

**Zone Electrophoresis.**—In order to confirm the existence of a negatively charged complex, zone electrophoresis was used. This technique involves moistening a suitable strip of paper with the solution to be investigated and applying a d.c. voltage to the ends of the strip.

The electrophoresis studies were carried out with varying ratios and concentrations of kojate and cadmium nitrate. In all cases, the solutions were adjusted to pH 10.5 with sodium hydroxide. For maximum efficiency, it is desirable to keep the ionic strength as low as possible, so no attempt was made to maintain constant ionic strength.

A 10 × 2.5 cm. strip of Whatman Glass Chromatography paper GF-B was cut into three pieces. The two end pieces were moistened with the kojate solution. The center piece was moistened with a cadmium solution containing the same concentration of kojate as the end pieces. The three pieces were placed in adjoining positions on a glass plate. Platinum electrodes were laid across the ends of the strip and the assembly covered with another glass plate. A regulated d.c. voltage was applied for several minutes. Hydrogen sulfide was used as a developer.

With a solution of 5.05 mM cadmium nitrate and 0.26 M kojate, under applied voltages of 200 v. for eight minutes or 250 v. for five minutes the cadmium zones moved about 2 cm. toward the positive electrode. The movement was irregular, the original rectangular shape being distorted. The results are shown in Fig. 4, B and C. A control paper, A, shows the movement of the zone with no potential applied. The two vertical lines near the center of each drawing indicate the boundaries between the three pieces of the strip. The shaded areas indicate the final position of the cadmium. The dashed lines show the position of the electrodes. D and E show the results when the solution con-

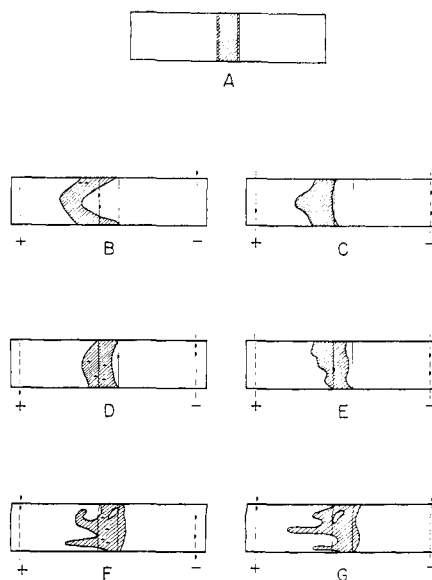


Fig. 4.—Zone electrophoresis of the cadmium kojate system.

tained 0.050 M kojate and 5.05 mM cadmium nitrate. In D, 220 v. were applied; in E, 250 v., for twenty minutes. Definite movement toward the positive electrode still occurred, although the movement was much less than in B and C, which contained five times as much kojate. Solutions containing 0.015 M kojate and 5.05 mM cadmium were run. The results are given in F and G (450 and 300 v. for fifteen minutes). In these cases, there was movement toward both the positive and negative electrodes. The zones were also very irregular on the positive side, with long streamers. This probably is due to local concentration gradients in the kojate caused by its movement.

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## Molecular Complexes and Their Spectra. XIII. Complexes of Iodine with Amides, Diethyl Sulfide and Diethyl Disulfide

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Spectrophotometric studies of solutions of iodine with acetamide, N,N-dimethylformamide, diethyl sulfide and diethyl disulfide have given results that are consistent with an interpretation of 1:1 charge transfer complex formation in all cases. The thermodynamic and spectral characteristics of these complexes have been determined. A discussion on the nature of the bonding responsible for the formation of these complexes is given. In addition a discussion on the general features of the spectra of iodine-donor complexes is presented.

### Introduction

Although extensive studies have been made on molecular complexes between iodine and organic compounds, there still remain some compounds whose interactions with iodine have not been carefully studied. Among them, amides, sulfides and disulfides seem to be of particular interest. The present paper gives the results of a spectropho-

metric investigation of iodine complexes formed from some of these compounds and also with di-*t*-butyl peroxide.

Amides are known to form complexes with metal ions,<sup>2</sup> the hydrogen ion<sup>3</sup> and electron-deficient molecules such as BCl<sub>3</sub>.<sup>4</sup> There is evi-

(2) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

(3) G. Frenkel and C. Niemann, *Proc. Natl. Acad. Sci., U. S.*, **44**, 688 (1958).

(4) W. Gerrard, M. F. Lappert, H. Pyszora and J. W. Wallis, *J. Chem. Soc. (London)*, 2144 (1960).

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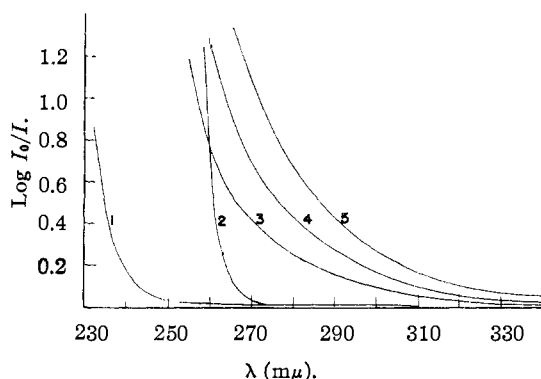


Fig. 1.—The ultraviolet absorption spectra of iodine-*N,N*-dimethylformamide solutions: solvent, dichloromethane; temperature, 20°; cell, 1 cm. Curves: 1, 0.000251 *M* iodine; 2, 1.413 *M* *N,N*-dimethylformamide; 3, 0.000268 *M* iodine and 0.181 *M* *N,N*-dimethylformamide; 4, 0.000268 *M* iodine and 0.362 *M* *N,N*-dimethylformamide; 5, 0.000268 *M* iodine and 0.723 *M* *N,N*-dimethylformamide.

dence in these papers that the oxygen atom in the amide molecule acts as the coordinating center in the complexing<sup>2-4</sup> and hence is regarded as more basic in amides than the nitrogen atom.

