Charge-transfer Complexes between Iodine and Various Aliphatic Amines

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In 1949 Benesi and Hildebrand[1] found an absorption band characteristic of the iodine complex with benzene. They demonstrated that this absorption band belongs to neither of the component molecules but is due to the interaction between them. Mulliken[2] succeeded in interpreting it as the intermolecular charge-transfer absorption, namely, the absorption inherent to the charge-transfer complex caused by the interaction between an electron donor and an electron acceptor. Since that time complexes of this kind consisting of various combinations of electron donors and acceptors have been studied from both experimental and theoretical points of view[3,4]. Especially, the complexes containing iodine as electron acceptor have been investigated extensively by many authors[3-7].

Nagakura[8] studied spectroscopically the complex between triethylamine and iodine in *n*-heptane. He concluded that the system does not exist as the ammonium salt like $(R_3IN)^+I^-$ but does as the charge-transfer complex represented by the resonance hybrid between the no-bond structure, $R_3N\cdots\cdots I_2$ and the dative (charge-transfer) structure, $R_3N^+-I_2^-$, and also showed that this complex is the most stable among the iodine complexes studied so far, as is seen from its great heat of formation of 12.0 kcal./mol. Further, Nagakura and Tsubomura[9] determined the dipole moment of this complex to be 11.3D in dioxane solution. This fact is conceivably interesting in showing that the contribution of the dative structure amounts to or probably exceeds 50% for this complex and that the complex may be regarded as an intermediate stage for the ammonium salt formation process shown as follows: $R_3N+I_2\rightarrow R_3IN^++I^-$. In fact it has been observed that the complex is easily converted into the corresponding ammonium salt when a slight amount of moisture is present.

In the present paper, the above-mentioned study is extended to iodine complexes with aliphatic amines other than triethylamine. The electron donors used in the present study are ammonia, methylamine, ethylamine, *n*-butylamine, dimetylamine, trimethylamine, tri-*n*-propylamine, tri-*n*-butylamine and piperidine. One of our principal purposes is to discuss the relation between the stability of the complexes and the structures of amine molecules as electron donors, special attention being concentrated on the effect of the alkyl group upon the electron donating power and steric repulsion of various amines. Another principal purpose is to obtain accurate and profound knowledge concerning the spectroscopic properties of the amine-iodine complexes. This is useful for discussing the mechanism of the complex formation.

Experimental

Purification of Materials.—Commercial iodine of G. P. grade was sublimed first with calcium oxide and potassium iodide, and sublimed again under nitrogen atmosphere. It was kept in a desiccator with phosphorus pentoxide as a drying agent. *n*-Heptane of Enjay Co. was shaken with sulfuric acid, dried with calcium chloride and sodium metal successively, and distilled with a distilling column of 60 plates made by Tokyo Kagaku Seiki Co.

1) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
2) R. S. Mulliken, ibid, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).
3) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).
4) S. P. McGlynn, ibid., **58**, 1113 (1958).
5) T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **80**, 578 (1959).
6) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954).
7) S. Aono, *Prog. Theor. Phys.*, **20**, 133 (1958).
8) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).
9) S. Nagakura and H. Tsubomura, *J. Chem. Phys.*, **27**, 819 (1957).

Ammonia generated from its aqueous solution by adding concentrated aqueous alkali was liquefied by coolng with dry ice and acetone mixture and dried with a piece of sodium metal. The dry ammonia thus obtained was led into *n*-heptane to prepare the stock solution. This stock solution was diluted to a desired concentration immediately before use. Methylamine, ethylamine, dimethylamine and trimethylamine were purified by distilling at low temperatures with activated alumina immediately before use for spectrophotometric measurements. The concentrations of ammonia, methylamine, dimethylamine and trimethylamine were determined by titration. *n*-Butylamine, diethylamine and piperidine were distilled twice with activated alumina to remove a trace of water. Tri-*n*-propylamine and tri-*n*-butylamine were shaken with acetic anhydride to remove primary and secondary amines contained as impurities, dried with activated alumina and then distilled twice under reduced pressure.

