STUDIES ON POSITIVE IODINE

by

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Submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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October, 1950

I should like to express my appreciation to Dr. Jacob Kleinberg and Dr. Calvin A. VanderWerf for their keen interest and guidance during the course of this work.

I should also like to thank the Upjohn Company and the University of Kansas for their financial aid during part of this work.

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INTRODUCTION

The halogens, especially fluorine and chlorine, are strongly electronegative, and form negative ions:

$$X_2 + 2e^- \rightarrow 2X^- .$$

With increasing size of the halogen atom, there is a decrease in electronegativity as is evidenced by the decreasing ionization potential and electron affinity. Iodine, the most electropositive of the halogens, has actually been shown to possess a unipositive oxidation state. Coordination compounds in which this oxidation state is exhibited have been prepared by the following reactions:

$$(1) \quad RCOOAg + I_2 + Py \rightarrow AgI + RCOOIPy$$

$$(2) \quad 2RCOOHg + 3I_2 + 6Py \rightarrow 2(HgI_2 \cdot 2Py) + 2RCOOIPy$$

The conductivity of solutions of iodine in various "active" solvents, i.e., those solvents in which iodine gives a brown solution, such as pyridine, has been explained theoretically on the basis of the dissociation of the dissolved iodine into positive and negative ions. The absorption spectra of such solutions have also been studied and the observed bands have been interpreted as being due to the formation of iodine-solvent complexes <u>via</u> the free electron pair.

The investigation herein described was undertaken

for the following reasons: (1) to study the mechanism by which free acid is formed in the reaction of iodine with heavy metal carboxylates in the presence of tertiary amines, and (2) to study the absorption spectra of pyridine coordinated positive iodine compounds to see whether they could be correlated with the spectrum of iodine in pyridine.

* * * *

HISTORICAL

A. The Positive Character of the Halogens

The concept of positive halogens is extremely useful, especially in explaining the mechanisms of various organic reactions. A careful distinction must be made, however, between the physical and chemical behavior of compounds in which the halogens merely exhibit some properties characteristic of the electro-positive elements, and those compounds in which the halogen is actually the cationic portion of the molecule. An attempt to clarify this distinction will be made in the succeeding discussion.

Cofman (1), in his study of the iodination of phenols with iodine monochloride, suggested that the hypoiodous acid formed by the reaction of iodine monochloride with water,

$$ICl + H_2O \rightleftharpoons IOH + HCl$$

was the active intermediate and that this substance functions as a labile base. He further postulated that the iodination of phenols is due to the presence of the iodine in the unipositive state and suggested the following mechanism for the reaction:

$$C_6H_5ONa + I_2 + H_2O \rightarrow C_6H_5OH + NaI + IOH$$

$$C_6H_5OH + IOH \rightarrow C_6H_4IOH + H_2O$$

Nef (2) reported that bromo- and chlorocyanogen gave potassium bromide and chloride, respectively, when boiled with potassium hydroxide, whereas iodocyanogen formed potassium iodate and iodide. These observations suggest that in these compounds the bromine and chlorine are negative whereas the iodine is positive. Chattaway and Wadmore (3) studied the action of hydrohalic acids on iodocyanogen and showed that the iodine has a positive character. The reactions they studied may be summarized in the following equations:

a. $\overset{-}{Br}\overset{+}{C}N + 2\ KOH \rightarrow KOCN + KBr + H_2O$

b. $\overset{-}{Cl}\overset{+}{C}N + 2\ KOH \rightarrow KOCN + KCl + H_2O$

c. $\overset{+}{I}\overset{-}{C}N + 2KOH \rightarrow KCN + KOI + H_2O$

$3KOI \rightarrow KIO_3 + 2\ KI$

d. $\overset{+}{I}\overset{-}{C}N + HCl \rightarrow HCN + \overset{+}{I}\overset{-}{C}l$

Clark and Streight (4) studied the electrolysis of cyanogen halides in the following solvents: acetonitrile, nitrobenzene, methanol, ethylene glycol, furan, pyridine, aniline, benzene, ethanol, quinoline, and pyrrole. In

every case, except in solutions of cyanogen iodide in pyridine, where iodine migrated to the cathode, the halogen was liberated at the anode.

