

show that the porphine skeleton of each molecule is distorted because of close contact with phenyl groups of neighboring molecules. These phenyl groups are directly above and below the porphine skeleton, as shown in Fig. 3.

ZnTPP·(H₂O)₂, on the other hand, cannot pack as closely as CuTPP because of the oxygen ligands, which are 2.45 Å. above and below the metal atom. The greater amount of void volume in the zinc porphyrin unit cell is illustrated by Fig. 3 and 4 which compare the ZnTPP·(H₂O)₂ and CuTPP crystal packing in the *x*- and *y*-directions. In the *z*-direction, the shortest Zn-Zn distance is 4.86 Å., whereas the shortest Cu-Cu distance is 3.76 Å. Since the ZnTPP·(H₂O)₂ molecules are farther apart, interference from phenyl groups is lessened and the porphyrin skeleton can remain planar. FeTPPOH·H₂O, with the oxygen ligands above and below the ring, packs in about the same way as the ZnTPP·(H₂O)₂ and is thus almost planar.

The packing and molecular interactions of nickel etioporphyrin I⁴ are illustrated by the 001 projection of isomorphous nickel etioporphyrin II given by Crute.⁷ There are no oxygen ligands above and below the ring, and close contact between neighboring molecules is possible. The close packing occurs with a slight loss of planarity. The ethyl and methyl groups, which are attached to atoms 2 and 3 of the pyrrole ring, are bent out of the plane of the ring. The interactions of these groups with neighboring molecules contribute to bending of the porphine nucleus. The interaction of overlapping pyrrole rings from neighboring molecules may also contribute to the nonplanarity.

The evident conclusion is that the porphine skeleton

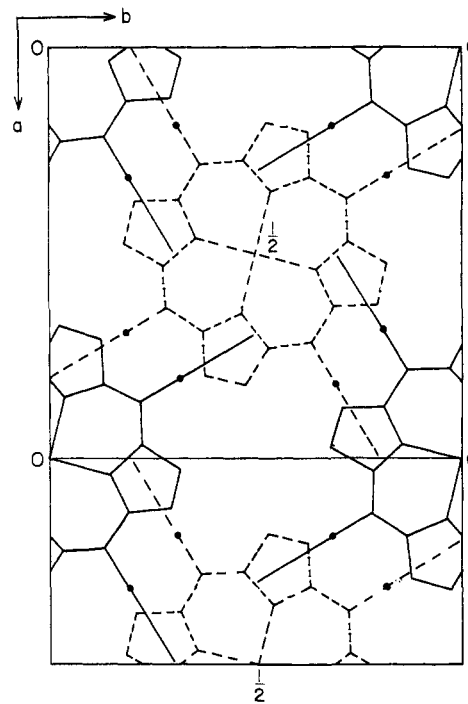


Fig. 4.—Projection of 1¹/₂ unit cells of ZnTPP·(H₂O)₂ on 001. The scale is the same for both the CuTPP and ZnTPP·(H₂O)₂ projections.

is quite flexible, since crystal packing forces can bend it easily. The shape of a particular porphyrin in a crystal appears to depend on the substituents and the type of packing. Porphine, since it has no substituents, would be expected to be nearly planar. The X-ray analysis of this compound is in progress.

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Molecular Addition Compounds of Amines and Iodine. Evidence for the Existence of a 2 : 1 Triethylamine-Iodine Complex

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Calorimetric studies of the triethylamine-iodine system in *n*-heptane revealed that the measured heat of reaction of the amine and iodine to form a 1:1 complex was strongly dependent upon the amine concentration. This result is explained in terms of the existence of a second iodine(I) complex, [(Et₃N)₂I⁺][I⁻], which is in equilibrium with the 1:1 complex. The molar heats of reaction that accompany the formation of 1:1 complexes were measured for seven amine-iodine systems in *n*-heptane by the method of thermometric titration and found to compare favorably with those values obtained by spectroscopic techniques. The sensitivity of iodine(I) compounds to hydrolysis and disproportionation is discussed.