Method. — A Cary recording spectrophotometer Model 14 was used for measuring absorption spectra. The temperature of the absorption cell was kept constant during the measurements by using the thermospacer through which water of constant temperature was circulating. A quartz cell with a glass stopper (10 ± 0.01 mm. light path) was used for the measurements in the ultraviolet region and a quartz cell with 100 ± 0.2 mm. light path was also used for the measurements in the visible region. In the present experiments, the concentrations of iodine and aliphatic amines were taken as low as possible. The actual values of the concentration were in the order of 10^{-5} and $10^{-3}\sim10^{-4}$ mol./l. for iodine and aliphatic amines, respectively. Under these conditions, the mixed solutions of iodine and amines were proved spectroscopically to exist in stable equilibrium for several hours. For the system of iodine and ammonia, however, the donor concentration amounted to the order of 10^{-2} mol./l., since the equilibrium constant for this system was rather small compared with those the other systems[10]. In this case the shape of the shifted visible band of iodine, which was used for the calculation of equilibrium constants in this case, was observed to be slightly dependent on the donor concentration. It was evident, however, that the effect was not so great as to affect the calculated equilibrium constants. Special care was taken to get rid of moisture in the procedure of preparing the mixed solutions, since even the existence of a slight amount of water is supposed to produce the I_3^- ion whose strong absorption peaks appear in the vicinity of the two kinds of absorption bands, namely the charge-transfer band and the shifted visible band of iodine.

Results and Discussion

Generally speaking, all the amine-iodine complexes under present consideration show the same spectroscopic features as the triethylamine–iodine complex described in the previous paper does[8]. Some typical examples of the absorption spectra measured in the present study are shown in Figs. 1—4. As is revealed from these figures, the absorption spectra of the iodine–amine systems commonly show two characteristic bands at 410~430 mμ and 230~280 mμ wavelength regions. By comparison with the iodine–triethylamine system reported in the previous paper[8], it is evident that the shorter and longer wavelength bands are respectively the charge-transfer band and the blue-shifted one of the visible band of iodine which ordinarily appears at 520 mμ in *n*-heptane. The maximum wavelengths (λ_{CT}, λ_{vis}) of these two kinds of absorption bands are given in Table I, together with the peak intensity (ε_{CT}) for the charge-transfer band. Further, from the analysis of these spectroscopic data, it was concluded that all the electron donors under consideration form stable 1 : 1 complexes with iodine in *n*-heptane. Since the details of the analytical method was described in the previous paper[8], it seems tedious to repeat

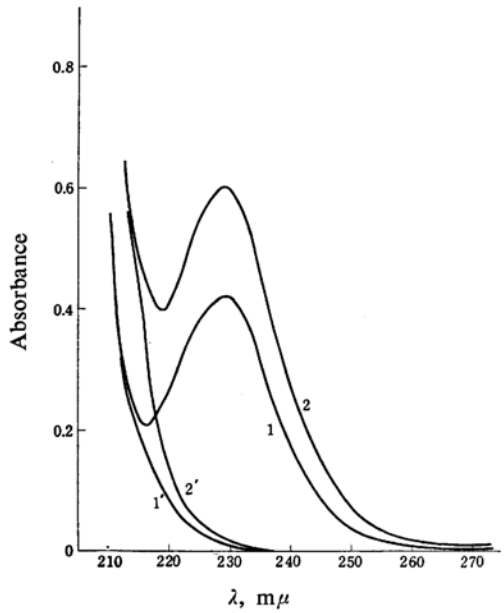

Fig. 1. The near ultraviolet absorption measured at 20°C with mixed solution of ammonia and iodine in *n*-heptane. The concentration of iodine is 7.35×10^{-5} mol./l. The concentrations of ammonia are 5.70×10^{-3} and 1.14×10^{-2} mol./. for curves 1 and 2, respectively. Curves 1′ and 2′ are the absorption curves for the pure ammonia solutions with the concentrations corresponding to curves 1 and 2, respectively. The iodine solution of 7.35×10^{-5} was used as reference with the measurement of curves 1 and 2. The light path was 10 mm. in all cases.

10) With the amine concentration over this limit value the shape of the two bands apparently changed and their peaks seemed to shift towards longer and shorter wavelengths for the charge-transfer band and the shifted visible band of iodine respectively. This phenomenon is the same as that observed by Reid and Mulliken in the case of pyridine-iodine system. In this case it is likely that complicated phenomena other than 1 : 1 equilibrium occur.