Extensive work has been done by McCullough and his co-workers on the halogen complexes of organic sulfides and selenides. They found that in the crystalline form of the complex between iodine and 1,4-dithiane the sulfur atom and the two iodine atoms of the molecule that complexes with this sulfur atom all lie in a straight line.<sup>5</sup> They have determined the equilibrium constants for the complexes between iodine and dimethyl sulfide,<sup>6</sup> dimethyl and various substituted diphenyl selenides<sup>7</sup> and some thiacycloparaffins.<sup>8</sup> They also determined the heats of formation of iodine complexes with dimethyl and substituted diphenyl selenides.<sup>9</sup>

### Experimental

**Purification of Materials.**—The purification of iodine and *n*-heptane is described in a previous paper.<sup>10</sup> The diethyl sulfide, diethyl disulfide and acetamide were Eastman reagent grade chemicals. The *N,N*-dimethylformamide and dichloromethane were Eastman spectrograde chemicals and the di-*t*-butyl peroxide Matheson, Coleman and Bell practical grade. Diethyl sulfide was dried with freshly activated silica gel and distilled with a Podbielniak column. Diethyl disulfide also was dried with silica gel and was distilled under reduced pressure. Dichloromethane was dried with Drierite and distilled with a Podbielniak column. Acetamide was recrystallized twice from pure dioxane and dried in a vacuum desiccator and the *N,N*-dimethylformamide was dried with silica gel and distilled under reduced pressure. The di-*t*-butyl peroxide was not further purified.

**Method.**—The experimental method of measuring the absorption spectra at various temperatures and deriving the equilibrium constants for the formation of the complexes is also described in the same previous paper.<sup>10</sup>

(5) G. Y. Chao and J. D. McCullough, *Acta Cryst.* (in press).

(6) N. W. Tidswell and J. D. McCullough, *J. Am. Chem. Soc.*, **79**, 1031 (1957).

(7) J. D. McCullough and D. Mulvey, *J. Phys. Chem.* (in press).

(8) J. D. McCullough and D. Mulvey, *J. Am. Chem. Soc.*, **81**, 1291 (1959).

(9) J. D. McCullough and I. C. Zimmerman, *J. Phys. Chem.* (in press).

(10) H. Tsubomura, *J. Am. Chem. Soc.*, **82**, 40 (1960).

### Results

**Amides.**—Non-polar solvents such as *n*-heptane or carbon tetrachloride dissolve only very small amounts of the amides and, therefore, could not be used as solvents for the present work. Chloroform has been found to be unsuitable because it reacts gradually with the complexes of iodine and amides. Finally dichloromethane was found to be inert toward the complexes and transparent further in the ultraviolet than chloroform. However, the low boiling point of dichloromethane may have changed the concentrations of the solutions slightly during the measurements, although the measurements always were made with freshly prepared solutions. It was found initially that the dichloromethane solutions of iodine and commercial grade amides showed a band at 360 *mμ* as well as the shifted visible iodine band and the ultraviolet absorption which is regarded as charge-transfer absorption. Recrystallization of the acetamide and distillation at reduced pressure of the *N,N*-dimethylformamide removed the absorption band at 360 *mμ* to a satisfactory extent.

In Fig. 1 the near ultraviolet spectrum of the iodine-*N,N*-dimethylformamide complex is given to show the type of spectroscopic data that were employed to calculate the equilibrium constants for the amide-iodine complexes. The solutions which contain only iodine show an absorption edge in the near ultraviolet at a wave length which is shorter than the contact charge-transfer absorption of iodine in *n*-heptane.<sup>11</sup> This can reasonably be explained as due to the contact charge transfer absorption of iodine-dichloromethane. Solutions containing both iodine and an amide have the ultraviolet cut-off shifted toward still longer wave lengths which indicates that the charge-transfer bands of the complexes appear in this region.

The determination of the equilibrium constant for the 1:1 complex formation of the complexes between iodine and the amide by the modified Benesi-Hildebrand plot<sup>10</sup> was not very easy for the following reasons: (1) the *K* is small (the percentage error in *K* increases as *K* becomes smaller), and (2) the charge-transfer band partly overlaps the strong absorption of the amide. In the case of acetamide its solubility limit is about 0.35 *M* so that the concentration of iodine would have to be increased to obtain a sufficiently strong charge-transfer band. Unfortunately iodine, at a concentration of 0.5 *mM* in dichloromethane, shows an absorbance ( $\log I_0/I$ ) of about 0.04 in the wave length region between 250 and 300 *mμ* which has been shown to be attributable to two overlapping bands, one of *I*<sub>2</sub> and one of *I*<sub>4</sub>.<sup>12</sup> This absorption, although quite weak, may still interfere with the Benesi-Hildebrand plot and hence the *K* value obtained for the iodine-acetamide complex is not very reliable.

The situation is better in the case of *N,N*-dimethylformamide because of its greater solubility in dichloromethane, permitting the iodine concentration to be reduced to half the value used in the acetamide solutions. The absorbance by the *I*<sub>2</sub>

(11) L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957).

(12) P. A. D. De Maine, *J. Chem. Phys.*, **24**, 1091 (1956).

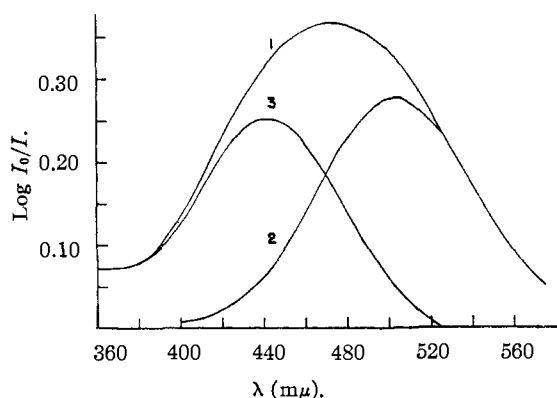


Fig. 2.—Resolution of the shifted visible iodine band of an iodine-*N,N*-dimethylformamide solution: solvent, dichloromethane; temperature, 20°; cell, 1 cm. Curves: 1, 0.000502 *M* iodine and 0.645 *M* *N,N*-dimethylformamide; 2, free iodine component of curve 1; 3, iodine-*N,N*-dimethylformamide complex component of curve 1.

and  $I_4$  was now only about 0.02 and its effect on  $K$  is almost within the experimental fluctuations. Modified Benesi-Hildebrand plots have been made for the iodine-*N,N*-dimethylformamide complex at three different temperatures. Five to six solutions were measured and the concentrations of the amide ranged approximately between 0.7 and 0.2 *M*. The points lie on a straight line within experimental error and the  $K$ 's and  $\epsilon$ 's determined from the plot are given in Table I. The plot of  $\ln K$  versus  $1/T$  gives a straight line and the resultant  $\Delta H^\circ$  is  $-4.03$  kcal./mole and  $\Delta S^\circ$  is  $-13.5$  e.u. In general the  $\epsilon$  values seem to increase with temperature, although two values at 10° are slightly larger than the corresponding values at 20°. This seems reasonable because our measurements were made on a side of the charge-transfer band and as the temperature increases the band usually becomes broader.