Introduction

Numerous studies have been made of the interaction of the halogens and interhalogens with nitrogen-containing bases.¹ The large heats of reaction that accompany the formation of 1:1 complexes of alkylamines and iodine²⁻⁴ and pyridine and iodine⁵ indicate that interaction is appreciable. The trialkylamine-iodine complexes^{3,4} are formed with the largest enthalpy loss (~12 kcal.) of all the iodine complexes for which thermodynamic constants have been measured.

Additional information germane to this study has been obtained from conductance studies and spectral investigations. The increase in conductance of pyridine with the addition of iodine,^{6,7} and of acetonitrile with the addition of iodine or iodine monochloride,^{8,9} leaves no doubt that ionic species are present. The nature of the ionic species as yet has not been established with certainty. Spectral evidence indicates that in solutions of iodine or iodine monochloride which contain a Lewis base, there exists one or more type of iodine(I) cation. Popov and co-workers^{10,11} have made

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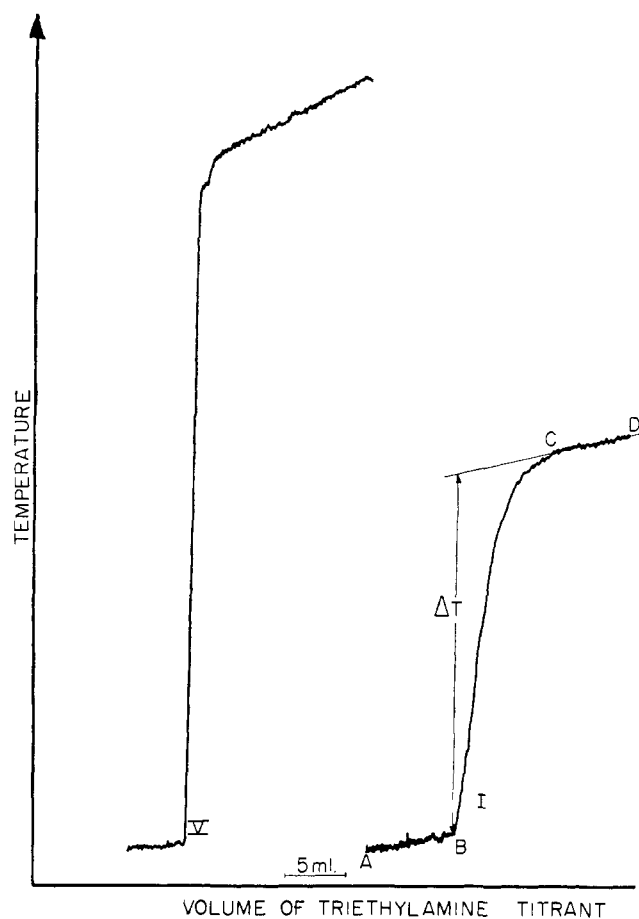


Fig. 1.—Typical titration curves for triethylamine-iodine system samples I and V of Table II: A, start of recorder chart drive; B, start of titration; C, end point of titration; C-D, portion of curve corresponding to excess titrant; ΔT , measured temperature change.