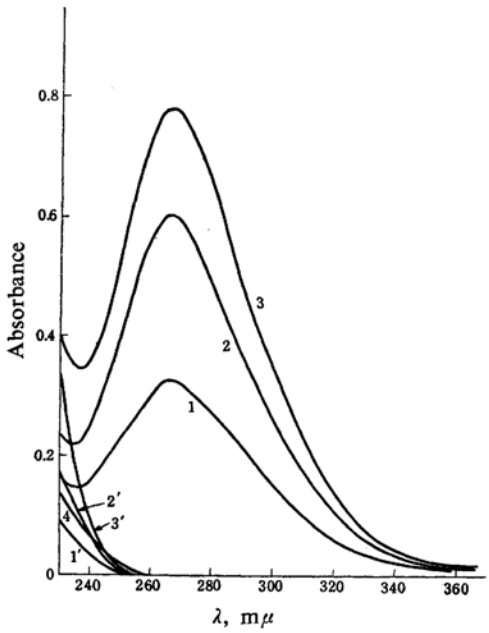

Fig. 2. The near ultraviolet absorption measured at 20°C with the mixed solution of trimethylamine and iodine. The concentration of iodine is 3.00×10^{-5} mol./l. The concentrations of trimethylamine are 2.04×10^{-4}, 4.08×10^{-4} and 7.45×10^{-4} mol./l. for curves 1, 2 and 3, respectively. Curves 1', 2' and 3' are the absorptions for the pure trimethylamine solutions with the concentrations corresponding to curves 1, 2 and 3, respectively. Curve 4 is for the pure iodine solution. The light path was 10 mm. in all cases.

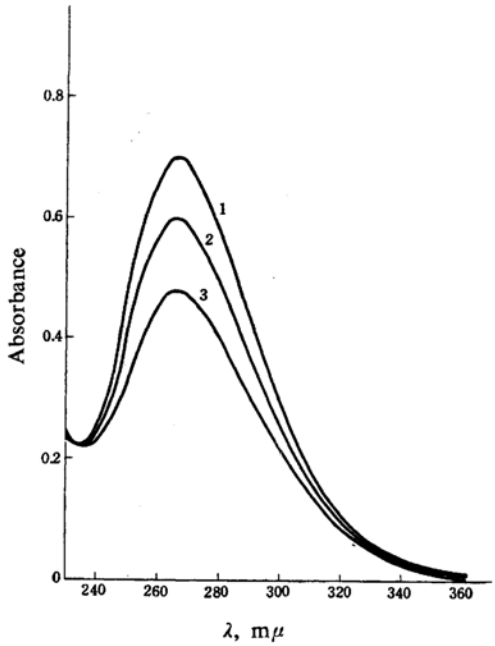

Fig. 3. The temperature dependency of the near ultraviolet absorption of the mixed solution of trimethylamine and iodine. The concentrations of iodine and trimethylamine are 3.00×10^{-5} and 4.08×10^{-4} mol./l., respectively. 10 mm. light path.

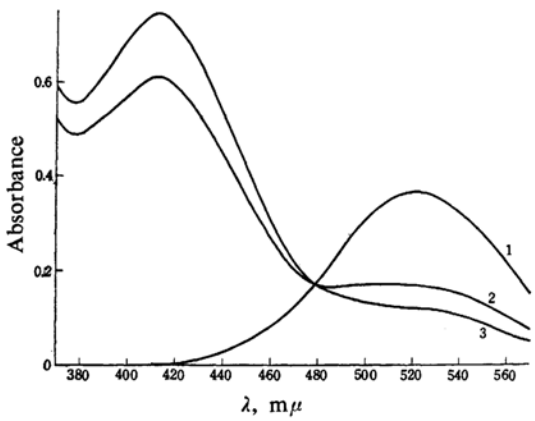

Fig. 4. The visible band of the mixed solution of tri-*n*-butylamine and iodine. The concentration of iodine is 3.97×10^{-5} mol./l. The concentrations of tri-*n*-butylamine are 0, 8.34×10^{-4} and 1.294×10^{-3} mol./l. for the curves 1, 2 and 3, respectively. 100 mm. light path.

here an account of it. Hence, our description on the evaluation of the equilibrium constants (K) will be made only in brief.

The actual evaluation of K was made by the two following methods; one is Benesi and Hildebrand's method and the other is the method which was applied successfully to some hydrogen-bonded systems and also to the triethylamine–iodine system[8,11]. Fig. 5 shows that Benesi and Hildebrand relation is satisfied for the systems under consideration. The K values obtained by these two methods were in complete agreement with each other within the range of experimental errors. For most of the systems under consideration, both the charge-transfer band and the shifted iodine visibie band were used for the evaluation of K. However, for the system containing ammonia or methylamine as the electron donor, K was evaluated from the blue-shifted iodine band alone. This is because the charge-transfer bands of these two systems, which appeared at shorter wavelengths compared with those of the other systems, overlap to some extent with the band at some 190 mμ pertinent to the electron donors and therefore are not suitable for the accurate evaluation of K. The K values at various temperatures obtained in the present study are given in Table I. Then the values of $R \ln K$ were plotted against the reciprocals of the absolute temperatures (T) at which

11) S. Nagakura, *J. Am. Chem. Soc.*, 76, 3070 (1954).

