

[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO]

## Molecular Complexes and their Spectra. VIII. The Molecular Complex between Iodine and Triethylamine<sup>1</sup>

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The interaction between triethylamine and iodine in very dilute solutions in *n*-heptane was studied spectrophotometrically. (In more concentrated though still dilute solutions, a water-soluble precipitate was quickly formed and the solutions became decolorized.) A new band due to neither of the components was observed at 278  $m\mu$  for the mixed solutions. At the same time, it was found that the visible band of iodine, which appears at 520  $m\mu$  in *n*-heptane, was shifted to 414  $m\mu$ . These phenomena are attributed to the formation of a 1:1 charge-transfer complex, whose equilibrium constant ( $K_c$ ), heat of formation ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were determined. The results are:  $\Delta H = -12.0$  kcal./mole;  $\Delta S = -23.5$  e.u.;  $K_c = 4.69 \times 10^3$  or  $4.61 \times 10^3$  (units, l./mole) from the charge-transfer band at 278  $m\mu$  and the blue-shifted visible band, respectively. These values show that the present complex is the strongest among the iodine charge-transfer complexes whose thermochemical constants have hitherto been established. The molar extinction coefficient of the charge-transfer band was shown to be only slightly temperature-dependent; the band was slightly broadened and flattened with rising temperature as expected theoretically.

### Introduction

It is well known that pyridine can form a stable 1:1 complex with iodine.<sup>3</sup> The heat of formation of this complex has been determined as 7.8 and 7.98 kcal./mole by Reid and Mulliken<sup>3</sup> and by Hartley and Skinner,<sup>4</sup> respectively. These values are apparently larger than those for other iodine complexes whose thermochemical constants have hitherto been measured. Furthermore, Reid and Mulliken found that the visible band of iodine, which appears at 520  $m\mu$  in *n*-heptane, shows a remarkably large blue shift as the result of complex formation and that the charge transfer (abbreviated CT hereafter) absorption band characteristic of the complex appears at somewhat shorter wave lengths than the values predicted from the relations presented by McConnell, Ham and Platt<sup>5</sup> and by Hastings, *et al.*<sup>6</sup> In these connections, it seemed interesting to study some properties of iodine-aliphatic amine systems, because the latter molecules may be expected to be even stronger electron donors than pyridine. For this purpose, triethylamine-iodine was selected.<sup>7</sup>

The mixed solution of triethylamine and iodine even when dilute in *n*-heptane is not stable, but we succeeded in finding conditions under which it was stable enough to give reproducible experimental results and to permit measuring the CT band

characteristic of the 1:1 complex. Furthermore, by using this absorption, we could evaluate the exact value of the equilibrium constant and of the heat of formation of the complex.

Solutions with triethylamine concentrations higher than  $10^{-2}$  mole/l. became turbid and gave precipitation immediately after preparation; at the same time decolorization of the solution occurred. The precipitate is soluble in water, which suggests that it may be an ionic substance.<sup>3</sup> A similarly water-soluble precipitate ("compound I") has been reported<sup>9</sup> to be formed slowly when iodine is dissolved in  $\gamma$ -picoline; whereas when water is added to a fresh solution of iodine in  $\gamma$ -picoline, a water-insoluble precipitate ("compound II"), soluble in organic solvents, is formed. Stoichiometrically, the picoline-iodine ratio is 2:1 in compound I and 1:1 in compound II. A water-insoluble 1:1 pyridine-iodine compound analogous to II is well known. Glusker and Miller<sup>9</sup> have examined both picoline-iodine compounds by X-ray radial distribution methods. Compound II shows covalent I-I bonds, compound I does not. They conclude that the latter solid has an ionic structure ( $Pc_2I^+$ ) $I^-$  but that the former is a  $Pc \cdot I_2$  complex presumably essentially similar in structure to the  $Pc \cdot I_2$  and  $Py \cdot I_2$  complexes<sup>3</sup> whose infrared and optical spectra have been studied in solution. From the foregoing one may infer that, although the first step in the interaction of  $I_2$  with amines is the formation of a non-ionic 1:1 CT complex, the latter may go over, more and more rapidly with increasing base strength [ $Et_3N(>NH_3)>Pc>Py$ ], to an ionic compound.