TABLE I  
EQUILIBRIUM CONSTANTS, MOLAR EXTINCTION COEFFICIENTS AND STANDARD ENTHALPY AND ENTROPY CHANGES FOR THE IODINE-*N,N*-DIMETHYLFORMAMIDE COMPLEX IN DI-CHLOROMETHANE

Temp., °C.	$\Delta H^\circ = -4.03$ kcal./mole; $\Delta S^\circ = -13.5$ e.u.				$K$ (l. mole <sup>-1</sup> )			$\epsilon$ (l. mole <sup>-1</sup> cm. <sup>-1</sup> )		
	(275 mμ)	(280 mμ)	(290 mμ)	Ave.	(275 mμ)	(280 mμ)	(290 mμ)	(275 mμ)	(280 mμ)	(290 mμ)
0	1.98	1.78	1.88	1.88	6320	5280	3210			
10	1.44	1.38	1.47	1.43	7040	5730	3500			
20	1.15	1.12	1.11	1.13	6970	5540	3630			

Although accurate  $K$  values cannot be obtained for the iodine-acetamide complex because of the reason stated above, modified Benesi-Hildebrand plots were tentatively made and approximate straight lines were obtained, leading to the following results: at 265  $m\mu$  and 22° the  $K$  (l. mole<sup>-1</sup>) is 0.61 and  $\epsilon$  (l. mole<sup>-1</sup> cm.<sup>-1</sup>) is  $1.50 \times 10^4$ , at 0° and 270  $m\mu$  the  $K$  is 1.15 and  $\epsilon$  is  $8.31 \times 10^3$ . Using the  $K$  values at 22° and 0° a  $\Delta H^\circ$  value of  $-4.61$  kcal./mole and a  $\Delta S^\circ$  value of  $-16.6$  e.u. have been obtained.

Using the  $K$  value of the iodine-*N,N*-dimethylformamide complex the shifted visible absorption

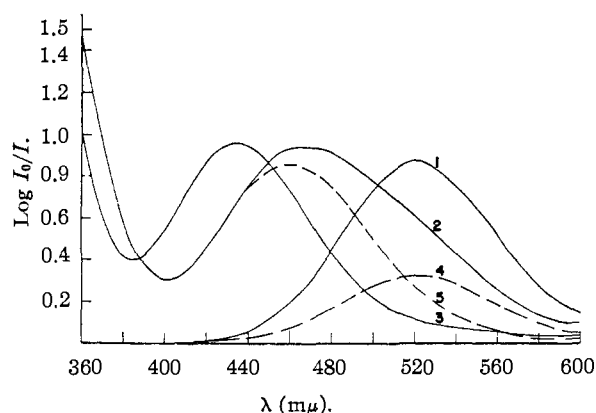


Fig. 3.—The visible absorption spectra of iodine-diethyl sulfide and iodine-diethyl disulfide solutions: solvent, *n*-heptane; temperature, 20°; cell, 1 cm. Curves: 1, 0.00100 *M* iodine; 2, 0.00100 *M* iodine and 0.300 *M* diethyl disulfide; 3, 0.00506 *M* iodine and 0.200 *M* diethyl sulfide; 4, free iodine component of curve 2; 5, iodine-diethyl disulfide complex component of curve 2.

band of iodine can be resolved into two components, one derived from free iodine and the other complexed iodine. Figure 2 is an example of such a resolution and shows that the complexed iodine band has a peak at 440  $m\mu$  and  $\epsilon_{\max}$  of 1185. A similar resolution of the visible spectrum can be done for the iodine-acetamide complex. Using  $K$  as 0.61 at 22° gives a smooth band with a peak at about 440  $m\mu$ .

**Diethyl Sulfide.**—Figure 3 shows the visible spectra of *n*-heptane solutions of iodine plus diethyl sulfide together with a solution of iodine. The visible band shifts from 525  $m\mu$  for iodine in *n*-heptane to 435  $m\mu$  for the iodine-diethyl sulfide solution which indicates strong complex formation. In Fig. 4 are shown the ultraviolet spectra of the *n*-heptane solutions of iodine and diethyl sulfide.

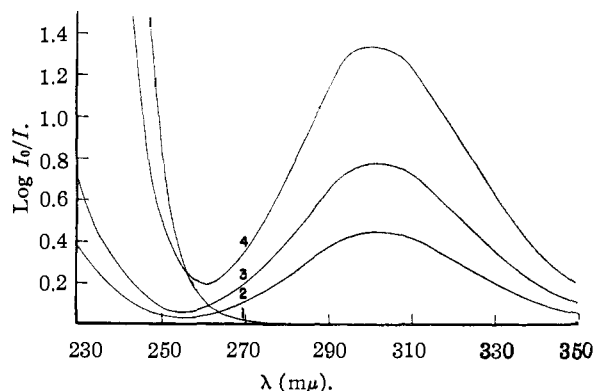


Fig. 4.—The ultraviolet absorption spectra of iodine-diethyl sulfide solutions: solvent, *n*-heptane; temperature, 20°; cell: 1 cm. Curves: 1, 0.100 *M* diethyl sulfide; 2, 0.0000506 *M* iodine and 0.00200 *M* diethyl sulfide; 3, 0.0000506 *M* iodine and 0.00500 *M* diethyl sulfide; 4, 0.0000506 *M* iodine and 0.0500 *M* diethyl sulfide.

The intense charge-transfer peak appears at 302  $m\mu$ . In contrast to the case of the amides, the donor absorption here does not overlap the charge-

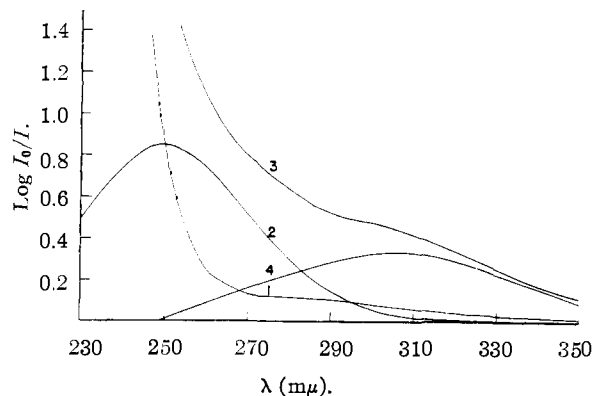


Fig. 5.—The ultraviolet absorption spectra of a diethyl disulfide-iodine solution: solvent, *n*-heptane; temperature, 20°; cell: 1 cm. Curves: 1, 0.00200 *M* iodine; 2, 0.00200 *M* diethyl disulfide; 3, 0.00200 *M* iodine and 0.00200 *M* diethyl disulfide; 4 the charge transfer band of the iodine-diethyl disulfide complex obtained by subtracting curves 1 and 2 from curve 3.

