[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, UNIVERSITY OF CHICAGO]

The Spectra of Iodine Solutions. I. The Effects of Low Temperatures upon Iodine Complexes[1]

BY JOE HAM[2]

RECEIVED FEBRUARY 2, 1954

A study has been made at liquid nitrogen temperatures in rigid glasses of solutions of iodine together with various aromatic hydrocarbons and other molecules, with which iodine forms charge-transfer complexes. Some attempts to study the Br_2 and ICN complexes at low temperatures were unsuccessful. At liquid nitrogen temperatures, the equilibrium constants are overwhelmingly in favor of complex formation for the iodine solutions so that dilute solutions of donors could be used in which, nevertheless, most of the iodine should have been in the form of complexes. The visible band of iodine complexes shifted to shorter wave lengths upon cooling. A glass consisting of 3-methylpentane and isopentane produced moderate red shifts in the charge-transfer bands of the benzene and toluene complexes upon cooling which may be explained by the altered index of refraction with contraction. A glass consisting of methylcyclohexane and isopentane, on the other hand, produced very large red shifts in these cases and no shifts or even blue shifts in other complexes. Measurements at intermediate temperatures showed that in those cases where bands shifted by large amounts, the shift was due to the appearance of a distinct new band which became increasingly intense and finally dominated the near ultraviolet spectra at low temperatures. This new band may be attributed to the absorption of a complex solvated by a methylcyclohexane molecule or molecules, although other possibilities cannot be ruled out completely. The large blue shift which occurred in the case of the hexaethylbenzene complex at low temperatures may possibly be due to two different forms of the iodine complex which exist because of the large steric hindrance of the ethyl groups. A discussion of the cause of the shift of the visible and infrared bands upon complexing and upon cooling is given.

Introduction

Iodine solutions have long attracted scientific attention because of the marked color changes in certain solvents. Iodine solutions are frequently violet, as is iodine vapor, yet the color varies in other cases from a reddish color (in benzene) to a pale yellow (in pyridine). The change from violet to other colors has long been attributed to the formation of 1:1 complexes. Benesi and Hildebrand[3] found that not only did the visible spectrum change for iodine in an aromatic solvent, but an intense new absorption appeared in a region of the ultraviolet where neither iodine nor the aromatic molecule has any absorption. By varying the concentrations of iodine and the aromatic molecule, both dissolved in an inert solvent such as *n*-heptane or carbon tetrachloride, they were able to show that the new ultraviolet peak arose from a 1:1 complex of iodine with the aromatic molecule and that this complex had a molar extinction coefficient $\epsilon_{\max} \sim 18{,}000$. The complex formation they attributed to a Lewis acid–base interaction.

Mulliken[4] has given a quantum-mechanical interpretation of the Lewis acid–base interaction which predicts the occurrence of a very intense band, called the charge-transfer (CT) band, appearing in the ultraviolet in cases like those discussed in the present paper. While this type of interaction occurs in many kinds of solutions,[4b,c] iodine solutions are a particularly valuable case to study, for several reasons. The iodine molecule has relatively little absorption throughout the near ultraviolet, is rather inert chemically, and forms complexes with numerous types of organic molecules, and these complexes have very strong CT bands. Most of the previous spectrophotometric measurements on iodine solutions have been made in solution near room temperature. In this and the following paper, the spectra are studied under conditions quite different from usual, namely, at liquid nitrogen temperatures in a rigid glass, and at room temperature under 2000 atmospheres pressure.

Already in a few instances in earlier work, quite large spectral effects have been observed in halogen solutions upon cooling to low temperatures. Prikhotko[5] observed a blue shift of 3500 kayser[6] for the visible band of iodine in alcohol and 1300 kayser for the visible band of bromine in pentane at liquid hydrogen temperatures (20°K.). More recently, Freed and Sancier studied a number of iodine complexes at low temperatures.[7] Of these, they studied the iodine complexes of cyclopropane and propene at liquid nitrogen temperatures. They observed, for the cyclopropane and propene complexes, respectively, blue shifts of the visible band by 770 and 2150 kayser, and red shifts of the charge-transfer band by 0 and 1320 kayser. In an effort to understand these frequency shifts, a number of iodine complexes at liquid nitrogen temperatures have been studied.