### Experimental

**Purification of Materials.**—J. T. Baker resublimed iodine was purified by subliming again under a nitrogen atmosphere and was kept in a desiccator with  $P_2O_5$ . Triethylamine and *n*-heptane were purified by the same method as described in a previous paper.<sup>10</sup> The reason we preferred triethylamine to trimethylamine as electron donor is that the former is liquid at room temperature and so is more convenient to handle.

**Methods.**—A Beckman quartz spectrophotometer and a Warren self-recording spectrophotometer whose wave length

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(3) C. Reid and R. S. Mulliken, *THIS JOURNAL*, **76**, 3869 (1954). Many other references on this complex can be found in this paper.

(4) K. Hartley and H. A. Skinner, *Trans. Faraday Soc.*, **26**, 621 (1950).

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

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

(7) At the 1955 Amsterdam International Conference on Coordination Compounds, Professor Mulliken learned of the following related work. (a) According to Professor L. J. Oosterhoff, Hantzsch in 1905 obtained crystals of a 1:1 complex of  $Br_2$  and of  $I_2$  with  $Me_3N$  (trimethylamine). Some years ago Mrs. Oosterhoff made some studies, and more recently studies on  $Me_3N \cdot I_2$  have been made in Oosterhoff's laboratory, indicating it to be like  $Py \cdot I_2$ . (b) Professor L. d'Or of Liege reported studies in his laboratory of  $I_2$  complexes with triethylamine, piperidine, thiophene and cyclohexene which disclosed ultraviolet presumably CT spectra agreeing fairly well with the formula of ref. 5.

(8) The mechanism of a similar reaction between ammonia and iodine has been studied by McAlpine.

(9) D. L. Glusker and A. Miller, *J. Chem. Phys.*, **26**, 331 (1957).

(10) S. Nagakura and M. Gouterman, *ibid.*, **26**, 881 (1957).

scale in the ultraviolet region was calibrated by using well-known absorption bands of benzene in heptane were used for measuring absorption spectra. In both instruments, the temperature of the absorption cell was kept constant during the measurements by using the thermospacer through which water of constant temperature was circulating. The quartz cell with a glass stopper ( $10 \pm 0.01$  mm. light path) was employed for the measurement in all wave length regions. In some cases, the glass cell with  $100 \pm 0.02$  mm. light path was also used for the measurements in the visible region. To minimize the effect of hydration upon the experimental results, the volumetric flasks, pipets and absorption cells were flushed with a jet of dry nitrogen (with a dew point below  $-20^\circ$ ) which was obtained from the Linde Air Products Company, and triethylamine was distilled from potassium hydroxide as drying agent immediately before preparing the solutions.

As has been mentioned, precipitation and decolorization occur rapidly in mixed solutions of triethylamine and iodine in *n*-heptane at triethylamine concentrations in excess of 0.01 mole/l. To avoid this unwanted side reaction, we used very dilute solutions with concentrations of the order of  $10^{-5}$  mole/l. of iodine and below  $10^{-2}$  mole/l. of triethylamine. Further, we found that the velocity of the side reaction was considerably slower in a quartz container than in a glass one. Hence, we removed the solution into the quartz cell, immediately after preparation in the glass flask. In every case, we finished the measurement within an hour after preparation of the mixed solution, although the absorption was found to remain almost constant during 2 or 3 hr.

### Results and Discussion

**Equilibrium between Triethylamine and Iodine in *n*-Heptane.**—Iodine has an absorption maximum at  $520 \text{ m}\mu$  in *n*-heptane, but its absorbance is very small in the wave length region from  $450$  to  $260 \text{ m}\mu$ . The absorption of triethylamine in this wave length region is also negligibly small. On the other hand, the situation is very different for the mixed solution of these two substances in the same solvent. As is easily seen from Fig. 1, where the ab-