transfer peak, and the absorption at this peak can be used for the determination of *K*. Under the experimental conditions employed the absorption near 302 *mμ* due to *I*<sub>2</sub> and *I*<sub>4</sub> and to diethyl sulfide was completely negligible. Five solutions of iodine and diethyl sulfide, with iodine at 0.0506 *mM* and sulfide ranging from 0.001 to 0.05 *M*, were used to make the modified Benesi-Hildebrand plots at four temperatures. The results for *K* and  $\epsilon$  are given in Table II. The  $\ln K$  versus  $1/T$  plot gave a straight line resulting in a  $\Delta H^0$  of  $-7.82$  kcal./mole and a  $\Delta S^0$  of  $-15.9$  e.u.

TABLE II

EQUILIBRIUM CONSTANTS, MOLAR EXTINCTION COEFFICIENTS AND STANDARD ENTHALPY AND ENTROPY CHANGES FOR THE IODINE COMPLEXES WITH DIETHYL SULFIDE AND DIETHYL DISULFIDE

Temp., °C.	$\Delta H^0 = -7.82$ kcal./mole, $\Delta S^0 = -15.9$ e.u. Diethyl sulfide		$\Delta H^0 = -4.62$ kcal./mole, $\Delta S^0 = -12.3$ e.u. Diethyl disulfide	
	<i>K</i> (l./mole)	$\epsilon$ (l./mole cm.)	<i>K</i> (l./mole)	$\epsilon$ (l./mole cm.)
0	562.5	$3.00 \times 10^4$	10.7	$1.42 \times 10^3$
10	343	$3.08 \times 10^4$	7.18	$1.48 \times 10^3$
20	210	$2.98 \times 10^4$	5.62	$1.59 \times 10^3$
30	135	$2.85 \times 10^4$	4.42	$1.56 \times 10^3$

**Diethyl Disulfide.**—The visible spectrum of the iodine-diethyl disulfide solution shown in Fig. 3 shows a shift of the visible iodine band from 525 *mμ* to 465 *mμ* which seems to indicate that the iodine-diethyl disulfide complex is not as strong as the iodine-diethyl sulfide complex. The ultraviolet spectrum of the iodine-disulfide solutions shows that the charge-transfer band has a large overlap with the diethyl disulfide absorption which extends to much longer wave lengths than the diethyl sulfide absorption. Consequently the absorption values for the modified Benesi-Hildebrand plots were taken at the tail of the charge-transfer band at 370 *mμ*. At this wave length the absorption due to the free iodine is completely negligible and the small absorption due to the disulfide was subtracted from the observed intensity

of the iodine-disulfide solutions. Five to six solutions of iodine and diethyl disulfide, with iodine at 0.00100 *M* and the disulfide ranging from 0.070 to 0.300 *M*, were employed for the modified Benesi-Hildebrand plots. The values for *K* and  $\epsilon$  at four temperatures are listed in Table II. The  $\ln K$  versus  $1/T$  plot gave a  $\Delta H^0$  of  $-4.6$  kcal./mole and a  $\Delta S^0$  of  $-12.3$  e.u.

From the *K* value at 20° a resolution of the shifted visible absorption band of iodine was made, analogous to the one for *N,N*-dimethylformamide, and is shown in Fig. 3 (curve 5). This resolution gives a peak at 460 *mμ* and  $\epsilon_{\max}$  of 1369 for the iodine band of the complex.

With the solutions used to determine the equilibrium constant the charge-transfer peak was hidden by the absorption of the disulfide. By reducing the disulfide concentration to 0.00200 *M* and increasing the iodine concentration to 0.00200 *M* an absorption curve was obtained, as shown in Fig. 5, which had an inflection indicating the location of the charge-transfer peak. In this solution the concentration of the complexed iodine should be very small compared to that of the free iodine. Then by subtracting off the absorption due to both free iodine and free disulfide the resultant charge-transfer band was constructed and gave a smooth curve with a peak at about 304 *mμ* (curve 4 of Fig. 5), which is about the same position as the charge-transfer peak of the diethyl sulfide-iodine complex, and  $\epsilon_{\max}$  of 15,000.

**Di-*t*-butyl Peroxide.**—Three *n*-heptane solutions of iodine at 0.506 *mM* have been measured containing 90, 50 and 20 volume per cent. of di-*t*-butyl peroxide. The absorption due to the peroxide does not permit any measurement of the ultraviolet charge-transfer band to be made. However, the slight shift of the iodine band indicates that the di-*t*-butyl peroxide interacts very weakly with iodine. Even for the solution which contains 90 volume per cent. peroxide the shift is only about 20 *mμ*.

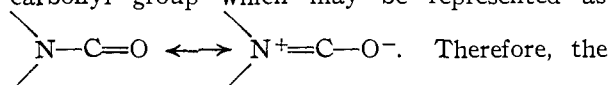
## Discussion

**Amides.**—Since aliphatic amines are among the strongest organic bases, their interaction with iodine might be expected to be relatively great. In fact, the iodine complex with triethylamine<sup>13</sup> is known to have the largest  $\Delta H^0$  value ( $-12.0$  kcal./mole) of all the iodine complexes whose  $\Delta H^0$ 's are known. As reported in a previous paper,<sup>10</sup>  $\Delta H^0$  for the iodine-*N,N*-dimethylaniline complex is  $-8.2$  kcal./mole. It was concluded in that paper that the nitrogen lone pair is the main site of donor action in *N,N*-dimethylaniline.

Two reasons can be considered for the decrease of the donor strength of dimethylaniline compared to triethylamine. First, by conjugation the lone pair orbital in dimethylaniline is spread to a certain extent over the benzene ring and consequently its overlap with the vacant molecular orbital of iodine is decreased. Second, the stabilization in the aniline molecule due to the conjugation between the lone pair and the ring is decreased by the intermolecular charge-transfer, and this will partly cancel the  $\Delta H^0$  for the complex formation.

(13) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

The amide molecules are almost planar,<sup>14</sup> and there is resonance between the nitrogen and the carbonyl group which may be represented as



Therefore, the donor strength of amides at the nitrogen atom is expected to be smaller than that of the alkyl amines for the same reason as given for the anilines. In the case of amides, a still larger decrease of the donor strength of the nitrogen atom is expected because of the large electronegativity of the carbonyl group. This may be the reason why the amide-iodine complexes have smaller  $-\Delta H^0$  values than the aniline-iodine complexes.