spectroscopic studies in which the results have been interpreted as evidence for the existence of a positive iodine species coordinated to two pyridine or pyridine-like molecules, or to a single dipyridine molecule. The fact that iodine(I) can have a coordination number of two is confirmed by the existence of such compounds as $[\text{Py}_2\text{I}]\text{ClO}_4$,¹² $[\text{Py}_2\text{I}]\text{NO}_3$,¹² $[\text{Py}_2\text{I}]\text{F}$,¹³ $[\text{Py}_2\text{I}]\text{SbF}_6$,¹³ $[\text{Py}_2\text{I}]\text{SO}_3\text{F}$,¹³ and $[(\gamma\text{-picoline})_2\text{I}]\text{I}$.¹⁴ The last compound is the *only* 2:1 amine-iodine complex that has been isolated. X-Ray radial distribution studies showed that the iodine-iodine bond is broken in this complex. Other workers^{5,15,16} have interpreted their spectroscopic data as evidence for a solvated iodine(I) species in which iodine is coordinated to a *single* pyridine molecule. Isolation of salts of the type $[\text{PyI}]\text{X}$, $[\alpha\text{-picoline-I}]\text{X}$, and $[\beta\text{-picoline-I}]\text{X}$ lends support to such a view.^{12,17} Hassel has questioned the conclusion, based on spectral studies, that 1:1 complexes of amines and iodine contain iodine(I) cations.¹⁸ X-Ray analysis of the 1:1 complexes of trimethylamine and iodine or iodine monochloride,

and of pyridine and iodine monochloride, show the N-I-X bonds are linear. The I-X bond is elongated and the N-I bond is of such length as to suggest the bond is essentially covalent. X-Ray analysis of the 1:1 pyridine-iodine complex gave similar results.¹¹ Despite these convincing arguments for the nonexistence of iodine(I) cations in solid 1:1 complexes, the effect of solvation and dielectric of the media cannot be discounted, and there remains the possibility that a $[\text{Am}\cdot\text{I}]^+$ cation exists, albeit in low concentration. Higher orders of coordination are possible but have been given no experimental verification. Spectroscopic studies have provided evidence for I_3^- in solutions of iodine dissolved in pyridine^{5,16} or iodine in quinoline.¹⁶ The anion ICl_2^- has been observed spectroscopically in solutions of iodine monochloride^{8-10,19} and nitrogen bases; IBr_2^- was observed in iodine monobromide solutions.¹⁰ The presence of iodide ions in the iodine solutions or of chloride ions in the iodine monochloride solutions has been assumed by several investigators. Such an assumption is reasonable although the concentration of these species is undoubtedly very small.

Calorimetric studies carried out in this laboratory revealed that the measured molar heats of reaction for a number of alkylamine-iodine systems were strongly dependent upon the concentration of the amine. This information suggested that more than a single complex species was present in the solutions of tertiary amines and iodine dissolved in "inert" solvents and prompted us to carry out a more detailed study of the concentration dependence of molar heats of reaction.

Experimental

Reagents.—Baker and Adamson resublimed iodine was ground with 25% by weight of potassium iodide and 10% by weight of calcium oxide. The mixture was sublimed; the iodine was collected and stored in a desiccator over phosphorus pentoxide.

Reagent grade carbon tetrachloride was shaken for several hours with a concentrated solution of potassium hydroxide, separated, and washed with distilled water. This process was repeated twice more. The reagent was then shaken with concentrated sulfuric acid, separated, and washed with distilled water. After the reagent had been washed free of the acid, it was dried by shaking over anhydrous U.S.P. grade calcium chloride. The dried liquid was fractionally distilled from a fresh quantity of calcium chloride and the constant-boiling center fraction retained.

Reagent grade *n*-heptane was shaken for intervals of 6 hr. with concentrated sulfuric acid and the acid separated. The procedure was repeated until the acid no longer became discolored. The *n*-heptane was then separated, washed with distilled water, and dried overnight over anhydrous calcium chloride. The dried solvent was fractionally distilled from fresh anhydrous calcium chloride and the constant-boiling center fraction retained. Comparison of the ultraviolet absorption spectra of the purified solvents with Spectrograde reagents was the criterion for purity.

Technical grade pyridine was refluxed for several hours over potassium hydroxide pellets and then distilled from fresh potassium hydroxide. The amines were Eastman Kodak White Label. These amines were purified by fractional distillation. The constant-boiling middle fraction was retained. Vapor phase chromatography indicated the amines were pure.