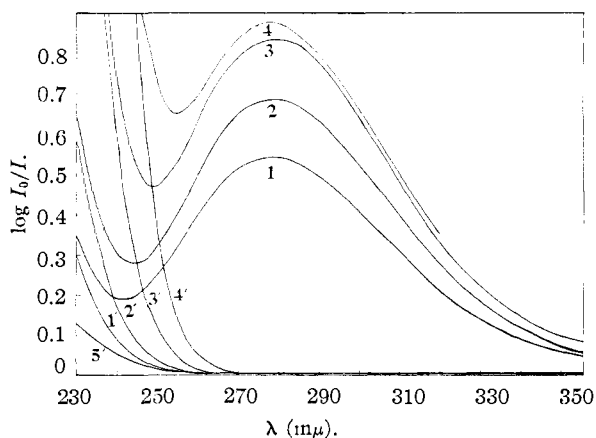


Fig. 1.—The near ultraviolet absorption measured at  $25^\circ$  with the mixed solution of triethylamine and iodine in *n*-heptane. The concentration of iodine is  $3.64 \times 10^{-5}$  mole/l. The concentrations of triethylamine are  $2.95 \times 10^{-4}$ ,  $5.90 \times 10^{-4}$ ,  $1.965 \times 10^{-3}$  and  $5.90 \times 10^{-3}$  for curves 1, 2, 3 and 4, respectively. Curves 1', 2', 3' and 4' are the absorption for the pure triethylamine solution with the concentration corresponding to curves 1, 2, 3 and 4, respectively. The curve 5' is for the pure iodine solution. The light path was 10 mm. in all cases.

sorption spectra of mixed solutions with a fixed concentration of iodine and varying concentrations of triethylamine are given, a new absorption maxi-

mum due to neither electron donor nor acceptor appears at  $278 \text{ m}\mu$ . This new band increases in intensity with the concentration of triethylamine. Furthermore, the absorbance of this band observed with the same solution decreases strongly as the temperature is increased (see Fig. 2). These facts can qualitatively be understood by regarding this new band as the CT absorption characteristic of the complex.<sup>11</sup>

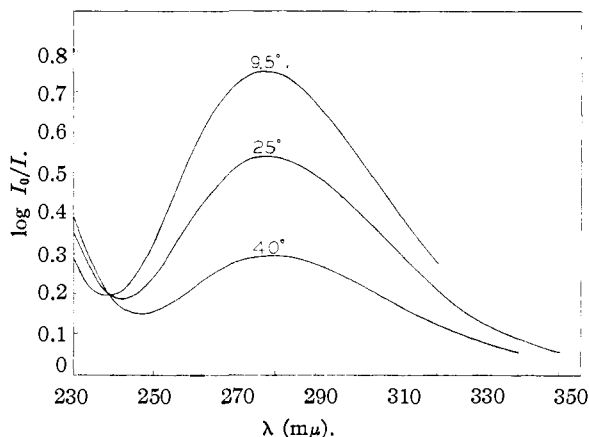


Fig. 2.—The temperature dependence of the near ultraviolet absorption of the mixed solution of triethylamine and iodine. The concentrations of iodine and triethylamine are  $3.64 \times 10^{-5}$  mole/l. and  $2.95 \times 10^{-4}$  mole/l., respectively; 10 mm. light path.

Parallel with the appearance of the CT absorption at  $278 \text{ m}\mu$ , a big change occurs in the visible band of iodine. As shown in Fig. 3, the band at  $520 \text{ m}\mu$  decreases in intensity with increasing con-

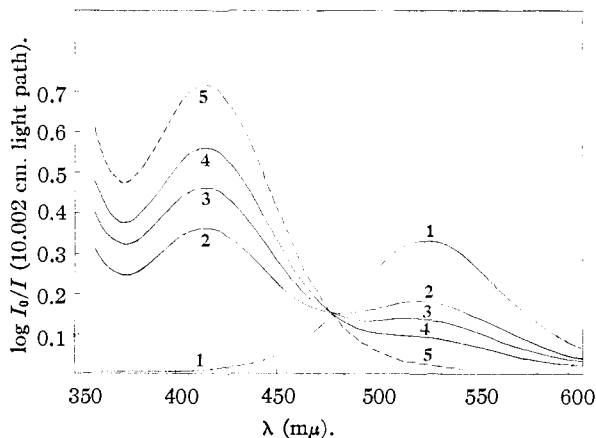


Fig. 3.—The visible band of the mixed solution. The concentration of iodine is  $3.55 \times 10^{-5}$  mole/l. The concentrations of triethylamine are 0,  $1.95 \times 10^{-4}$ ,  $3.90 \times 10^{-4}$  and  $7.80 \times 10^{-4}$  mole/l. for the curves 1, 2, 3 and 4, respectively. Curve 5 is for the absorption due solely to the complexed iodine molecule.