Cyanogen iodide seems to behave as an electromer, ionizing reversibly as follows: $\overset{+}{I}\cdot\overset{-}{C}N \rightleftharpoons \overset{-}{I}\cdot\overset{+}{N}C$

Clark and Streight brought out the fact that while there is no direct correlation between the concentration of the two electromers present in the solution and the dielectric constant of the solvent, the latter does play an important and undetermined role in characterizing the behavior of the iodine.

B. Coordination Compounds of Positive Iodine

Carlsohn and co-workers (5) pioneered in the field of coordination compounds of positive univalent iodine. Reasoning that if in IOH the iodine does function as a cation, they concluded that such a cation might be stabilized by coordination with pyridine. They succeeded in preparing a series of salts of the hypothetical bases IPyOH and IPy_2OH.

In 1924, Carlsohn was able to isolate the stable salt $I(Py)_2ClO_4$ by the reaction of silver perchlorate with iodine in the presence of pyridine using chloroform as a solvent. The same compound was prepared from the mercurous salt using benzene as a solvent. Utilizing these reactions, Carlsohn prepared the following coordination compounds of inorganic acids:
IPyOH, $IPyNO_3$, $I(Py)_2OH$, $I(Py)_2ClO_4$, $I(Py)_2NO_3$, $I_2(Py)_3SO_4$, $I(Py)_2HPySO_4$.

He also showed that substances of the type RCOOI could also be stabilized by coordination with pyridine to form compounds of the type I(Py)OOCR. The reaction by which he prepared these compounds is the following:

$$RCOOAg + I_2 + Py \xrightarrow{CHCl_3} I(Py)O-\overset{\overset{O}{\|}}{C}-R + AgI$$

If the mercurous salt is used in benzene solvent, the

same product is obtained.

$$(RCOO)_2Hg_2 + 3I_2 + 6Py \rightarrow I(Py)\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R + 2(HgI_2 \cdot 2Py)$$

Carlsohn prepared a whole series of these compounds and made a thorough study of their properties. He found that these compounds liberate iodine from potassium iodide, and in the presence of water undergo autooxidation-reduction, forming iodine and pyridinium iodate. They immediately attack an acidic solution of phenol to yield iodophenol. Carlsohn tested the hypothesis of Finkelstein(6), who measured the decomposition potentials of ICl, IBr and ICl_3 and the electrode potentials of these substances against the iodine electrode. His measurements demonstrated that the I^+ ion should be placed with the noble metals in the electromotive series. Treatment of a chloroform solution of dipyridine iodine (I) nitrate with metallic zinc, iron, magnesium, copper, silver, gold and mercury, revealed that all were immediately dissolved. It cannot be said that iodine is more noble than silver since the iodine coordination compound is prepared by the replacement of silver with iodine. Apparently, in the case of silver, the reaction can go both ways. The reaction probably proceeds in both directions because in either case the precipitation of silver iodide removes the replaced element from the reaction.

Carlsohn also found that when an electric current

is passed through methanol or chloroform solutions of these compounds, the iodine migrates toward the cathode. This is excellent evidence that the iodine is the positive constituent of the salt.

In acetone and methanol, the nitrate complexes were found to have appreciable conductance and their conductivity was not found to be appreciably affected by the addition of pyridine. The conductivity of the benzoate however, was found to be increased tremendously by the addition of pyridine. The nitrate ion is an extremely poor coordinating ion and would not be expected to form a coordinate bond as easily as the benzoate ion. The nitrate is without any doubt more salt-like and ionic and considerably more highly dissociated.

Zingaro, et. al. (7) studied the reaction of silver carboxylates with iodine in the presence of various tertiary amines and made the following observations: (1) certain of the positive iodine salts could not be prepared, or only in very low yields and (2) even under extremely anhydrous conditions, the formation of free acid is a competing reaction. These two observations have been at least partially explained in this work.

C. The Nature of Iodine Solutions

Solutions of iodine in pure solvents can broadly be classified into two groups according to color. Hydrocarbons, chloro- and bromohydrocarbons and carbon disulfide give violet solutions with iodine, whereas alcohols, ethers, ketones, organic acids, nitriles, nitrogen bases and certain sulfur compounds dissolve iodine to form brown solutions. On the basis of careful molecular weight determinations, Beckmann (8) showed that iodine is present in the diatomic state in both types of solvents.