Apparatus for Calorimetric Studies.—The apparatus was essentially that developed by Jordan and co-workers.^{20,21} For work in nonaqueous solvents with small heat capacities it was found necessary to introduce a simple, but important, modification to the apparatus. It is essential in this procedure that titrant and titrate be near thermal equilibrium prior to titration. All at-

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TABLE I
 SUMMARY OF THERMODYNAMIC DATA FOR 1:1 MOLECULAR ADDITION COMPOUNDS OF IODINE

Lewis base, B:	Solvent	$B: I_{2(solv)} + I_{2(solv)}$	K_f	$B: I_{2(solv)} + \Delta H_f$	$-\Delta H_f, \text{kcal./mole}$	$-\Delta H_f, \text{kcal./mole}$
		K_f (temp., °C.), 1./mole		$-\Delta H_f, \text{kcal./mole}$		
N,N-Dimethylpropionamide ^b	CCl ₄		3.9 ± 0.2 (25)	4.0 ± 0.3		Not measurable
N,N-Dimethylaniline ^c	<i>n</i> -Heptane		18.8 (27)	8.2 ± 0.3		Not measurable
N,N-Dimethyl- <i>p</i> -toluidine ^c	<i>n</i> -Heptane		41.9 (21.3)	8.3 ± 0.2		Not measurable
Pyridine ^d	<i>n</i> -Heptane		290 (16.7)	7.8 ± 0.2		8.1 ± 0.7
Pyridine ^e	CCl ₄		97 (25)			8.0 ± 0.5
Triethylamine ^f	<i>n</i> -Heptane		4690 (25)	12.0		11.8 ± 0.7
Tri- <i>n</i> -propylamine ^g	<i>n</i> -Heptane		1390 (20)	12.1		12.0 ± 0.6
Tri- <i>n</i> -butylamine ^g	<i>n</i> -Heptane		1600 (20)	12.3		11.6 ± 0.7
Tri- <i>n</i> -amylamine	<i>n</i> -Heptane					12.1 ± 0.3
Diethylamine ^g	<i>n</i> -Heptane		7120 (20)	9.7		8.8 ± 0.2
Ethylamine ^g	<i>n</i> -Heptane		720 (20)	7.4		7.5 ± 0.6

^a Determined by thermometric titration; the value of ΔH_f is for the temperature 22 ± 2°. Deviations are standard deviations. R. S. Drago, private communication, 1963. ^c See ref. 2. ^d See ref. 5. ^e See ref. 11. ^f See ref. 4. ^g See ref. 3.

 TABLE II
 EFFECT OF TRIETHYLAMINE CONCENTRATION ON THE
 MAGNITUDE OF ΔH_f MEASURED IN *n*-HEPTANE

No.	Concn. of Et ₃ N ^a titrant, mole/l.	Final Et ₃ N ^b concn., mole/l. × 10 ²	Moles of I ₂ titrated × 10 ⁴	ΔH_f (mean), ^c kcal./mole	Condition of titrated solution
I	0.0890	0.810	2.919	11.8 ± 0.7	Clear
II	0.233	2.12	1.271	12.6 ± 0.4	Clear
III	0.363	3.30	1.568	14.0 ± 0.4	Clear
IV	0.489	4.44	2.154	13.9 ± 0.6	Faintly turbid
V	0.698	6.35	4.000	14.9 ± 0.3	Turbid
VI	0.990	9.00	2.714	15.1 ± 0.3	Turbid
VII	1.416	12.9	3.321	15.1 ± 0.3	Turbid
VIII	0.932 ^d	8.48 ^d	3.704	12.6 ± 0.3	Clear

^a Concentration of triethylamine titrant before dilution. ^b Concentration of triethylamine titrant after dilution by a factor of 15.0/165 but before equilibrium was established. This is equivalent to the value C_{Am} in eq. 6-8. ^c Deviations expressed in terms of standard deviation. Deviations are based on four to five replicates. ^d Total concentration of triethylamine plus N,N-dimethylpropionamide. The final triethylamine concentration was 0.014 *M*.