centration of triethylamine, and at the same time a new band at  $414 \text{ m}\mu$  becomes gradually predominant; and there is an isosbestic point where the absorption curves for different solutions with a fixed concentration of iodine cross each other. This

(11) R. S. Mulliken, *THIS JOURNAL*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

seems to mean that the 414  $m\mu$  band is due to a 1:1 complex formed by the iodine molecule with triethylamine and that in the mixed solution this is in equilibrium with free iodine and triethylamine.

As the first step in a quantitative consideration, the relation between  $1/C_D$  and  $C_A/k$  for the CT band (where  $C_D$ ,  $C_A$  and  $k$  are, respectively, the initial concentrations of triethylamine and of iodine and the absorbance value of the CT band measured with the mixed solution) was checked by Benesi and Hildebrand's method.<sup>12</sup> The results are shown in Fig. 4. From this figure, it is seen that a straight

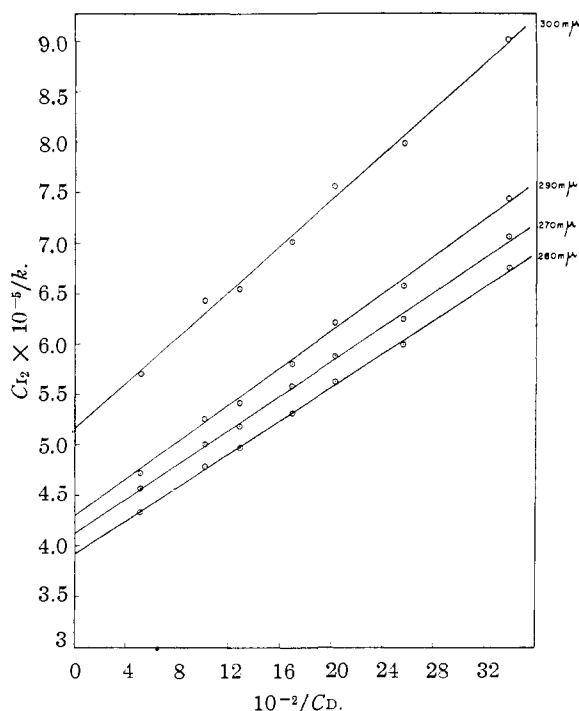


Fig. 4.—The relation between  $C_{I_2}/k$  and  $1/C_D$  (at 25°).

line relationship is completely satisfied between  $1/C_D$  and  $C_A/k$ . Then, by following the usual procedure,<sup>12</sup> we could evaluate the molar extinction coefficient of the CT band and the equilibrium constant ( $K_c$ ) for complex formation (in liters/mole). The results are given in Table I.

TABLE I  
EQUILIBRIUM CONSTANT ( $K_c$ ) AND MOLAR EXTINCTION COEFFICIENT ( $\epsilon$ ) OF THE CT BAND EVALUATED BY BENESI AND HILDEBRAND'S METHOD (AT 25°)

Wave length ( $m\mu$ )	$K_c \times 10^{-3}$	$\epsilon \times 10^{-4}$
300	4.59	1.94
290	4.62	2.35
280	4.71	2.56
270	4.80	2.43

Av. value of  $K_c$ :  $4.68 \times 10^3$

We also have used another method for evaluating the equilibrium constant from the CT band, *viz.*, the method which was applied successfully to some hydrogen-bonded systems.<sup>10,13</sup> According

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

(13) S. Nagakura, *ibid.*, **76**, 3070 (1954).