Experimental

Low Temperature Cell.—A metal Dewar cell was used similar in design to that described by Potts,[8] but embodying several improvements. It consisted of an absorption cell partially surrounded by the coolant chamber in such a manner (see Fig. 1) that the light did not pass through the coolant. This assembly was attached to the lid of a metal can which was evacuated, for thermal insulation, by a mechanical vacuum pump. One of the improvements over the previous design consisted of making the wall of the metal can gasketed with an "O" ring to the lid and inner assembly, thus facilitating disassembly. The Dewar was taller and therefore had less heat conduction losses than in the earlier design. The windows were cemented onto the invar holders (Figs. 1c and 1d) using araldite cement. The small thermal contraction of invar permitted rapid cooling and warming with little danger of breaking the windows. An improvement over screwing a threshold window holder against the Teflon gasket was made by using eight screws

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[1] This work was assisted in part by the Office of Ordnance Research under Project TB2-0001 (505) of Contract DA-11-022-ORD-1002 with The University of Chicago.

[2] Atomic Energy Commission predoctoral fellow, 1951–1953. Jackson Laboratory, E. I. du Pont de Nemours and Co., Wilmington, Del.

[3] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[4] (a) R. S. Mulliken, *ibid.*, **72**, 600 (1950); (b) **74**, 811 (1952); (c) *J. Phys. Chem.*, **56**, 801 (1952).

[5] A. Prikhotko, *Acta Physicochim. U.R.S.S.*, **16**, 125 (1942).

[6] Kayser (formerly $cm.^{-1}$). See Transactions of the Joint Commission for Spectroscopy, *J. Opt. Soc. Am.*, **43**, 410 (1953).

[7] S. Freed and K. M. Sancier, THIS JOURNAL, **74**, 1273 (1952).

[8] W. J. Potts, *J. Chem. Phys.*, **21**, 191 (1953).

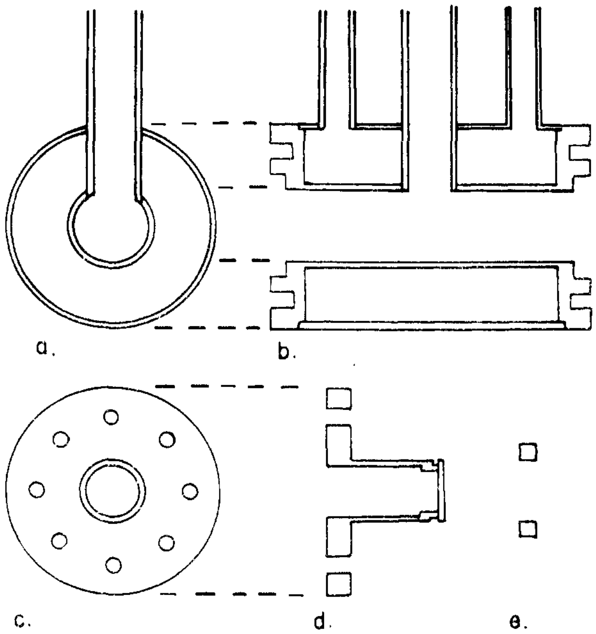

Fig. 1.—Cross sections of the inner cell assembly of the low temperature Dewar. Cross sections a and b show the coolant chamber surrounding the cell and the various filling tubes. The window holders (shown in c and d) fit into each end of b to form the cell. Each cell holder is pulled against a Teflon gasket, e, by eight screws. This entire inner assembly is surrounded by a metal can with quartz windows and the intervening space is evacuated to produce a Dewar.

to pull the window holder against the gasket (Fig. 1e) without twisting, which made a tight seal that could be repeatedly warmed and cooled without leaking. Path lengths could be varied up to about 7 cm. by choosing differently shaped window holders. A cell length of 1 cm. was used for the present work.

Since the body of the cell was made of copper, which reacted slowly with iodine solutions, it and the invar holders were coated with a thin coat of araldite cement. This reduced the rate of fading of iodine solutions to about 1% per hour at room temperature.

By filling the cooling jacket with metal shot, the heat capacity of the cell was increased sufficiently so that measurements could be taken at intermediate temperatures. The thermocouple, which was calibrated at the CO_2 sublimation point and the O_2 boiling point, was attached on one of the window holders in the inset, so that its thermal connection with the coolant chamber was principally through the solution. This guaranteed that the measured temperature would be no lower than the solution temperature in the light path. The coldest temperature measured was 85°K. (liquid nitrogen boils at 77°K.). Liquid nitrogen was poured into the coolant chamber until the solution reached the desired intermediate temperature. Spectral measurements could be taken at about 10 wave lengths before the temperature had drifted 2° in the worst cases. By taking measurements from longer to shorter wave lengths and then in the opposite direction, much of the effect of the thermal drift could be corrected by taking an average of the two sets of readings.