tempts to obtain thermal equilibrium between titrant and titrate by thermostatic control of a titrant reservoir external to the dewar adiabatic titration cell were unsuccessful. By introducing a 17-ml. titrant reservoir filled with titrant into the dewar filled with the solution to be titrated, thermal equilibrium was achieved within 1 hr. The exact shape of the reservoir depends upon the capacity of the dewar and the spatial restrictions within it. Our reservoir resembled a miniature cylindrical wash bottle with a straight mouthpiece. The reservoir was connected to a hypodermic syringe by a short length of Tygon tubing to form an airtight system. For the experiments reported herein the titrant was forced from the reservoir at a constant rate of 7.65 ml. min.⁻¹ as the syringe plunger was moved forward. The delivery rate was faster than that usually employed in order to reduce heat losses during titration.

Procedure.—A standardized stock solution of iodine in the appropriate solvent was prepared of such a concentration as to contain approximately 10⁻⁴ mole of iodine per 10 ml. of solution. Iodine solutions for use in thermometric titration were prepared by diluting 10-ml. aliquots of the standard solution to 150 ml. in the dewar flask. The amine solutions were prepared by weighing the amines into volumetric flasks and adding the appropriate solvent. The titrant reservoir, filled with the amine solution, was fitted into the dewar filled with titrate and the system allowed to come to thermal equilibrium. The heat capacity of the system was determined in a typical fashion by passing a fixed current for a measured time through a Manganin coil of known resistance immersed in the titrate. The actual titration was then carried out followed by remeasurement of the heat capacity of the system. Because of the significant increase (5-8%) in heat capacity of the system which accompanied the addition of the titrant, it was necessary to use a value for the heat capacity that represented an average of the system's heat capacity for the period during which

heat evolution was recorded, B-C in Fig. 1. The heat capacity of the system at point C was computed knowing the volume of the titrant at this point and assuming the heat capacity varied linearly with the volume of titrant. The average heat capacity, C_p^{av} , used in computation was for the region B-C of Fig. 1. The heat of reaction, $-\Delta H_f$, was computed from the relationship

$$-\Delta H_f = \frac{C_p^{av} \Delta T}{N} = q_M \quad (1)$$

where q_M corresponds to the heat evolved in the formation of 1 mole of product and ΔT to the increase in the temperature of the system with the formation of N moles of product. Because the equilibrium constants for 1:1 complex formation are sufficiently large and the amines were in large excess, the moles of product were taken to be equal to the amount of iodine present.

Figure 1 shows typical titration curves for triethylamine-iodine. The portion B-C is never quite linear even for the most concentrated amine titrant solution. The curvature is more pronounced with the dilute solutions, but the end points remain remarkably well defined. The excess reagent line C-D is linear.

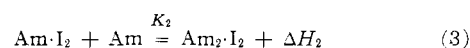
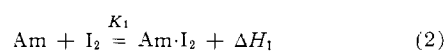
Reference to Table I shows that the average heats of reaction determined by thermometric titration agree well with the values obtained by spectroscopic methods. The values for H_f given in Table I are for the amine concentrations and iodine concentrations which approximate as closely as possible those concentrations used in the studies to which comparisons were made. These results demonstrate the reliability of the calorimetric method.

Results

The dependence of the measured molar heats of reaction upon the concentration of the amine in alkylamine-iodine systems was investigated in detail for triethylamine-iodine. The data, summarized in Table II, for this system show an increase in the molar heat of reaction from 11.8 to 15.1 kcal. mole⁻¹ as the titrant concentration was increased from 0.089 to 0.990 *M*. Special care was taken to control the volume of solutions in these experiments in order to be able to compute amine concentrations at the termination of a titration.

Discussion

A plot of the average values for the heat of reaction and the final triethylamine concentration reveals a near linear relationship at low amine concentrations. An explanation for this relationship, which is consistent with all experimental observations, is based on an equilibrium between $Am \cdot I_2$ and $Am_2 \cdot I_2$ complexes according to eq. 2 and 3.