to this, the equilibrium constant ( $K_c$ ) can be determined by the use of the equation

$$K_c = [C_D(k_0 - k') + C'_D(k - k_0)]/[C_D C'_D(k' - k)] \quad (1)$$

where  $k_0$ ,  $k$  and  $k'$  are the absorbances, measured at a fixed wave length, with solutions whose concentrations of iodine are equal and whose concentrations of triethylamine are 0,  $C_D$ , and  $C'_D$ , respectively. This method has advantage in that the effect of superposed absorption belonging to either of the components (in this case, iodine) is considered explicitly in the equation. The reason for this is clear from the fact that eq. 1 can be derived from the relations under the assumption described in ref. 10:

$$K_c = C_C/[(C_D - C_C)(C_A - C_C)] = C'_C/[(C'_D - C'_C)(C_A - C'_C)] = [C_C C'_D - C'_C C_D]/[(C'_C - C_C)C_D C'_D]$$

$$k = C_C(\epsilon - \epsilon_A) + k_0; k' = C'_C(\epsilon - \epsilon_A) + k_0$$

where  $C_C$  and  $C'_C$  are concentrations of the complex in solutions whose concentrations of triethylamine are  $C_D$  and  $C'_D$ , respectively, and  $\epsilon$  and  $\epsilon_A$  are molar extinction coefficients of the complex and iodine, respectively. Another advantage of this method is that the equilibrium constant can be obtained independently of the molar extinction coefficient ( $\epsilon$ ).<sup>14</sup> The values of  $K_c$  at 25° evaluated with the aid of eq. 1 are shown in Table IIb. Comparing Tables I and IIb, the  $K_c$  values obtained by the two methods are seen to be in good agreement. We employed only the second method for further determination of  $K_c$  at different temperatures. The results are shown in Table II.

TABLE II  
EQUILIBRIUM CONSTANTS ( $K_c$ ) AT DIFFERENT TEMPERATURES EVALUATED BY EQ. 2

	$\lambda(m\mu)$	$K_c \times 10^{-3}$	
(a) At 20.5°	300	6.10	
	290	6.19	
	280	6.47	
	270	6.50	Av. $6.32 \times 10^3$
(b) At 25.0°	300	4.62	
	290	4.61	
	280	4.71	
	270	4.80	Av. $4.69 \times 10^3$
(c) At 30.0°	300	3.41	
	290	3.22	
	280	3.32	
	270	3.28	Av. $3.31 \times 10^3$
(d) At 40.0°	300	1.85	
	290	1.75	
	280	1.66	
	270	1.71	Av. $1.74 \times 10^3$

Further, by the use of the data given in Table II, we can plot the relation between  $R \ln K_c$  and  $1/T$  as shown in Fig. 5. Then drawing a straight line to fit all points as well as possible (actually by the use of the least squares method), the heat of formation ( $\Delta H$ ) and entropy change ( $\Delta S$ ) can be obtained from its slope and its intersection with the

(14) According to Benesi and Hildebrand's method,  $1/\epsilon$  and  $1/K_c\epsilon$  are respectively obtained from the intersection of the straight line in Fig. 4 with the abscissa and from its slope. Therefore, the evaluated  $K_c$  value is very sensitive to  $\epsilon$ .