There is another possibility, namely, that a lone pair of oxygens may have a greater donor strength toward iodine than the nitrogen atom of the amide. It is known that aliphatic ketones are rather weak donors. The  $\Delta H^0$  of the iodine-acetone complex, for instance, has not been determined either spectroscopically or calorimetrically, but its  $K$  at 30° in carbon tetrachloride has been determined from infrared measurements to be 0.28 (l./mole.<sup>15</sup> The  $K$ 's for ethyl alcohol and diethyl ether are both larger than this (0.37 and 0.76 l./mole at 30°, respectively) and their  $\Delta H^0$ 's are -2.1 and -4.3 kcal./mole, respectively.<sup>16</sup> Hence we would expect that the  $\Delta H^0$  for the iodine-acetone complex would be less than 2 kcal./mole. Although this value is much smaller than the experimental  $\Delta H^0$  for the amide-iodine complexes, it is expected that the amide resonance would increase the electron density at the oxygen atom and fortify the donor strength of the oxygen lone pair.

Infrared studies of amide-metal ion complexes by Muetterties,<sup>2</sup> and n.m.r. studies of amides in sulfuric acid<sup>3</sup> and of an amide- $\text{BCl}_3$  complex<sup>4</sup> suggest strongly that the oxygen atom in amides acts as the donor toward electron acceptors.

**Sulfide, Disulfide and Peroxide.**—Tideswell and McCullough measured the equilibrium constant for the formation of the iodine-dimethyl sulfide complex in carbon tetrachloride.<sup>6</sup> Their value at 25° is 71 l./mole which is considerably smaller than the  $K$  value for the iodine-diethyl sulfide complex at 30° obtained in the present work. This is understandable as a result of greater electron release by the ethyl group as compared to the methyl group.

The present results indicate that diethyl sulfide has a much greater donor strength than the corresponding ether. The  $\Delta H^0$  obtained for the sulfide is -7.82 kcal./mole compared to -4.3<sup>1,16</sup> and -4.2<sup>17</sup> kcal./mole for the ether. Also, as shown in Table III, the visible band is shifted more toward the blue in the sulfide complex than in the ether complex. These results indicate a stronger complexing for the sulfide compared to the ether.

(14) (a) From microwave work with formamide the H-N-H plane is shown to form an angle of 15° with the N-C-O plane. This means that the axis of the lone pair orbital of nitrogen also makes a small angle with that of the  $\pi$  orbital of the carbonyl group. (b) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

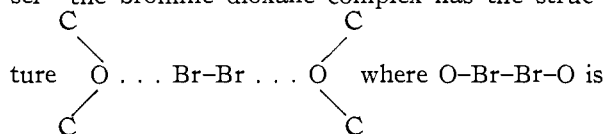
(15) H. Yamada and K. Kozima, *J. Am. Chem. Soc.*, **82**, 1543 (1960).

(16) P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1192 (1957).

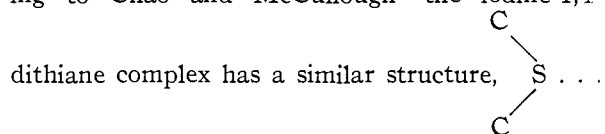
(17) M. Brandon, M. Tamres and S. Searles, *J. Am. Chem. Soc.*, **82**, 2129 (1960).

The iodine-dimethyl selenide complex has still larger  $K$  and  $\Delta H^0$  values; according to McCullough and Zimmerman<sup>9</sup> the  $K$  at 15.3° is 910 l./mole and  $\Delta H^0$  is -8.5 kcal./mole. It may be expected that the decreasing ionization potentials of the  $\text{Et}_2\text{X}$  type molecules in the order  $\text{X} = \text{O}, \text{S},$  and  $\text{Se}$  play a part in the above-mentioned order of donor strengths. According to Walsh and Price,<sup>18</sup> the observed lowest ionization potentials of diethyl sulfide and diethyl ether are 9.3 and 10.2 e.v., respectively. Their difference is 0.9 e.v. Although their value for diethyl ether is 0.7 e.v. higher than that of Watanabe,<sup>19</sup> it seems to be true that the sulfides have smaller ionization potentials than the ethers. The wave lengths of the charge-transfer peaks of the iodine complexes with these donors are also found to be separated by an amount corresponding to 0.9 e.v.

The structures of some halogen complexes with ethers and with sulfides in the solid state have been determined by X-ray analysis. According to Hassel<sup>20</sup> the bromine-dioxane complex has the struc-



linear and the bromine molecule lies in a plane bisecting the C-O-C angle and its axis makes an angle of about 33° with the C-O-C plane. According to Chao and McCullough<sup>5</sup> the iodine-1,4-



I-I where I-I-S also is linear and the iodine molecule lies in a plane bisecting the C-S-C angle. However, it can be calculated from their data that the angle between the I-I-S line and the C-S-C plane is about 80° which is considerably larger than the corresponding angle in the bromine-dioxane complex.

The difference in the above-mentioned angles for the ether complex and the thioether complex may be due mainly to the difference in the crystal fields of these two complexes. But it might be due mainly to the spacial distribution and energy of the lone pairs which are considered to differ appreciably between ethers and thioethers, as is expected from the fact that the C-S-C angle in thioethers is considerably smaller than the C-O-C angle in ethers. The 3p-3d hybridization which is thought to be present in sulfides may also possibly play some role in this matter.<sup>21</sup>

Another interesting result obtained in the present research is that diethyl disulfide has a much smaller donor strength than diethyl sulfide. A very similar decrease of donor strength also has been found for di-*t*-butyl peroxide compared to diethyl ether. Although it was impossible to obtain the  $K$  and  $\Delta H^0$  values for the peroxide-iodine complex, it is clear

(18) A. Walsh and W. Price, *Nature*, **148**, 372 (1941).

(19) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(20) O. Hassel, *Proc. Chem. Soc.*, 250 (1957).

(21) R. S. Mulliken, *J. Am. Chem. Soc.*, **77**, 887 (1955).

from the very small change in the visible iodine band that this complex has a very small  $K$ .