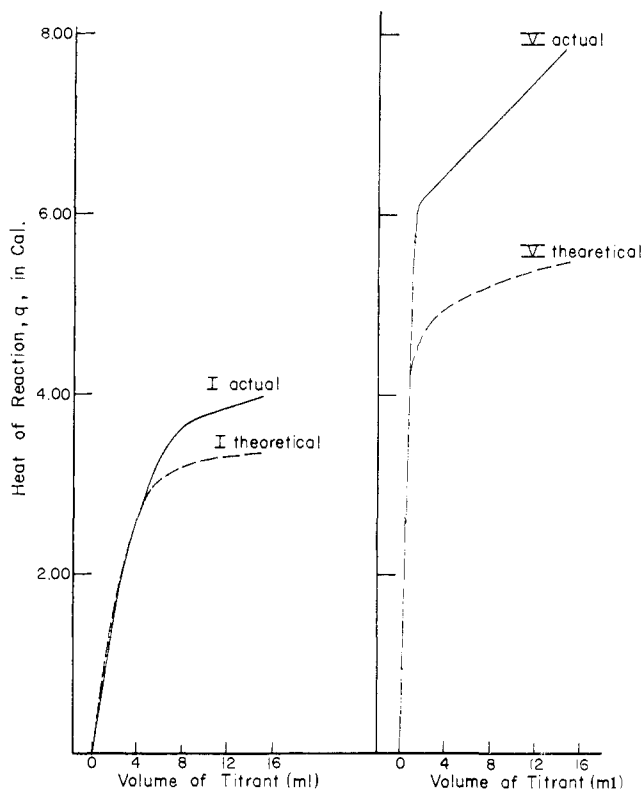


Fig. 2.—Comparison of theoretical titration curves with experimental curves.

The measured heat evolved, q , would be equal to

$$q = m_1\Delta H_1 + m_2\Delta H_2 \quad (4)$$

where m_1 is the number of moles of $\text{Am}\cdot\text{I}_2$ initially formed and m_2 , the number of moles of $\text{Am}_2\cdot\text{I}_2$ formed in the titration. The symbols ΔH_1 and ΔH_2 are the corresponding molar heats of reaction given in eq. 2 and 3. Substituting concentrations for moles in eq. 4 gives

$$q = \frac{v}{1000} [C_1\Delta H_1 + C_2\Delta H_2] \quad (5)$$

where v is the volume of the solution in the dewar titration cell. The concentration of the 1:1 complex at equilibrium, C_1 , is equal to the initial concentration of the 1:1 complex, C_{1i} , minus the concentration of the 2:1 complex that has formed, C_2 , and the equilibrium amine concentration is equal to the initial amine concentration, C_{Am_i} , less the concentration of the 1:1 complex initially formed and the 2:1 complex. The equilibrium constant for the second equilibrium is therefore

$$K_2 = \frac{(C_2)}{(C_1 - C_2)(C_{\text{Am}_i} - C_1 - C_2)} \quad (6)$$

The value⁴ for K_1 is large, 4600 l. mole⁻¹, and the amine is present in large excess relative to the iodine so that it is a reasonable approximation to make the initial concentration of the 1:1 complex, C_{1i} , equal to the initial iodine concentration, C_{1i} . Furthermore, the concentration of the 2:1 complex is small relative to the amine so that $(C_{\text{Am}_i} - C_1 - C_2)$ is equal approximately to $C_{\text{Am}_i} - C_{1i}$. Using these approximations eq. 6 becomes

$$K_2 = \frac{(C_2)}{(C_{1i} - C_2)(C_{\text{Am}_i} - C_{1i})} \quad (7)$$

Rearranging eq. 7 to give an expression for C_2 , substituting into eq. 5, and rearranging gives the equation

$$\frac{1000}{v} \frac{q}{C_{1i}} = \Delta H_1 + \frac{(K_2 C_{\text{Am}_i} - K_2 C_{1i}) \Delta H_2}{1 + K_2 C_{\text{Am}_i} - K_2 C_{1i}} = \Delta H_r \quad (8)$$