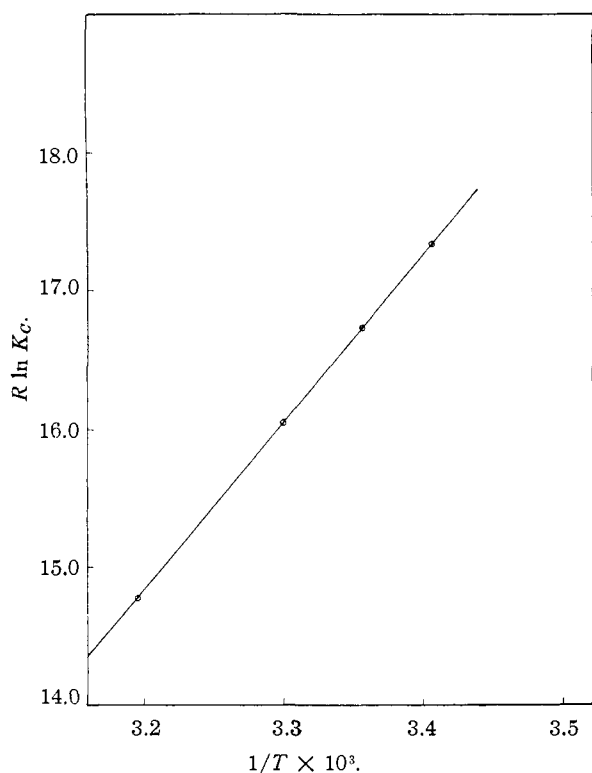


Fig. 5.—The relation between  $R \ln K_c$  and  $1/T$ .

abscissa, respectively.  $\Delta H$  and  $\Delta S$  obtained thus are  $-12.0$  kcal./mole and  $-23.5$  e.u., respectively. From a comparison of these values with the corresponding values in the case of the pyridine-iodine complex, it is concluded that triethylamine can form a more stable complex than pyridine. Therefore, it may be expected that the contribution of the dative configuration in the normal state of the present complex is larger than for the pyridine-iodine complex, for which Reid and Mulliken suggested 25% as a plausible estimate. In this connection, it may be interesting to measure the dipole moment and the infrared absorption spectrum for the present system, because the expected big charge transfer in the normal state may conceivably exert a remarkable effect upon these two properties. The experimental result obtained by Tsubomura and the present author shows that the  $R_3N \cdot I_2$  complex has a large dipole moment of  $11.3 D$ . It seems evident from this value that the magnitude of charge transfer in the complex is undoubtedly larger than 50% and probably amounts to 60%.<sup>15</sup>

According to results obtained by Autrey and Connick and by Buckles, *et al.*, the  $I_3^-$  ion has absorption maxima at  $365$  and  $295 m\mu$ .<sup>16</sup> Thus if any  $I_3^-$  is present, superposition of its shorter wave length band on the  $R_3N \cdot I_2$  CT absorption should cause an error in the above quantitative considerations. Under our experimental conditions, however, we did not find any absorption

(15) H. Tsubomura and S. Nagakura, *J. Chem. Phys.*, **27**, 819 (1957).

(16) A. D. Autrey and R. E. Connick, *THIS JOURNAL*, **73**, 1842 (1951); R. E. Buckles, J. P. Yuk and A. I. Popov, *ibid.*, **74**, 4379 (1952).

maximum near  $365 m\mu$  and, moreover, the absorbance at this wave length is small (see Figs. 1 and 3). This seems to mean that the concentration of  $I_3^-$  in the mixed solution is very small and that the effect of the ion upon the evaluated equilibrium constant value is not serious. Further support for this argument is given by the agreement in  $K_c$  values from both the CT absorption and the blue-shifted visible band of iodine which will be described in the following section. But the slight change of  $K_c$  with wave length (see Table II) may be due to the existence of a small amount of  $I_3^-$ .

Let us now turn to a second determination of the equilibrium constant from the visible iodine band of the complex. This band has been used for the determination of  $K_c$  for some complexes, for instance, iodine complexes with pyridine,<sup>8</sup> pyridine N-oxide and its derivatives.<sup>17</sup> In these cases  $K_c$  could not be obtained from the CT absorption band, because the latter overlapped the absorption of the electron donor itself. For the present system, however,  $K_c$  could be determined with high accuracy both from the CT and the visible band. The value obtained from the latter by using eq. 1 was  $4.61 \times 10^3$  at  $25^\circ$ . This value is very close to that evaluated from the CT band ( $4.69 \times 10^3$  or  $4.68 \times 10^3$ ) as given above in Tables I and II.

**Position of the CT Absorption Band of the Triethylamine-Iodine System.**—The CT absorption band of the complex at  $25^\circ$  is depicted in Fig. 6.

