association equilibrium constants and molar extinction coefficients were obtained for all systems, while ΔH and ΔS values were calculated for the latter three systems. The results were found to agree with the "electron vibration" model developed principally for charge-transfer (CT) complexes, if one assumes that the H-bond lengths increase in going from ether to selenide or to telluride. The thermodynamic properties and the comparison of the spectral data with literature data reported for typical CT complexes show that CT constitutes only part of the over-all H-bond interaction.

In recent years, much experimental and theoretical work has been devoted to the study of charge-transfer (CT) complexes, and in particular to their spectral properties.¹⁻³ To interpret the intensification of the infrared stretching vibration of the electron-acceptor molecule on CT complex formation, the so-called "electron-vibration" model was developed.⁴⁻¹⁰ The dative or charge-transfer form contributes to the over-all state of the complex, and the relative weight of this contribution is conveniently described by the coefficient of the wave function descriptive of this dative form which enters the linear sum of terms constituting the over-all wave function of the complex.^{2,3} The electron vibration model recognizes that this weighting or dative coefficient, b , varies during the electron-acceptor stretching vibration and in phase with it. This variation in turn is equivalent to a change of the over-all or effective dipole moment, again in phase with the stretching vibration, and leads to the observed intensification of the corresponding infrared band.

Interestingly, the recent and rigorous treatment of the problem by Friedrich and Person¹⁰ should be useful to explain the intensification of typical X-H stretching vibrations on H-bonding as well. In fact, the authors recognized that there are conceptual similarities between

their treatment and those presented by others who were specifically interested in H-bonding.¹¹⁻¹³

A complete test of the Friedrich and Person theory as applied to H-bonding does not seem feasible at this time,¹⁴ but accurate intensity data used in the light of the approximate results of the formal treatment¹⁰ may well serve to estimate the relative importance of charge transfer compared to the other contributions to the H-bond strength in a series of structurally similar H-bonded complexes.

This more limited objective is the goal of the present study. Literature data alone, however extensive,¹⁵ cannot be used to this end. For one, the methods used to determine integrated molar absorption coefficients differ widely in various laboratories,^{16,17} and systematic errors cannot ordinarily be estimated and removed. Secondly, the selection of H-bonding partners is critical, even for a limited comparison of theory and experiment. Frequently, and, for example, in the case of trialkylamines, there is a definite parallelism between charge-transfer donor strength and electron-donor electrostatic action.² In the present series, the accumulation of negative charge on the electron-donor moiety decreases in going from O to Se or Te, while the charge-transfer tendency should increase. This means that the trends observed within series of complexes as studied here should show which of these two effects is more important, and this reasoning led to the present selection of H-bonding partners. In addition, it seemed important to get some H-bonding data for the heavier chalcogenide ethers; little work seems to have been done on these compounds.¹⁵

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