Solvents.—The solvents used in this study were two mixtures of hydrocarbons which freeze to stable rigid glasses at low temperatures.[8] One was composed of 1 part of 3-methylpentane to 3 parts of isopentane which will, hereafter, be called MP, and the other was composed of 1 part of methylcyclohexane to 3 parts isopentane which will be called MCH. As these solutions cooled they gradually contracted until at liquid nitrogen temperatures they had shrunk about 25% in volume compared with room temperature. These solvents were Phillip's Pure grade purified by a method described by Potts.[9]

The solubility of iodine is quite low in saturated hydrocarbons at low temperatures. The data given by Hildebrand,[10] when extrapolated to liquid nitrogen temperatures, give a solubility in *n*-heptane of about 10^{-11} molar. Those solvents which complex with iodine, however, have much smaller temperature coefficients of solubility; for example, iodine in ether has an extrapolated solubility of 2×10^{-4} molar at liquid nitrogen temperatures. This no doubt means that the complexes are much more soluble at low temperatures than free iodine.

The very low solubility of iodine in the glasses prevented any measurements on the spectra of uncomplexed iodine at low temperatures. When such measurements were attempted, the solutions took on a cloudy appearance and acquired a weak absorption throughout the near ultraviolet, characteristic of iodine crystals. For complexed iodine, on the other hand, the high intensity of the charge-transfer band permitted the use of solutions only 2 to 5×10^{-5} molar of iodine in a 1-cm. cell, provided enough donor was used to give a crystal-free solution. The amount of donor required for this purpose varied from 200 to 600 times the iodine concentration in most cases.

Experimental Problems.—Only very approximate absorption intensities could be measured. Although the proportions of iodine present as complex were unknown at low temperatures, these should have been close to 100% except, perhaps, in the few cases of large donor molecules where the low solubility of the donor necessitated extremely low donor concentrations. Table I gives the values of the equilibrium constant at 77°K. for several complexes calculated from the ΔS and ΔH values observed near room temperature.[11] The large variation among these values indicates, for example, that a much less donor is required for a study of the *p*-xylene-iodine complex than is required for the benzene-iodine complex. The equilibrium constant for the benzene-iodine complex given in Table I predicts that, for typical benzene concentrations, 85% of the iodine was complexed at 77°K. The absence of iodine crystals and the low solubility of iodine in the glass suggest that a much greater percentage of the iodine was in the complex. Since the solutions became rigid glasses at liquid nitrogen temperatures, it is likely that the equilibrium was frozen in at some higher temperature. This temperature could depend to some extent upon the rate of cooling.

TABLE I[a]

ESTIMATED VALUES OF THE EQUILIBRIUM CONSTANT $K = (C_{AD})/(C_A C_D)$ AT LIQUID NITROGEN TEMPERATURES

C_A and C_{AD} are the respective concentrations of the acceptor (iodine) and complex expressed in moles per liter, and C_D is the concentration of the donor expressed as mole fraction.

Donor	K (at 298°K.)	ΔH	ΔS	K (at 77°K.)
Benzene	1.21	−1300	− 4.0	640
Toluene	2.24	−1800	− 4.4	13000
Xylene	2.96	−2000	− 4.9	47000
Dioxane	9.30	−3500	− 7.3	1.9×10^8
Pyridine	1250.00	−7800	−12.0	3.1×10^{19}

[a] Data taken from ref. 11, with the exception of data on the pyridine complex taken from C. Reid and R. S. Mulliken, THIS JOURNAL, 76, 3869 (1954).

In addition to the problem of the concentration of the complex, one also had the problem of background probably produced by scattering from density fluctuations in the glass. This was particularly bad when the solutions contained large donor concentrations. Therefore, the recorded intensities given below in Table III may be in error by as much as 30%.

At times, concentrations of donors above the solubility limit at low temperatures were used. In these cases, the solutions could be kept crystal-free for extended periods, but when the cell was warmed slightly, it filled with crystallites. In a few cases, the complex was so weak and/or the solubility of the donor was so small that no concentration of donor would give crystal-free solutions. Examples of this type of donor are ethyl iodide, naphthalene and pyridine. It may be that in the case of some complexes, the

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(9) W. J. Potts, *J. Chem. Phys.*, **20**, 809 (1952).