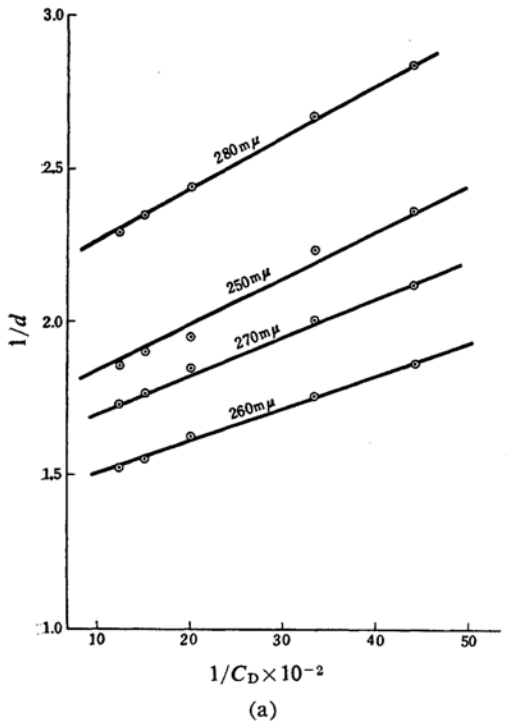

Fig. 5. Benesi-Hildebrand's plots for the diethylamine-iodine complex: a, at 10°C; b, at 30°C. C_D and d are the concentration of electron donor and the absorbance of the solution.

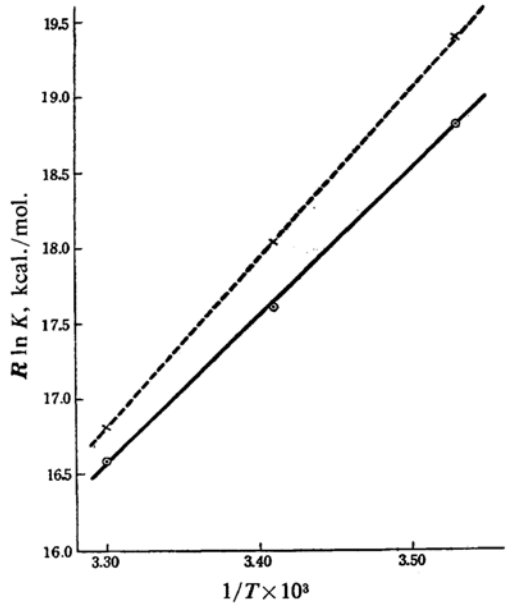

Fig. 6. The relations between $R \ln K$ and $1/T$ for the diethylamine (—○—) and piperidine (---×---) complexes.

equilibrium constants were obtained. The linear relationship between these two quantities is shown in Fig. 6 for some typical systems. The heat of formation (ΔH) and the entropy change (ΔS) for the complex formation were obtained from the slope of the straight line and its intersection with ordinate, respectively (actually by the use of the least squares method). The results are shown in Table I, together with the ionization potentials (I_p) cited from literatures[12,13] for convenience of discussion. Some notable facts deduced from the results in Table I will be discussed below.

Heat of Formation and Entropy Change.— The $|\Delta H|$ values change widely from 4.8 kcal./mol. for the ammonia complex to 12.3 kcal./mol. for the tri-*n*-propylamine complex. A similar tendency can also be seen with $|\Delta S|$. Moreover, it is evident from Table I that both of these quantities generally increase with the decreasing ionization potential of the electron donor. This relationship between $|\Delta H|$ and I_p is completely consistent with the expectation from Mulliken's charge-transfer theory. Therefore this fact certainly supports the interpretation that the iodine–amine complexes under consideration are of Mulliken's charge-transfer type.

It is worthy of notice that the values of $|\Delta H|$ and $|\Delta S|$ increase regularly by replacing

12) K. Watanabe and J. R. Mottle, *J. Chem. Phys.*, **26**, 1773 (1957).
13) K. Higasi, I. Omura and T. Tsuchiya, *Monograph Series of the Research Institute of Applied Electricity, Hokkaido University*, No. 4 (1954—7), Appendix.