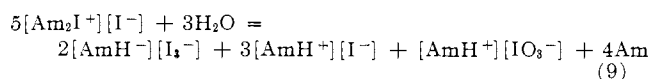
As the concentration of the amine increases, the value of $(K_2 C_{\text{Am}_i} - K_2 C_{1i})$ in the denominator of the second term becomes increasingly significant. It soon predominates so that the value of the second term approaches ΔH_2 . The expression for ΔH_r in eq. 8 then approaches a constant equal to $\Delta H_1 + \Delta H_2$, which is equivalent to the heat of reaction of the amine and iodine to form the $\text{Am}_2\cdot\text{I}_2$ complex. Unfortunately, in these experiments at high amine concentrations the superposition of heat of crystallization of a solid amine-iodine complex upon the heat of reaction eliminates the possibility of measuring an accurate value for ΔH_2 .

At low initial amine concentrations it may be shown that the curvature of a line connecting plots of ΔH_r vs. C_{Am_i} is only very slight for values of ΔH_2 ranging from 2 to 4 kcal. mole⁻¹ and values of K_2 ranging from 20 to 50. (The values for ΔH_2 and K_2 are approximate values for the triethylamine-iodine system obtained from the experimental results.) A theoretical titration curve was derived by solving eq. 2 and 3 simultaneously. Reasonable values for the constants $K_1 = 4700$ l. mole, $K_2 = 25$ l. mole, $\Delta H_1 = -11.4$ kcal./mole, and $\Delta H_2 = -3.7$ kcal./mole were assigned. Theoretical curves are plotted in Fig. 2 for solutions I and V (Table II). The theoretical and experimental curves are in fair agreement in view of the assumptions and approximations that were necessary in deriving the theoretical curve. At low concentrations of amine the agreement is quite satisfactory and there is a definite end point in the theoretical curve. The theoretical treatment makes no allowance for heat developed by crystal formation nor for heat changes resulting from a slight difference in temperature of the titrate and titrant.

It is apparent from eq. 8 that when the value for C_{Am_i} is equal to C_{1i} , the second term in eq. 8 cancels, and the heat of reaction is equal to ΔH_1 . Despite the very slight curvatures at low initial amine concentration, a linear extrapolation in a ΔH_r vs. C_{Am_i} plot would yield a value for ΔH_1 that more nearly represents the correct value for this term than the values previously reported for which no compensation was made for the presence of the $\text{Am}_2\cdot\text{I}_2$ species. It was possible to obtain a value for ΔH_1 of -11.4 kcal. mole⁻¹ for triethylamine-iodine in this manner.

That the increased heat of reaction was not due to increased Coulombic interactions between the highly polar $\text{Am}\cdot\text{I}_2$ complex and amine molecules (or that this contribution was relatively small) was demonstrated by substituting polar *N,N*-dimethylpropionamide molecules ($\mu = 3.80$ D.) for some of the less polar triethylamine molecules ($\mu = 0.75$ D.). Reference to sample VIII in Table I shows that the heat of reaction depends solely on the amine concentration and is insensitive to the presence of the more polar *N,N*-dimethylpropionamide molecules.