(10) J. H. Hildebrand, *ibid.*, **20**, 190 (1952).

(11) C. van de Stolpe, Thesis, Amsterdam, 1953.

complex can crystallize before either component crystallizes, but no such behavior was noted in the iodine solutions.

Impurities in the donor presented a very serious problem. The presence of a trace of an impurity in a weak donor can take up all of the iodine in solution. For example, a trace of ether in the benzene completely eliminated the absorption of the benzene–iodine complex near 300 mμ at low temperatures.

It is known that oxygen forms complexes with a number of saturated and unsaturated hydrocarbons, giving rise to ultraviolet absorption.[12] These absorptions are mostly at wave lengths shorter than the wave lengths where the iodine complexes have their absorption. Nevertheless, it seemed desirable to determine whether dissolved oxygen had anything to do with any of the phenomena observed. To test this, oxygen was passed into the benzene–iodine solutions before freezing. There was no effect upon the absorption spectra at low temperatures. Boiling, or passing pure nitrogen (less than 0.01% O_2) through the solution before freezing, also showed no effect, although both these methods removed much of the dissolved oxygen,[12] as was determined by room temperature measurements near 210 mμ on the pure solvents. These tests showed clearly that oxygen played no role in the phenomena studied here. Hence for the remaining experiments, no efforts were made to eliminate dissolved oxygen other than by sealing off the cell at room temperature before cooling.

Experiments with Br_2 and ICN Complexes.—Spectral measurements of the Br_2 and ICN complexes were attempted at low temperatures. Both of these molecules reacted too readily with the solvents in ultraviolet light at the very low concentration which had to be used for low temperature work, so that no reliable results could be obtained.

Results on Iodine Complexes

Table II gives the positions of the CT band and visible bands in a number of iodine complexes at room temperature, and at liquid nitrogen temperatures in the MCH glass. The position of the visible band at room temperature could not be determined very accurately for the aromatic complexes, since the correction for the uncomplexed iodine was large and the resulting position was sensitive to errors in the equilibrium constant. At room temperature, the visible band was observed at increasingly short wave lengths for the donors with more methyl groups in the series benzene, toluene, etc. At low temperatures, the visible band shifted in all these cases to much shorter wave lengths (near 450 mμ) and the order of peak positions in relation to the number of methyl substituents was reversed. The positions of the visible band for the three olefin complexes studied at low temperatures were at still shorter wave lengths (about 430 mμ).

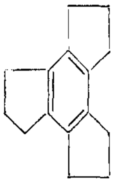
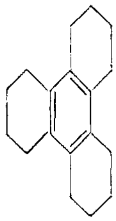
In the ether complex, the weak band corresponding to the $^3\Pi - {}^1\Sigma^+$ transition of I_2 can be seen at low temperatures near 530 mμ.[13] Here it has shifted to the blue about 4300 kayser from its position at room temperature in uncomplexed iodine, as compared with a shift of 3900 kayser for the main iodine visible band (which corresponds to $^3\Pi_0{}^+ - {}^1\Sigma^+$ plus a weaker $^1\Pi - {}^1\Sigma^+$ transition).[13]

The peak molar extinction coefficient of the main visible band at low temperatures was almost the same for all complexes. For aromatic complexes, it appeared to be about ϵ 1600, for the olefin complexes slightly larger, ϵ 1800, and for the ether and alcohol complexes slightly smaller, ϵ 1400. The peak intensities of the CT band at low temperatures were 13,000 and 15,000 for the benzene and toluene complexes, respectively (each is the average of three runs). The intensities of the CT band for the heavily substituted benzene complexes, such as the hexamethylbenzene complex, dropped to around 6000. Within the uncertainties of the data, the CT intensities are the same at low temperatures as at room temperature (see Table III).

TABLE II

EFFECT OF TEMPERATURE UPON THE POSITION OF THE CT AND VISIBLE MAXIMA OF IODINE COMPLEXES

The absorption of uncomplexed iodine has been subtracted from the observed spectra to obtain the room temperature data for the visible band.