TABLE I. SPECTROSCOPIC AND THERMAL DATA OF VARIOUS IODINE-AMINE COMPLEXES OBTAINED IN THE PRESENT EXPERIMENT, TOGETHER WITH THE IONIZATION POTENTIAL DATA (I_p)

Electron donor	λ_{CT}^{obs} mμ	ε_{CT} $\times 10^{-4}$	λ_{vis}^{obs} mμ	K 10°C	20°C	25°C	30°C	40°C	$-\Delta H$ kcal./mol.	$-\Delta S$ e.u.	I_p[12,13] eV.
Ammonia	229	2.34	430	89	67				4.8	8.0	10.154
$MeNH_2$	245	2.12	418		530		330		7.1	12.3	8.97
$EtNH_2$	246	2.26	417		720	560	480	320	7.4	12.3	8.86
n-$BuNH_2$	247	2.48	417		1230		770	480	8.4	14.8	8.71
Me_2NH	256	2.68	412		6800		4200	2560	9.8	15.9	8.24
Et_2NH	260	2.50	410	13000	7120		4260		9.7	18.4	8.01
piperidine	260	2.97	410	16200	9400		4900		10.3	16.1	
Me_3N	266	3.13	414		12100	7540	6240	4370*	12.1	22.6	7.82
Et_3N[8]	278	2.56	414		6320	4690	3310	1740	12.0	23.5	7.50
n-Pr_3N	281	2.38	414	2930	1390		740		12.1	26.6	7.23
n-Bu_3N	281	2.50	414	3900	1600				12.3	27.8	

* This value was obtained at 35°C.

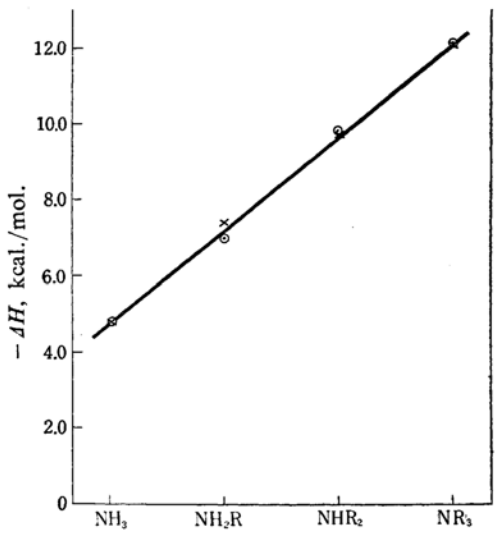

Fig. 7. The effect of successive substitution of alkyl groups for hydrogen atoms of ammonia on the heat of formation.

○: R=Me ×: R=Et

successively hydrogen atoms of ammonia by fixed kinds of alkyl groups. A typical example exhibiting such a tendency is given in Fig. 7. This figure shows that $|\Delta H|$ changes linearly with the number of the methyl or ethyl group introduced into the ammonia molecule. This seems to be interesting in meaning that the effect of the alkyl substitution upon the magnitudes of this quantity may be additive. According to the present experimental results, the $|\Delta H|$ value increases by 2.4 kcal./mol. by replacement of a hydrogen atom of ammonia by a methyl or ethyl group.

Next let us add some notes on the direct relation between $|\Delta H|$ and $|\Delta S|$. As was already pointed out by several authors[14], ΔH's are often known to change in a linear fashion with ΔS's for a series of related reactions or equilibria involving moderate changes in structure. For example, Keefer and Andrews[15]

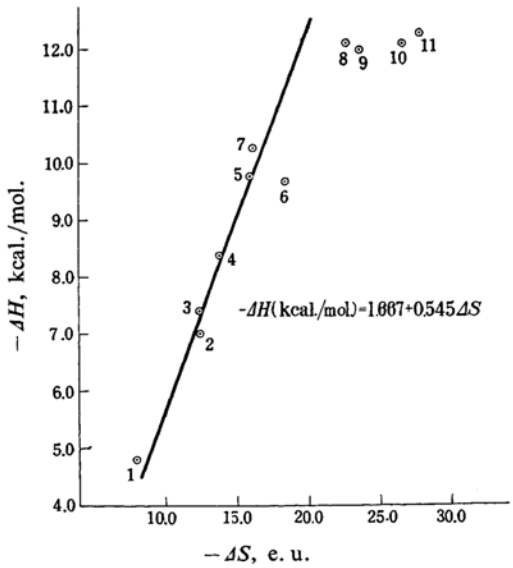

Fig. 8. The relation between the heats of formation and entropies. The numbers in Figs. 8-10 represent the kind of electron donors: 1, ammonia; 2, methylamine; 3, ethylamine; 4, *n*-butylamine; 5, dimethylamine; 6, diethylamine; 7, piperidine; 8, trimethylamine; 9, triethylamine 10, tri-*n*-propylamine; 11, tri-*n*-butylamine. The value for triethylamine is taken from Ref. 11.