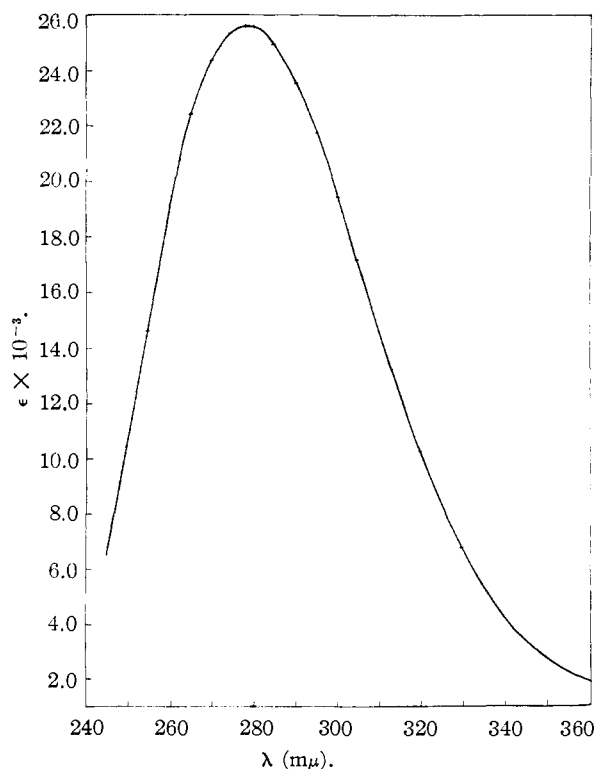


Fig. 6.—The CT absorption band (at  $25^\circ$ ).

Its maximum is at  $278 m\mu$ . The molar extinction coefficients necessary in drawing this figure were

(17) T. Kubota, private communication.

evaluated by using the average value of  $K_c$  given in Table II in connection with the absorption spectra (Fig. 1) of mixed solutions with known initial concentrations of both components.

It is known that the position of any CT absorption band can in many cases be predicted well from ionization potential ( $I_D$ ) of the donor using semi-empirical relations given by McConnell, Ham and Platt<sup>5</sup> or by Hastings, Franklin, Schiller and Matzen.<sup>6</sup> In the present case, using the observed  $I_D$  of 7.50 e.v.,<sup>18</sup> these relations give (for an iodine complex), respectively, 3.12 e.v. and 3.75 e.v., as compared with the observed value of 4.44 e.v. (278  $m\mu$ ). However, the value  $I_D = 7.50$  e.v. is an adiabatic one, and Watanabe's data indicate that in ammonia and the aliphatic amines the vertical  $I_D$  is considerably larger. Since theoretical considerations indicate that a vertical value or even a somewhat larger value of  $I_D$  would be appropriate in CT complex formation by aliphatic amines,<sup>19</sup> perhaps a value of 8.0 or even 8.5 e.v. similar to the mass-spectroscopic value<sup>20</sup> would be suitable for  $I_D$  here. With  $I_D = 8.5$  e.v., the MHP and HFMS equations predict 3.80 and 3.85 e.v., respectively, which still are considerably lower than the observed value. Similar discrepancies have been found for the iodine complexes with pyridine<sup>3,21</sup> and with pyridine N-oxide or its derivatives.<sup>17</sup>

From the foregoing examples, it appears likely that the MHP and HFMS iodine-complex equations no longer hold very well and give too small predicted frequencies, for very strong complexes. However, this is not surprising since, as Mulliken has strongly emphasized,<sup>22</sup> no theoretical reason is apparent why the empirical parameters appearing in these equations even for a particular acceptor should be at all constant except for closely related group of donors.

**Molar Extinction Coefficient of the CT Absorption.**—The observed value of the molar extinction coefficient of the CT band at its maximum (278  $m\mu$ ) is  $2.42 \times 10^3$ ,  $2.45 \times 10^3$ ,  $2.56 \times 10^3$  and  $2.56 \times 10^3$  at 40.0, 30.0, 25.0 and 20.5°, respectively. From these values it is seen that the molar extinction coefficient decreases as the temperature becomes higher. However, its decrease in passing from 20.5 to 40.0° is only 5.5% and may be explained by an expected temperature broadening of the band. The molar extinction coefficient at 330  $m\mu$  is 6630 and 6270 at 40.0 and 20.5°, respectively. Thus, the order at this wave length is the reverse of that at 278  $m\mu$ . This fact shows that

(18) K. Watanabe, photoionization: private communication.