Donor	At room temp. in *n*-heptane		At liquid nitrogen temp. in MCH glass[a]	
	CT	*vis*	CT	*vis*
Benzene[b]	288	500	324	452
Toluene[b]	299	496	322	452
p-Xylene	303	495	323	453
Mesitylene	327	493	330	456
Hexamethylbenzene	366	..	368	478
	373	...	373	476
	378	...	375	...
Hexaethylbenzene	372	..	319	455
Hexene-1	274	..	304	439
Cyclohexene	286	..	310	440
Tetramethylethylene	338	..	345	438
t-Butyl alcohol	233	460	235	425
Diethyl ether	250	475	250	433

[a] The CT maxima for the benzene (see Fig. 2) and toluene complexes in the MP glass are at 297 and 315 mμ, respectively. [b] See also Figs. 3 and 4.

TABLE III

PEAK MOLAR EXTINCTION COEFFICIENTS OF THE CT BAND OF THE BENZENE, TOLUENE AND HEXAMETHYLBENZENE COMPLEXES OF IODINE AT ROOM AND AT LOW TEMPERATURE

Donor	Solvent	ϵ_{max} at room temperature				ϵ_{max} at 77° kayser in MCH
		Ref. 1[a]	Ref. 11	Ref. 22	Ref. 23	
Bz	C_nH_{2n+2}[b]	18,000	16.700	....	....	13.000
	CCl_4	15.400	....	16,400	14.700	
Tol	C_nH_{2n+2}	....	11.800	....	....	15,000
	CCl_4	....	....	16.700	....	
Hm[b]	C_nH_{2n+2}	....	....	....	....	6.000
	CCl_4	....	....	8,200	6.690	

[a] The same experimental data were later analyzed by T. M. Cromwell and R. L. Scott, THIS JOURNAL, **72**, 3825 (1950), to give ϵ 14,000 for both solvents. [b] Either *n*-heptane or *n*-hexane.

The position of the CT band at low temperatures depended upon the glass. In the MP glass at low temperatures, the respective CT bands of the benzene and toluene complexes shifted slightly to 297 and 315 mμ compared with 288 and 299 mμ in heptane at room temperature. The visible band is at

[12] D. F. Evans, *J. Chem. Soc.*, 345 (1953).

[13] J. S. Ham, THIS JOURNAL, **76**, 3886 (1954).

about the same position for the benzene–iodine complex in the MP glass as in the MCH glass, although the low solubilities in the MP glass prevented an accurate study.

In the MCH glass, the complexes of iodine with partially methylated benzenes showed temperature shifts of the CT band at low temperature toward longer wave lengths, such that at low temperature its position became almost independent of the number of methyl groups. The olefin complexes showed a similar tendency. In hexamethylbenzene and tetramethylethylene, the CT bands were at longer wave lengths than for the less methylated compounds at all temperatures, although the temperature shifts in these cases were small. The ether and alcohol complexes, which are of a different classification type than the hydrocarbon complexes,[4] did not show a red shift upon cooling. The hexaethylbenzene complex, with a large blue shift, formed a special case which will be discussed later.

Figure 2 shows the absorption spectrum of the benzene–iodine complex in *n*-heptane at room temperature and in two rigid glasses at liquid nitrogen temperature. In determining ϵ, all of the iodine was assumed to be in the form of the complex at low temperatures.

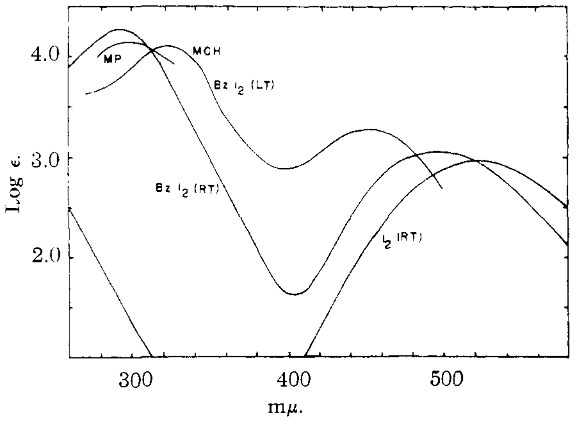


Fig. 2.—Molar extinction coefficients of the benzene–iodine complex at room temperature in *n*-heptane and in the MCH glass at low temperatures. The spectrum of the complex in the MP glass is shown only at the CT peak because the low solubility of the components in this glass prevented further spectra from being taken. Also shown is the absorption of iodine in *n*-heptane at room temperature.