14) For example, see J. E. Leffler, *J. Org. Chem.*, 20. 1202 (1955).

15) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, 77, 2164 (1955).

reported that such a linear relationship holds good for a series of substituted benzene-iodine complexes.

As is clear from Fig. 8, the linear relationship between $|\Delta H|$ and $|\Delta S|$ seems to hold for most amine complexes studied in the present paper, too. However, the points for the complexes including diethylamine and four tertiary amines as electron donors apparently deviate rightwards from the straight line. In the complex formation of iodine with these amines involving bulky substituent groups, the steric strain may actually bring about a great decrease of freedom in the motion of the substituent groups. This is probably the reason why the complexes including these amines as electron donors show greater entropy change than that expected from the linear relationship in Fig. 8. Such deviation from the linear relationship was also observed by Keefer and Andrews with the hexaethylbenzene-iodine complex[15]. Excluding the members deviating from the straight line, one can evaluate the isokinetic temperature[14] to be 545°K for amine-iodine systems.

The Relation between $|\Delta H|$ and Hammett's Constant. — When the linear relationship is satisfied between ΔH and ΔS in a series of related reactions or equilibria, the same relationship is known to be always satisfied between Hammett's substituent constant σ and ΔH, too. In fact, on the basis of the experimental results by Brown et al.[16], Taft[17] pointed out that ΔH values of Me_3BNR_3 complexes change linearly with the σ^* values of substituent groups of amines, so far as the steric strain due to the substituent groups may be regarded as small. A similar relation may be expected to hold for the present case. In Fig. 9 are plotted the heats of formation of the iodine-amine complexes against σ^* values for alkyl groups of various amine components. The σ^* values taken here are the same as those employed by Taft[18] for the trimethylboron-amine complexes. Inspection of the figure reveals to us that, as expected from Hammett's rule, the linear relationship is well satisfied for almost all the points except for those of triethyl-, tri-*n*-propyl-, tri-*n*-butyl-amines. The discrepancy observed with these three tertiary amine complexes may reasonably be thought to be caused by the steric strain. This fact is consistent with the conclusion derived from the $|\Delta H|-|\Delta S|$ relationship mentioned in the preceding paragraph. Taft also pointed out the existence of a similar discrepancy for the $Me_3B\cdot NR_3$ complexes. By excluding the cases of the donors deviating from the straight line in Fig. 9, the value of reaction constant ρ can be calculated to be -4.84 for the amine-iodine complexes.

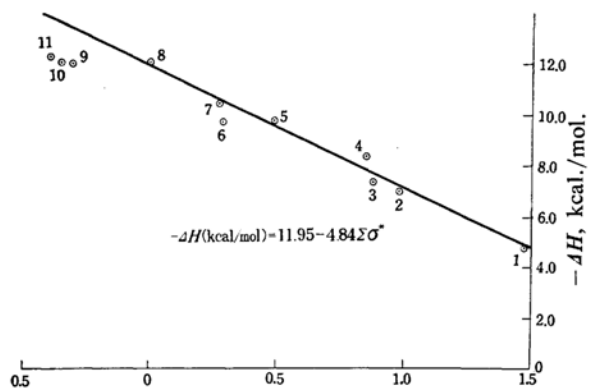

Fig. 9. Hammett's plot between the heat of formation and σ^*. The straight line is drawn by applying the least squares method to the points 1—5 and 7.

The Relation between Wavelengths of Charge-transfer Bands and Ionization Potentials of Electron Donors.—In Fig. 10 the transition energies ($h\nu_{CT}^{obs}$) of the charge-transfer spectra are plotted versus the ionization potentials of electron donors. As is clearly seen from this figure and Table I, the lower the ionization potentials of electron donors are, the smaller the transition energies of the charge-tranfer bands. This tendency can naturally be expected from Mulliken's theory and has already been observed by several investigators for iodine complexes with aromatic hydrocarbons and other electron donors[14,15]. However, the present results are thought to be more reliable and systematic compared with results obtained with some other iodine complexes, because for the present systems the charge-transfer bands appear at the suitable wavelength region where the bands do not overlap with those inherent to the component molecules and therefore the accurate determination of the maximum wavelength is possible.

Concerning the relation between the ionization potential of the electron donor and the transition energy of the charge-trasfer absorption band, Mulliken's charge-transfer theory gives the following formula:

$$h\nu_{CT}=I_p-A+2\beta^2/(I_p-A) \qquad (1)$$

16) H. C. Brown and R. B. Johannesen, *ibid.*, 75, 16 (1653) and other papers.
17) R. W. Taft, Jr., "Steric Effects in Organic Chemistry", Edited by M. S. Newman, John Wiley & Sons, Inc., New York (1956), p. 632.
18) Ref. 17, p. 619. $\Sigma\sigma^*$ for piperidine is assumed to be the sum of σ^* values of ethyl and *n*-propyl groups.
19) R. S. Mulliken, *Rec. trav. chim. Pays-Bas*, 75, 845 (1956).