Spectroscopic studies of amines and iodine in *n*-heptane have established the existence of a 1:1 triethylamine-iodine complex⁴ and other 1:1 tertiary alkylamine-iodine complexes.³ Direct evidence for 1:1 complexes of tertiary amines and iodine was provided by Hassel, who isolated crystals of $(\text{CH}_3)_3\text{N}\cdot\text{I}_2$.¹⁸ The isolation of a 2:1 triethylamine-iodine complex was undertaken in order to provide direct evidence for its existence. Nagakura reported that for triethylamine-iodine solutions in *n*-heptane the solutions become turbid and a precipitate readily formed when the amine concentration was in excess of 10^{-2} M.⁴ The precipitate was reported "water-soluble." We too have observed such a phenomenon. Solutions of I_2 and Et_3N in *n*-heptane, with concentrations comparable to samples IV-VI used in thermometric titrations, developed a turbidity within the time of titrations. Eventually a brown, gummy material separated from the solution and the solvent was left colorless. The gummy material solidified upon standing. This solid material was readily soluble in acetonitrile but insoluble in common organic solvents of low dielectric constant. Every attempt to recrystallize this material from acetonitrile led to the isolation of colorless, needle-like crystals of triethylammonium iodide, identified by melting point, elemental analysis, and X-ray spectroscopy. Despite our repeated failure to isolate the 2:1 complex, the behavior of the product during recrystallization suggested the possibility that an ionic triethylamine-iodine complex analogous to $[(\gamma\text{-picoline})_2\text{I}]\text{I}^{14}$ is responsible for these experimental results. These iodine(I) compounds are thought to be particularly sensitive to hydrolysis and subsequent disproportionation according to the equation



The iodine as I_3^- which is formed in this reaction would be rapidly and strongly coordinated by the basic amine which is present in large excess so that some ionic iodine(I) species would be regenerated. Hydrolysis and disproportionation of the iodine(I) species would again set in. This process would continue until all the triiodide is consumed. This mechanism is similar to that proposed by Carlsohn to account for the instability to moisture of salts containing the dipyridinoiodine(I) cation.¹² Previous success in isolating the 2:1 picoline-iodine complex is thought to be due to the reduced chemical activity of iodine coordinated to heterocyclic

amines arising from the distribution of the positive charge of iodine throughout the aromatic rings. It should be pointed out that hydrolysis of iodine(I) accompanied by disproportionation (eq. 9) would not change the apparent concentration of titratable iodine. One equivalent of iodate ion would be generated for each equivalent of iodine that had disproportionated. The possibility that the iodine(I) species reacts with the acetonitrile solvent has not been discounted. A slow iodination of pyridine is thought to occur when iodine is dissolved in pyridine.^{7,16} A reaction of this type would result in the loss of titratable iodine.

Early workers attributed the time-dependent change in conductivity of an iodine solution in pyridine to a slow ionization of a highly polarized species, such as $\text{PyI}^{\delta+}-\text{I}^{\delta-}$.^{6,7} This model has been given a refined theoretical treatment by Mulliken.²² According to Mulliken there are two types of charge-transfer complexes, the "outer complex," $\text{B}\cdot\text{X}_2$, and the "inner complex", $[\text{BX}^+][\text{X}^-]$. Mulliken proposed that in the case of pyridine-iodine, the slow increase in conductance is due to a slow passage from outer to inner complex over an energy barrier of considerable height. The slow transition from "outer" to "inner" complex has been used repeatedly to account for time-dependent spectral changes.^{5,8,22} An explanation of the data from our calorimetric studies requires the existence of two amine-iodine complexes. But more significantly it requires that the two species achieve equilibrium in the time that it takes to mix the reagents. Experimentation showed that the measured heats of reaction obtained at the fastest feed rates were in agreement with those at slower rates. From this we concluded that attainment of equilibrium between the 1:1 and 2:1 complexes is essentially instantaneous. An explanation for this phenomenon is consistent with the Mulliken theory if it is allowed that the energy barrier for the transition from an outer complex, $\text{Am}\cdot\text{I}_2$, to an inner complex, $[\text{Am}_2\text{I}^+][\text{I}^-]$, is small.

The complexity of amine-iodine systems has been pointed up by the results of this study. There appears now to be good evidence in support of the existence of at least two complex amine-iodine species. Further investigation is necessary to test the hypothesis that the interaction of 1:1 and 2:1 complexes is responsible for frequently reported time-dependent changes in conductance and spectra of iodine solutions in nitrogen-containing basic solvents.

(22) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).