The structures of the disulfides are not well established. Stevenson and Beach,<sup>22</sup> in their calculation of the structural parameters from an analysis of the electron diffraction data for dimethyl disulfide, assumed that the two C-S bonds lie in a plane and are *trans* to each other. On the other hand, Baudler<sup>23</sup> concluded from the Raman spectra of hydrogen disulfide that in this molecule the two H-S bonds are perpendicular to each other just like the two O-H bonds in hydrogen peroxide. This conclusion seems reasonable on account of the probably strong repulsion between the two lone pair  $p\pi$  orbitals of the sulfur atoms. However, in diethyl disulfide and di-*t*-butyl peroxide the structures are still in doubt. Anyway, by inspection of molecular models it appears that there is no steric repulsion toward an approaching iodine molecule in the case of diethyl disulfide, whatever the orientation of the S-C<sub>2</sub>H<sub>5</sub> groups around the S-S axis, and even in the case of di-*t*-butyl peroxide steric repulsion toward iodine does not seem to be large. Therefore, the decrease of the donor strengths of the peroxide and the disulfide should be explained in some other way.

Let us consider first the case where the two O-C bonds in peroxides or the two S-C bonds in disulfides are perpendicular to each other. In this case, the lone pairs on the oxygen or sulfur atoms are orthogonal to each other and no direct interaction exists between them. For this case the decrease of the donor strength may be explained in the following way. In an ether or a sulfide the donor properties of the oxygen or sulfur atom are enhanced by the inductive effect of the alkyl groups. In a peroxide or a disulfide this effect diminishes to approximately one half and the substitution of a more electronegative oxygen or sulfur atom for a carbon atom will diminish the electron density at the other oxygen or sulfur atom and hence decrease the donor strength at this other atom. Although from Pauling's electronegativity scale the sulfur atom has an electronegativity equal to that of carbon, it appears from the dipole moments of alkyl sulfides that a sulfur atom in a sulfide is more electronegative than a carbon atom. Also, the electronegativity calculated by Skinner and Pritchard, based on Mulliken's electronegativity scale, gives a larger value for sulfur than for carbon ( $sp^3$ ).<sup>24</sup>

Secondly, let us consider the case where the two lone pairs of the oxygen or sulfur atoms are parallel or at least not completely perpendicular. In this case, the two lone pairs can interact with each other and form two molecular orbitals, the one with the lower energy being symmetric and the other with the higher energy being antisymmetric with respect to the exchange of the two oxygen or sulfur atoms. The higher energy molecular orbital should have only a small overlap integral with a  $\sigma$  acceptor like I<sub>2</sub> because of its antisymmetric nature, while the

lower energy molecular orbital can have a strong overlap with a  $\sigma$  acceptor but has a higher ionization potential compared to the ether or sulfide. In this way the weak donor strength can perhaps be understood. Of course, the inductive effect mentioned above will also work in this case.

Both of these explanations imply an increase of the ionization potentials of the donating electrons in a disulfide or a peroxide compared to a sulfide or an ether. The experimentally found close agreement of the wave lengths of the charge-transfer peaks of the iodine-sulfide and iodine-disulfide complexes (Table III) may be partly explained by the change in the charge-transfer energy due to the resonance interaction of the "no bond" and "dative" wave functions (second order perturbation term) which gives a greater spectral transition energy, and hence shorter wave length, the stronger the complex, or by some other minor effects such as solvent effects, etc.

**General Features of the Spectra of Iodine- $n$ -donor Complexes.**—Table III shows the  $K$  and  $\Delta H^0$  of a number of iodine complexes with  $n$ -donors together with  $\lambda_{\max}$ ,  $\epsilon_{\max}$ , half width ( $\Delta\bar{\nu}_{1/2}$ ), oscillator strength ( $f$ ) and matrix element of the transition dipole moment ( $D$ ) of both the charge-transfer bands and the visible iodine bands of these complexes as obtained by the present authors and by others. From this table a certain number of regularities can be found, namely, as  $-\Delta H^0$  increases: (1)  $\epsilon_{\max}$ ,  $f$  or  $D$  of the charge-transfer band increases, (2)  $\lambda_{\max}$  of the visible iodine band decreases and (3)  $\epsilon_{\max}$ ,  $f$  or  $D$  of the iodine band increases. The quantities  $f$  and  $D$  are calculated by the formulas

$$f = 2,302.6 \frac{c^2 M_e}{e^2 N_0 \pi} \epsilon_{\max} \Delta\bar{\nu}_{1/2} = 4.319 \times 10^{-9} \epsilon_{\max} \Delta\bar{\nu}_{1/2}$$

and

$$D = \sqrt{10^8 \frac{C}{N_0} \frac{3\hbar}{8\pi^2 \bar{\nu}_{\max}} \epsilon_{\max} \Delta\bar{\nu}_{1/2}} = 0.9582 \sqrt{\frac{\epsilon_{\max} \Delta\bar{\nu}_{1/2}}{\bar{\nu}_{\max}}}$$

where  $c$  is the velocity of light in cm. sec.<sup>-1</sup>,  $M_e$  is the mass of the electron in g.,  $e$  is the charge of the electron in abs. e.s.u.,  $N_0$  is Avogadro's number,  $\hbar$  is Planck's constant in erg sec.,  $\epsilon_{\max}$  is the molar extinction coefficient at the peak of the band in l. mole<sup>-1</sup> cm.<sup>-1</sup>,  $\Delta\bar{\nu}_{1/2}$  is the half width of the band in cm.<sup>-1</sup> and  $\bar{\nu}_{\max}$  is the wave number at the peak of the band in cm.<sup>-1</sup>.

Rule 1 holds very well, with the one exception of the pyridine-iodine complex. This rule can be explained by the charge-transfer theory of Mulliken.<sup>25</sup> For rather strong complexes the intensity of the charge-transfer band is mainly determined by  $a^*b$ , where  $a^*$  and  $b$  are the coefficients of the following wave functions of the complex for the ground and excited states

$$\Psi_g = a\Psi_0 + b\Psi_{ct}, \text{ and } \Psi_e = b^*\Psi_0 - a^*\Psi_{ct}$$

where  $a \approx a^*$ , and  $b \approx b^*$

As the complex gets stronger  $a^*b$  increases and hence the intensity of the charge-transfer band is

(22) D. P. Stevenson and J. Y. Beach, *J. Am. Chem. Soc.*, **60**, 2872 (1958).

(23) M. Baudler, *Diss. Göttingen* (1946).