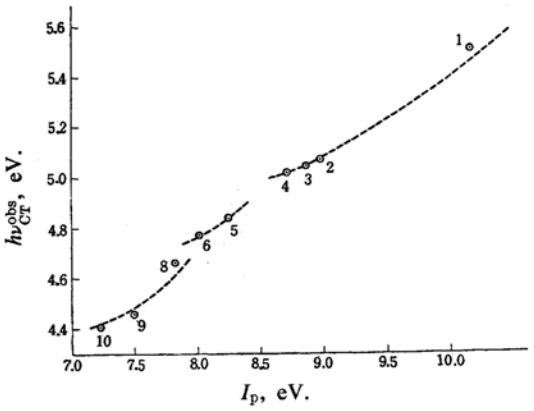

Fig. 10. The relation between the transition energies ($h\nu_{CT}^{obs}$) of the charge-transfer absorption bands and the ionization potentials of the electron donors (I_p).

where β means the exchange integral between electron donating and electron accepting orbitals, and A represents the electron affinity of the acceptor plus the attraction energy between the component molecules in the charge-transfer structure. Hastings et al.[15] found empirically that Eq. 1 with constant A and β fits well the observed $h\nu_{CT}$ values of the complexes of a large number of donor molecules with iodine. However, in the present iodine complexes where the value of $|I_p-A|$ can not be thought to be considerably large as compared with $|\beta|$ and the interaction between the component molecules is apparently great as revealed from the ΔH values, it looks better to adopt the following equation which can be derived by treating the resonance interaction of the no-bond structure with the dative (charge-transfer) structure with the aid of a variation method:

$$h\nu_{CT}=\sqrt{(I_p-A)^2-4s\beta(I_p-A)+4\beta^2}/(1-s^2) \quad (2)$$

where s means the overlap integral between the electron donating and accepting orbitals, and the other notations in Eq. 2 are the same as those in Eq. 1. From either of these formulas, the linear relationship between I_p and $h\nu_{CT}$ may be expected when the magnitude of I_p-A is overwhelmingly greater than $|\beta|$. In fact, Ham, Platt and McConnell[20] pointed out that the expected relationship is fulfilled for the $h\nu_{CT}^{obs}$ and I_p values observed with a number of iodine complexes.

By the first glance at Fig. 10, it may be revealed that all the points in the figure fit fairly well a straight line. However, in view of the fact that the observed $h\nu_{CT}^{obs}$ values of iodine complexes with various primary or tertiary amines show a tendency to converge to a constant value (5.0 and 4.4 eV. for primary and tertiary amines respectively), it looks better to interpret the results as follows: All the points in Fig. 10 are divided into three parts, according to whether the electron donor is ammonia and primary amines, secondary amines, or tertiary amines. Further, each part of them can conceivably be represented by a hyperbola as expected from Eq. 2.

In other words, it may be said that no parameter in Eq. 2 is a constant commonly used for all the iodine complexes under consideration but rather a constant characteristic of each part. In this connection, it seems interesting to evaluate the actual values of these parameters in such a manner as to fit the observed relationship between I_p and $h\nu_{CT}^{obs}$ as well as possible.

Under the reasonable approximation that the exchange integral β is proportional to the overlap integral s, namely $\beta=\alpha s$, Eq. 2 can be changed as follows:

$$(1-s^2)h\nu_{CT}=\{(I_p-A)^2-4(I_p-A)\alpha s^2+4\alpha^2 s^2\}^{1/2} \quad (3)$$

Here α is a constant which may be commonly determined independently of the kind of amine. The structure of the trimethylamine-iodine complex was studied by Strømme[22] with the aid of X-ray crystal analysis method and was determined as shown in Fig. 11. On the basis

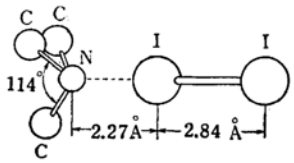

Fig. 11. The spatial configuration for the trimethylamine-iodine complex based on Strømme's X-ray crystal analysis[22].