Measurements of several complexes were taken also at intermediate temperatures. The data for the benzene and toluene complexes are shown in Figs. 3 and 4. In Fig. 3 (benzene complex) it is apparent that the large shift was really due to a new band appearing at longer wave lengths than the CT band that is found at room temperature. This new band became stronger as the temperature was lowered until it became dominant in the near ultraviolet spectrum at the lowest temperatures. It was not resolved clearly in Fig. 4 (toluene complex), although the shape of the absorption curve at 133°K. indicates that the same type of phenomenon was probably occurring here as for the benzene complex. The iodine was largely uncomplexed at the higher temperatures, resulting in a very small total absorption by the complex. For the other aromatic complexes, the shifts were too small compared with the width of the CT band for studies at intermediate temperatures to permit distinguishing between the appearance of a new band and a continuous shift. Some of the olefin complexes showed large shifts which are probably a similar new band (see Table II). The shifts discussed in this paragraph were not connected with the vitrification of the solvent, since they occurred at temperatures well above the freezing point.

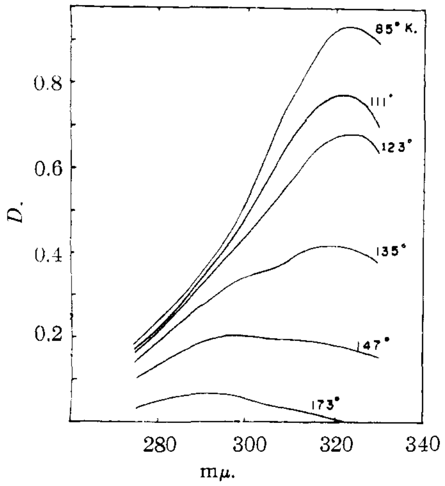


Fig. 3.—The optical density of iodine solutions at intermediate temperatures in the MCH glass containing a small amount of benzene. The background absorption of the cell and solvent are subtracted. At the highest temperatures shown, the CT band appears weakly at the same wave length where it appears at room temperature but, at temperatures below 147°K., a separate band arises near 320 mμ.

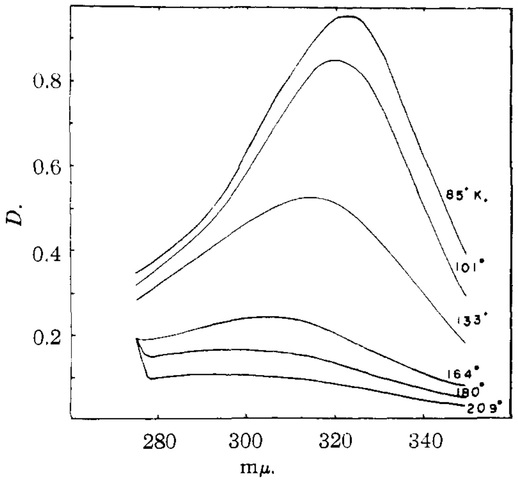


Fig. 4.—Same as Fig. 3 except with toluene instead of benzene. In this case, the two peaks are not resolved, but their existence may be inferred by the breadth of the band at intermediate temperatures.

Discussion of the Shifts in the Charge-transfer Band

One of the most striking things found at low temperature was the new band in complexes which appeared in the MCH glass at low temperatures but did not appear in the MP glass. The small shifts observed in the MP glass are probably similar to the shifts correlated with changes in the index of refraction, discussed in the following paper.[14] The glasses contract about 25% in going from room temperature to liquid nitrogen temperatures, which produces a large change in the index of refraction of the solvent. Shifts of 8 or 9 mμ are readily explained in terms of this effect.[14]

The new band observed in the MCH glass in the benzene and toluene complexes at low temperatures indicates that there is a different absorbing species at low temperatures than is present at room temperature in at least these two cases. This may conceivably be a multiple complex of several donor molecules with one iodine molecule, it may be an aggregation of several complexes, or it may be a solvent-assisted complex consisting of one or more methylcyclohexane molecules solvating the complex. The various possibilities are not easy to separate experimentally. Evidence of 2:1 complexes has been obtained in other types of complexes such as the nitroaromatic aniline[15] and the silver ion aromatic complexes.[16] But since variations of the benzene concentration over a fourfold range in the MP glass failed to show any effect upon the position of the CT band, the shift is probably not the result of 2:1 complex formation. It is difficult to see why an aggregation of complexes should take place in the MCH glass but not in the MP glass since the solubility of iodine and donor are much greater in the MCH glass and presumably the relative solubilities of the complex should be in the same order.