(19) For example, in  $R_3N \cdot BCl_3$ , the RNR angles should be approximately tetrahedral, hence somewhat smaller than in free  $R_3N$ , whereas in the free  $R_3N^+$  ion, they should be larger, perhaps even 120° (planar ion). In a strong complex  $R_3N \cdot I_2$ , they should be intermediate between those in  $R_3N \cdot BCl_3$  and those in free  $R_3N$ . (Private communication from Professor R. S. Mulliken.)

(20) Professor Higasi at Hokkaido University (private communication) finds 8.88 e.v. for trimethylamine, as compared with Watanabe's photoionization value 7.82 e.v. (*J. Chem. Phys.*, **26**, 542 (1957)).

(21) It should be noted that Watanabe's value (in ref. 20) for pyridine is 9.23 e.v., whereas a mass-spectroscopic value of 9.8 e.v. was used in ref. 3. However, it is likely that 9.23 e.v. represents  $\pi$ -electron ionization and that the lone-pair  $I_D$  needed for the  $Py \cdot I_2$  complex is higher. In any event the discrepancy remains.

(22) R. S. Mulliken, *Rec. trav. chim. Pays-Bas*, **75**, 815 (1956).

the CT band becomes broader with increasing temperature. It is expected theoretically that the total integrated area, or  $f$  value, of the band may be nearly independent of temperature. From the above mentioned fact it is inferred that the assumption of the temperature independence of the peak molar extinction coefficient, which has been employed by several authors for determining the heat of formation of some CT complexes,<sup>23</sup> is not far from being correct if the measurements are made in a narrow range of temperature, e.g. 20–40°.

**Blue Shift of the Visible Band of Iodine Caused by Complex Formation.**—As mentioned above, the magnitude of the blue shift of the visible iodine band from free iodine to the iodine-triethylamine complex is large enough to permit the accurate determination of the equilibrium constant. Let us consider the mechanism of this blue shift. This problem already has been discussed by Mulliken.<sup>22</sup> His explanation is that the  $\sigma_u$ MO of iodine, which is the excited orbital for the visible band under consideration, produces a strong non-bonded repulsion toward amine partner in complex formation, because of its big size.

A similar explanation can be given from the present writer's LCMO approximation. According to this method, the CT attraction originates from the interaction between the above mentioned  $\sigma_u$ MO and the non-bonding orbital on the nitrogen atom of triethylamine. As the result of this interaction, the former orbital becomes higher in energy (and the latter lower). Thus the visible band of iodine is shifted toward shorter wave lengths, assuming that the energy of the  $\pi_g$ MO, the lower orbital corresponding to the visible band of iodine, is not appreciably changed by the triethylamine partner in the complex. It may be conceivable that triethylamine approaches an iodine molecule in such a manner that the interactions between the  $\pi_g$ MO of the latter and the filled orbitals of the former become as small as possible, because these interactions would result in a repulsive force.

Curve 5 in Fig. 3 represents the visible absorption band of the complexed iodine molecule as obtained from the equilibrium constant and the absorption curves 1 and 3 in the same figure. As easily seen from this figure, the intensity of the visible band of iodine is undoubtedly larger for the complexed than for the free molecule (a similar effect is found for the  $Py \cdot I_2$  complex)<sup>3</sup>. Unfortunately, in the wave length region of 350 to 450  $m\mu$ , some CT absorption is superposed on the visible band under consideration, so it is difficult to treat this increase quantitatively.

**Acknowledgments.**—The author wishes to express his sincere thanks to Professor Mulliken for his kindness in reading and suggesting changes in the manuscript and in other helpful discussions and suggestions. His thanks are also due to Professor Platt and other members of the laboratory for the hospitality shown during his stay at Chicago.

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(23) T. M. Cromwell and R. L. Scott, *THIS JOURNAL*, **72**, 3825 (1950); W. G. Barb, *Trans. Faraday Soc.*, **49**, 143 (1953); A. Kuboyama and S. Nagakura, *THIS JOURNAL*, **77**, 2644 (1955).