of this structure, the overlap integral s_t for the tertiary amine-iodine complex system can be evaluated at 0.293. In this case, the 5p σ^* antibonding orbital of iodine and the s-p hybridized nonbonding electron orbital of nitrogen are assumed to be electron accepting and donating orbitals, respectively. In that case the proportion of s-p hybridization was determined from the $\angle$C-N-C bond angle. By the use of the value of s_t and the observed $h\nu_{CT}^{obs}$ and I_p values, the parameter A_t for the tertiary amine complexes and the common

20) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).
21) S. H. Hastings, J. L. Schiller and F. A. Matsen, *J. Am. Chem. Soc.*, **75**, 2900 (1953).
22) O. Strømme, *Acta Chem. Scand.*, **13**, 268 (1959).

parameter α can be evaluated at 7.60 and -7.14 eV., respectively. Further, by applying commonly this α value to the secondary and primary amine systems, the parameters for these systems (s_s, s_p, A_s and A_p) can be determined. These results are tabulated in Table II, together with the values of β_p, β_s and β_t.

TABLE II. THE CALCULATED VALUES OF PARAMETER IN EQ. 3

	A (eV.)	s	β (eV.)
Primary amines and ammonia	9.85	0.327	-2.32
Secondary amines	8.21	0.308	-2.20
Tertiary amines	7.60	0.293	-2.09

From Table II it is clear that A, s and $|\beta|$ values decrease in the order of primary amine > secondary amine > tertiary amine. The explanation for this tendency will be given below. The bulky alkyl groups attached to the nitrogen atom of the amine molecule probably cause the increase in the steric repulsion with the opponent iodine molecule. Actually the existence of the steric hindrance for the cases of the triethylamine, tri-*n*-propylamine and tri-*n*-butylamine complexes was shown in the preceding paragraph. This steric repulsion may conceivably bring about the increase in the N–I distance of the complex, in the order of the primary amine<secondary amine < tertiary amine. This means that s, $|\beta|$ and the magnitude of the electrostatic attraction in the dative (charge-transfer) structure decrease in the following order: primary amine > secondary amine > tertiary amine. Moreover, A is considered to be the sum of the electron affinity of electron acceptor and the electrostatic attraction between component molecules in the complexed state. Therefore the values of A turn out to decrease in the above order, even if the electron affinity of iodine may be regarded as a constant. Since the latter value is usually assumed to be 1.8 eV.[23], it is easily seen from the A values given in Table II that the absolute values of the electrostatic attraction terms then amount to some 8.0, 6.4 and 5.8 eV. for the complexes including ammonia and primary amines, secondary amines, and tertiary amines, respectively.

Summary

Mulliken's charge-transfer type molecular complexes between iodine and various aliphatic amines were studied spectrophotometrically in *n*-heptane solutions. The electron donor components used in the present study include ammonia, primary amines (methyl-, ethyl- and *n*-butyl-), secondary amines (dimethyl-, diethyl- and piperidine), and also tertiary amines (trimethyl-, tri-*n*-propyl- and tri-*n*-butyl-). The charge-transfer absorption bands characteristic of molecular complexes of this kind appeared between 229 and 281 mμ depending on the kind of amines used as electron donors. The stable equilibria of 1 : 1 complex formation were verified for all the systems. The equilibrium constants (K) were determined at various temperatures and the heats of formation (ΔH) and entropy changes (ΔS) were evaluated. The values of ΔH range from -4.8 kcal./mol. for ammonia complex to -12.3 kcal./mol. for tri-*n*-butylamine complex, and ΔS also changes from -8.0 e. u. for the former and -27.8 e. u. for the latter. The effect of successive replacement of hydrogen atoms of ammonia by methyl or ethyl groups on the value of ΔH was shown to be additive. From the data of ΔH and ΔS it was concluded that there exists a linear relation between these two quantities for the iodine complexes with all the primary amines and secondary amines having rather small substituent groups like methyl. The deviation from the linear relation was observed with the complexes including diethylamine and tertiary amines as electron donors. These amines with bulky substituent groups may be expected to exert a great steric hindrance in the case of the molecular complex formation. Further it was shown that the plots of ΔH's against σ^*'s (Hammett's substituent constant) fit the straight line, except for those of the iodine complexes with triethylamine, tri-*n*-propylamine and tri-*n*-butylamine. With the aid of the spatial configuration derived from X-ray crystal analysis data for the trimethylamine-iodine complex, one could evaluate the three parameters (overlap integral (s), exchange integral (β) and effective electron affinity (A)) which are necessary for explaining reasonably the relation between the transition energies of the charge-transfer bands and the ionization potentials of electron donors. For example, the β values thus estimated were -2.09, -2.20 and -2.32 eV. for the complexes with primary, secondary and tertiary amines, respectively.

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