(24) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

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

TABLE III  
 THE SPECTRAL CHARACTERISTICS OF THE IODINE COMPLEXES WITH *n*-DONORS

Donors (solvent)	$K$ ( $20^\circ\text{C}$ ) (l. mole <sup>-1</sup> )	$-\Delta H^*$ (kcal. mole <sup>-1</sup> )	Charge-transfer band			Shifted visible iodine band						
			$\lambda_{\text{max}}$ ( $m\mu$ )	$\epsilon_{\text{max}}$ (l. mole <sup>-1</sup> cm. <sup>-1</sup> )	$\Delta\nu_{1/2}$ ( $\text{cm.}^{-1}$ )	$D$ (Debyes)	$\lambda_{\text{max}}$ ( $m\mu$ )	$\epsilon_{\text{max}}$ (l. mole <sup>-1</sup> cm. <sup>-1</sup> )	$\Delta\nu_{1/2}$ ( $\text{cm.}^{-1}$ )	$D$ (Debyes)		
<i>n</i> -Heptane <sup>a</sup>	~0	~0					522	897	3200	0.0124	1.17	
Carbon tetrachloride <sup>a</sup>	~0	~0					512					
Dichloromethane <sup>a</sup>	~0	~0					502					
Methyl alcohol <sup>16</sup> (carbon tetrachloride)	0.473	1.90	242.8	8,360	2300	0.0829	2.07	440	973	4250	.0179	1.29
Ethyl alcohol <sup>16</sup> (carbon tetrachloride)	0.451	2.10	243.3	10,800	2500	.117	2.46	443	1082	4500	.0210	1.41
Tri- <i>n</i> -butyl phosphate <sup>20</sup> ( <i>n</i> -heptane)	20.0	2.94	<220					456	1280	4200	.0232	1.50
<i>N,N</i> -Dimethylformamide <sup>a</sup> (dichloromethane)	1.13	4.03	<255	>7,000				441	1189	4300	.0221	1.44
Diethyl ether <sup>16</sup> (carbon tetrachloride)	0.971	4.30	249	5,700	6900	.170	2.99	468	873	4100	.0155	1.24
Diethyl ether <sup>17,21</sup> ( <i>n</i> -heptane)	1.16	4.2	252	5,650	6900	.168	3.00	462	950	4100	.0168	1.29
Diethyl disulfide <sup>a</sup> ( <i>n</i> -heptane)	5.62	4.62	304	15,000	7200	.466	5.49	460	1369	4100	.0242	1.54
Diethyl sulfide <sup>a</sup> ( <i>n</i> -heptane)	210	7.82	302	29,800	5400	.695	6.68	435	1980	4200	.0352	1.80
Pyridine <sup>22</sup> ( <i>n</i> -heptane)	269	7.8	235	50,000	5200	1.12	7.48	422	1320	4300	.0245	1.48
Dimethyl selenide <sup>7</sup> (carbon tetrachloride)	661	8.5 <sup>b</sup>						430	~2600	~4500	~.05	~2
Triethylamine <sup>14</sup> ( <i>n</i> -heptane)	6460	12.0	278	25,600	7700	0.851	7.09	414	2030	5700	.0501	2.10

<sup>a</sup> Present work.

expected to increase.<sup>26</sup> From this point of view the intensity of the charge-transfer band should reach a maximum when  $a \approx b$  and  $a^* \approx b^*$  and decrease for a very strong complex where  $b \gg a$ . From dipole moment measurements and assumed geometry of the triethylamine-iodine complex<sup>27</sup> and the pyridine-iodine complex,<sup>28</sup> it is calculated that  $b^2$  in these complexes is, respectively, about 59 and 25%. From these facts, keeping in mind that the  $b^2$ 's obtained here are rather rough, it can be seen that  $a^*b$  will be near its maximum for the triethylamine-iodine complex and about equal or smaller for the pyridine-iodine complex since the change in  $a^*b$  with  $b$  is rather small. Therefore, the observed strong intensity of the CT band of the latter complex apparently must be due to some other cause. It is interesting to see that the  $f$  values of the CT bands of some of the strong complexes shown in Table III are quite large, comparable to those of the strong intramolecular CT bands.

Rule 2 has more exceptions but the general trend toward decreasing  $\lambda_{\text{max}}$  is clear. The reason why rule 2 holds already has been discussed by Mulliken.<sup>29</sup> Rule 3 also holds roughly. The reason why this rule holds is not clear at present but a plausible explanation would be that the wave function of the upper level of the iodine band receives an admixture of that of the charge-transfer band, so that the iodine band acquires added intensity, which becomes stronger for stronger complexes, from the latter. The deviations from rule 3 might then be attributable to effects of variations in geometry on the extent of mixing of the two wave functions.

(26) For weak complexes such as those between iodine and aromatic hydrocarbons  $b$  is very small, and part of the intensity of the observed CT band is believed to be caused by a different mechanism.<sup>14</sup> J. N. Murrell, *J. Am. Chem. Soc.*, **81**, 5037 (1959).

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

(28) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3860 (1954).

(29) R. S. Mulliken, *Rec. Trav. Chim.*, **75**, 845 (1956).

It is remarkable that both the visible and ultraviolet bands of the iodine-diethyl ether complex have  $\epsilon_{\text{max}}$  values that are much smaller than those of the other iodine complexes having about the same  $\Delta H^0$  values. That two different measurements for this complex have given about equal  $K$ ,  $\Delta H^0$  and  $\epsilon_{\text{max}}$  values seems to prove that these measurements are fairly accurate. At present it seems difficult to explain why the  $\epsilon_{\text{max}}$ 's are so small.

As can be seen in the table, the  $K$  values generally parallel the  $-\Delta H^0$  values, except for the tri-*n*-butyl phosphate complex. The quite large  $K$  value of this complex compared to those of other complexes having the same order of magnitude for  $\Delta H^0$  seems to suggest that this complex may be rather different in nature from the other iodine complexes.

The half width of both the CT and visible iodine bands broadens rather remarkably as the complexes become stronger. Although this broadening seems to be related to the shape of the potential energy curves of the upper states (CT and iodine excited states), with respect to the internuclear distance, a detailed discussion of these phenomena is rather difficult at present. The broadening of the iodine band may be related to the blue shift caused by the complexing, which was explained by Mulliken<sup>29</sup> as due to the exchange repulsion between the "swollen" excited iodine molecule and the donor molecule; namely, this repulsion changes the upper state potential energy of the complex, with respect to the internuclear distance near its equilibrium point, causing not only a blue shift of the iodine band as a whole but a broadening of the band, and as the complexing becomes stronger the broadening of the band, according to this explanation, will probably be increased. Further consideration of the cause of the broadening of both the CT and

(30) H. Tsubomura and J. M. Kliegman, *J. Am. Chem. Soc.*, **82**, 1314 (1960).