There remained the possibility that the MCH glass molecules solvated the complex. Although saturated hydrocarbons are usually considered to be quite inert, there is evidence that the cyclic ones, in particular, have some donor properties. Iodine forms a complex with cyclopropane which has a definite peak at 240 mμ at low temperatures.[7] At room temperature there is strongly increasing absorption of an iodine solution in *n*-heptane at 242 mμ as the heptane is replaced by cyclohexane. Using this increase in absorption, Hastings, *et al.*,[17] have deduced an equilibrium constant $K = 0.013$ (in liters/mole units) and $\epsilon_{\max}$ 19,000 for a cyclohexane–iodine complex. Even the iodine absorption appearing in normal paraffin solvents is not present down to 210 mμ in solutions of iodine in perfluoroheptane.[18] While this absorption might be attributable to a shift in the iodine N, V transition to the red in solutions with higher dielectric constant, it might also be due to CT transitions in very loose complexes of iodine with the normal paraffins, especially since the ionization potentials of saturated hydrocarbons predict that the CT band for the iodine complex should be in this region.[19]

Similar increases in absorption are found in the bromine vapor spectra in the same wave lengths region when various foreign gases are present.[20] It is not clear at present if these halogen absorptions near 230 mμ are CT transitions or perturbed halogen transitions. The electronic excitation corresponding to 230 mμ is almost as great as the excitation energy of the solvent, so that large interactions may occur. These interactions might result in unusual deviations from Beer's law.[21]

The CT band of the hexaethylbenzene complex showed the very large shift of 53 mμ to shorter wave lengths upon cooling. Measurements at intermediate temperatures indicated that the shifted band was a new band different from the CT absorption at room temperature. Only if there were 10% or more impurities in the donor could this shift have been due to impurities complexing with the iodine. The same possibilities exist in this case as discussed above, but there is also a possibility that here two types of 1:1 complexes are capable of formation because of the large steric effects of the ethyl groups, one of these being more stable at room temperature and the other more stable at low temperature. Just what these two types of complexes could be is not clear at present. To test this hypothesis, a series of heavily substituted benzenes were studied.

Hexamethylbenzene has a planar carbon skeleton and forms a very stable iodine complex.[22,23] By joining the adjacent substituents with saturated hydrocarbon chains of different lengths, models indicate that the planarity of the carbon skeleton should be decreased and the possible steric hindrance effect upon complexing should increase. The room temperature equilibrium constant for the hexaethylbenzene complex is anomalously small, presumably as the result of the ethyl groups sterically hindering complex formation.[22,23] The substituted benzene with three five-membered rings, tricyclopentenobenzene, is almost planar, but when an additional methylene group is added in each side ring to give *sym*-dodecahydrotriphenylene, a sizeable deviation from planarity should occur. While there was a slight red shift in the CT band of the hexamethylbenzene–iodine complex, and no shift in the slightly less planar molecule, there was a slight blue shift of the CT band of the dodecahydrotriphenylene–iodine complex upon cooling. In hexaethylbenzene, the bulky ethyl groups should create much more steric hindrance than in other cases, and here there was a remarkably large shift of the CT band to shorter wave lengths at low temperature. Studies of the complexes of the molecule containing three seven-membered side rings, trispentamethylenebenzene, should be interesting since this molecule should have steric effects almost as great as those of hexaethylbenzene. And, if the blue shifts are related to steric hindrance, the CT band of the iodine complex should shift to the blue by an amount almost as large as was observed in the hexaethylbenzene complex.

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(14) J. S. Ham, THIS JOURNAL, **76**, 3881 (1954).

(15) J. Landauer and H. McConnell, *ibid.*, **74**, 1221 (1952).

(16) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949).

(17) S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, *ibid.*, **75**, 2900 (1953).

(18) Unpublished data.

(19) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

(20) N. S. Bayliss and A. L. G. Rees, *Trans. Faraday Soc.*, **35**, 792 (1939).

(21) Another example of this type of effect may be the phenomena described by J. S. Ham, *J. Chem. Phys.*, **21**, 756 (1953).

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

(23) M. Tamres, D. R. Virzi and S. Searles, *ibid.*, **75**, 4358 (1953).

Conceivably of relevance to some of the phenomena reported above is the fact that, theoretically, more than one CT band may exist, resulting from the several possible ionization potentials of the donor. The splitting of the lowest ionization potential of toluene by the methyl group, however, was too small to produce a measurable broadening of the CT band. An example where two different types of donor electrons may give rise to two CT bands perhaps exists in some complexes between substituted anilines and chloranil (tetrachloro-*p*-benzoquinone), where two new bands are observed in the mixtures of the components.[24]

Unlike most complexes, the iodine complexes have the CT band well separated from the region of strong donor absorption. This permitted a considerable spectral region to be searched for higher frequency CT absorptions. For the tetramethylethylene–iodine complex, which has the CT peak very well separated from the donor absorption, a search was made from the CT band at 345 mμ down to 230 mμ at low temperatures. No new charge transfer band was found. The second ionization potential of tetramethylethylene, which is of a σ-type, has been calculated to be at 12.80 e.v.,[25] which would correspond to a CT absorption at much shorter wave lengths than 230 mμ. The first (π) ionization potential is at 8.52 e.v.[25]

The Shifts in the Visible Band

Figure 5 shows the heat of formation of the iodine complex plotted against the position of the visible absorption peak. There is a fairly good correlation between these two quantities indicating that the more stable the complex, the more the visible band shifts upon complexing.

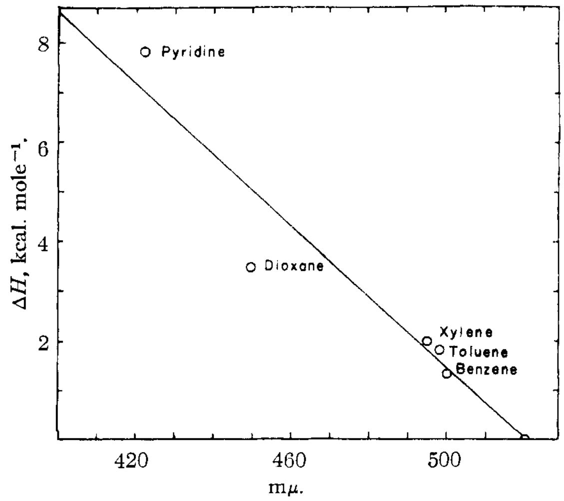

Fig. 5.—Heats of formation of iodine complexes *vs.* the visible absorption maxima of the iodine complexes at room temperature (see Tables I and III).

Why the visible band of iodine should shift to the blue upon complexing and shift even more when the solution is cooled, has never been adequately explained. Bayliss and Rees have attempted to explain the blue shift of the visible band of halogen solutions by assuming that the solvent molecules form a cage which compresses the interatomic distance of the halogen molecule in its ground state.[26] Using Franck–Condon arguments, Bayliss predicts the visible absorption to shift to shorter wave lengths upon compression. Prikhotko has applied this theory to explain the shift in the iodine visible spectrum at low temperatures.[5]

This theory is difficult to reconcile with several facts. The visible spectrum of iodine in heptane is not affected by increasing the pressure on the solution to 2000 atmospheres[14] although the internal pressures of solutions are of this same order of magnitude or smaller. In addition, the theory of Bayliss does not specifically take into account the 1:1 nature of the complexes.

In contrast to the cage theory of the shifts in the visible band, the charge transfer theory predicts a slight increase in the I–I bond distance when the iodine is in a complex.[4] This is because the transferred electron in the dative structure ($D^+ - I_2^-$) goes into the lowest unfilled orbital of the iodine molecule, which is an antibonding orbital. The antibonding character of this orbital tends to increase the bond distance in the ground state of the complex because the ground state contains a small admixture of dative structure wave function.

Both the visible and near infrared bands are observed to shift by about the same amount (3900 and 4300 kayser) in going from uncomplexed iodine to iodine in the ether complex at low temperatures.[13] The upper states of these two transitions have a common electronic configuration. This common electronic configuration includes an antibonding (σ) orbital as the excited molecular orbital. Complexing and cooling seem to affect the energy of this orbital by large amounts by some unknown mechanism.

If this is so, one would also expect a comparable blue shift of the N, V band near 190 mμ since the V state has the same excited molecular orbital. The smaller absorption of some complexes near 230 mμ than for free iodine in heptane[27,28] may be due to this blue shift of the N, V band; or, the smaller absorption of the complex at these wave lengths may be just the disappearance of the CT band of a weak complex between heptane and iodine (see above for a discussion of this possibility).

The author wishes to thank all those who helped make this work possible. Special thanks are due Prof. J. R. Platt who offered much assistance and encouragement, and to Prof. R. S. Mulliken who sponsored this research. The cyclically substituted benzenes were furnished by Prof. W. G. Brown and his group, who suggested their possible value in determining the role of steric effects in complexes.

WILMINGTON, DELAWARE

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