(31) M. Tamres and M. Brandon, *ibid.*, **82**, 2134 (1960).

iodine bands seems to be worthwhile for a better understanding of the nature of these upper states.

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[CONTRIBUTION OF THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT, AND UNIVERSITY OF MISSOURI, COLUMBIA, MISSOURI]

## The Acid Decomposition of Tris-(2-pyridinalalkylimine)-iron(II) Compounds<sup>1</sup>

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The rate of acid dissociation of tris-(2-pyridinalalkylimine)-iron(II) compounds is first order in complex over at least 95% of the reaction. No intermediates were observed indicating that the rate of dissociation of the first ligand  $k_1 \gg k_2$  or  $k_3$ . The acid dependence parallels that of  $[\text{Fe}(\text{bipy})_3]^{+2}$  and may be explained on the basis of either "half-bonded" or "protonated" intermediates. With either intermediate, complete ligand dissociation apparently precedes hydrolysis of the Schiff base. Evidence is presented for the existence of paramagnetic "protonated" species in concentrated acid solutions. The rate of decomposition is dependent on the alkyl group and increases in this order: (MePI), (EtPI), (BuPI), (PrPI). Thus the rate is inversely proportional to the base strength of the amine. Evidence for isomerization is presented with (QEtPI) and a large difference in rate of dissociation is noted between the isomers.

### Introduction

In recent years there has been considerable interest in the mechanism of the formation and decomposition of  $[\text{Fe}(\text{o-phen})_3]^{+2}$  and  $[\text{Fe}(\text{bipy})_3]^{+2}$ .<sup>3-7</sup> Although the decomposition of the former is essentially acid independent, there is an important  $\text{H}^+$  dependence in the latter. This has been explained on the basis of the greater flexibility of the ligand allowing one coordinating nitrogen to dissociate while leaving the other intact ("half-bonded" structures).<sup>5,6</sup> Another postulated intermediate is the "protonated" species.<sup>3,4</sup> Mechanisms based on either intermediate will satisfy the  $\text{H}^+$  dependence of the dissociation of  $[\text{Fe}(\text{bipy})_3]^{+2}$ , but it is necessary to assume the presence of a large fraction of the total complex in the "protonated" form using the latter concept. The inability of several investigators to demonstrate the presence of "protonated" species lends credence to the alternate mechanism. It has been shown<sup>8</sup> that 2-pyridinalalkylimines form compounds with Fe(II) which are structurally similar to  $[\text{Fe}(\text{bipy})_3]^{+2}$ . It was thought that kinetic studies of the decomposition of a series of these compounds might distinguish between the "half-bonded" and "protonated" intermediates. Since the mechanism presented by Basolo, *et al.*,<sup>6</sup> and supported by Krumholz<sup>5</sup> postulates the partial regeneration of the original complex from the "half-bonded" intermediate and since Schiff bases are known to hydrolyze rapidly in acid solution,<sup>9</sup>

the rate of dissociation might be expected to include a contribution from the hydrolysis of the "half-bonded" intermediate and thus have a modified  $\text{H}^+$  dependence.

Since the ligands are unsymmetrical, two isomers of the tris-complexes are possible. It was of interest to determine whether both isomers are formed and to what extent their rates of dissociation differ. For this purpose, the *n*-propyl derivative was selected as having sufficient size to give isomers with measurable solubility differences while steric effects would not unduly affect the stability. While the major emphasis was on (PrPI),<sup>10</sup> various other alkyl-2-pyridinalimines were studied for a comparison.

### Experimental

$[\text{Fe}(\text{o-phen})_3]^{-2}$  and  $+3$  and  $[\text{Fe}(\text{bipy})_3]^{+2}$  and  $+3$  perchlorates were prepared by methods in the literature.<sup>11</sup>

The alkyl-2-pyridinalimine complexes of the type  $[\text{Fe}(\text{RPI})_3](\text{ClO}_4)_2$  were all prepared by the same general method. To 0.1 mole of pyridine-2-aldehyde dissolved in 50.00 ml. of acetone was added 0.09 mole of the amine (with the lower boiling amines the equivalent amount of a concentrated water solution of the amine was used). After standing at room temperature for 15 minutes, 0.10 mole of  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  dissolved in 50 ml. of water was added. The deeply colored solution was stirred for 15 minutes, filtered to remove suspended particles and slowly treated with a slight excess of 20% aqueous  $\text{NaClO}_4$  to precipitate the product. Recrystallization from water (occasionally containing  $\text{NaClO}_4$ ), followed by drying under vacuum at room temperature gave dark purple micro-crystals. The yields varied from 20–90% of theoretical depending on the solubility characteristics.

$[\text{Fe}(\text{PrPI})_3](\text{ClO}_4)_2$ : a mixture of 0.29 g. of *n*-propyl amine and 0.60 g. of pyridine-2-aldehyde was added to 0.50 g. of  $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$  dissolved in 100 ml. of water. After filtration and cooling to 0°, an excess of chlorine was added. Four ml. of a 30% aqueous  $\text{NaClO}_4$  solution was slowly

(1) Taken in part from the Ph.D. thesis of Edward A. Healy, University of Connecticut, 1958.

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(3) J. H. Baxendale and P. George, *Nature*, **162**, 777 (1948); **163**, 725 (1949); *Trans. Faraday Soc.*, **46**, 736 (1950).

(4) P. Krumholz, *Nature*, **163**, 724 (1949); *Anais. acad. brasil. cienc.*, **22**, 263 (1950).

(5) P. Krumholz, *J. Phys. Chem.*, **60**, 87 (1956).

(6) F. Basolo, J. C. Hayes and H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 3807 (1954).

(7) E. A. Healy and R. K. Murmann, *ibid.*, **79**, 5827 (1957).

(8) J. C. Bailar, Jr., and D. H. Busch, *ibid.*, **78**, 1137 (1956).

(9) This was substantiated by measurements in our Laboratories.

(10) (MePI), (EtPI), (PrPI), (BuPI), (*i*-PrPI), (QEtPI) and (AQPI) refer to 2-pyridinalalkylimines in which the alkyl group is methyl, ethyl, *n*-propyl, *n*-butyl, *i*-propyl,  $\alpha$ -phenylethyl and 8-aminquinoline, respectively; (o-phen) = 1,10-phenanthroline, (bipy) = 2,2'-bipyridine.

(11) F. P. Dwyer and E. C. Gyrfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 263 (1950); F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).