The physical properties of brown solutions differ markedly from those of the violet. In general, iodine is much more soluble in solvents which give brown solutions than in others. Hildebrand and co-workers (9) have shown that the violet solutions form a series of "regular solutions", i.e., solutions which are formed from their components with the same change in entropy as occurs in the formation of an ideal solution of the same concentration. Studies of solubility curves of brown solutions indicate that new molecular species are formed in such solutions. The heats of solution of iodine in solvents which form brown solutions are much higher than the values in violet solutions (10).

A great deal of spectrophotometric work has been

carried out for the purpose of obtaining further information concerning the nature of violet and brown solutions. The latter are non-absorbing at the red end of the spectrum, but absorb heavily in the violet, whereas the former absorb strongly in the longer wave-length portion of the visible spectrum and transmit both violet and all the infrared light beyond 1200 mμ. Violet solutions have an absorption spectrum very similar to that of iodine vapor; and the spectrum of brown solutions at elevated temperatures shows a shift of equilibrium toward the region where absorption is observed for violet solutions. Getman (11) found that in the visible region of the spectrum, these solutions fall into two groups: violet, with absorption maxima ranging from 520 mμ to 540 mμ as in n-C_6H_{14}, benzene, toluene, carbon disulfide, carbon tetrachloride, chloroform, and nitrobenzene; and brown, with maxima from 460 to 480 mμ as in ethyl alcohol, isopropyl alcohol, acetone, acetophenone pyridine and water. Getman also confirmed previous observations that the spectra of brown iodine solutions change with time.

Most investigators have assumed that in brown solutions, the iodine exists chemically bound with the solvent in equilibrium with free iodine. This seems to be a logical assumption in view of the fact that each of the solvents in which iodine forms brown solutions

contains an element, e.g., nitrogen, oxygen or sulfur, capable of a forming a coordinate covalent bond by virtue of the free electron pair.

Hildebrand and Glascock (12) have presented the most convincing evidence for the existence of solvated iodine in brown solutions. They studied the freezing point of solutions of iodine in an "inactive" (violet) solvent and the change in freezing point brought about by the addition of a small amount of a third substance, itself being either an "inactive" or "active" (brown) solvent. They showed that only in the case of the "active" solvents did a large deviation from the calculated freezing-point lowering occur. In those cases in which the lowering is less than that calculated for the iodine on the basis of the dilution law, these investigators concluded that there must be at least partial combination of iodine with the second solvent.

The precise nature of the binding between the iodine and the solvent molecule is not yet well understood. Conductivity studies by Audrieth and Birr (13) have shed some light on the nature of the binding between iodine and pyridine. They found a steady increase in conductivity of such solutions with the passage of time. In a very dilute solutions, a constant value is quickly obtained, and the limiting molar conductance of 130-132 is twice as great as can be explained on the basis of a simple dissociation into positive and negative ions. To explain

the experimental data, the authors postulate the gradual conversion of the initially formed, non-conducting addition compound into a ternary salt, and believe that solutions of iodine in pyridine contain the following species in equilibrium:

$$Py + I_2 \rightleftharpoons IPy^+ + I^- \rightleftharpoons Py^{++} + 2I^-$$

$$2(Py \cdot I_2) \rightleftharpoons IPy^+ + I \cdot PyI_2^-$$

Fairbrother, in some recent investigations (14) on the dielectric polarization of iodine in violet and brown solutions, has presented evidence in support of the hypothesis of Audrieth and Birr. His results indicate that the formation of a red or brown solution is accompanied by polarization of the iodine molecule. The proximity of an electron-donor may very well stabilize one of the possible ionic structures, $\overset{+}{I}$--$\overset{-}{I}$ and $\overset{-}{I}$--$\overset{+}{I}$, of an iodine molecule. Thus, if a partial polarization of the iodine molecule takes place, the positive end of the molecule may be stabilized by coordination with a molecule of the solvent.

Iodine in brown solutions is much more reactive than that in violet solutions. The iodine in violet solutions can be activated by the addition of solvents which change the color of such solutions to brown.

Brown solutions of iodine in ether, alcohol, dioxane, cyclohexanol and cyclohexene have been found to react with

the silver derivative of saccharin to precipitate the theoretical amount of silver iodide. Violet solutions have been found to react only very slowly or not at all.

EXPERIMENTAL

1. Preparation of Some New Positive Iodine Compounds

A. Preparation of the Reagents

The acids used either were Eastman white label products or were purchased from the Department of Chemistry of the University of Illinois. All the acids were subjected to a series of recrystallizations from ethanol-water mixtures until a product giving the correct melting point on succesive recrystallizations was obtained.

Pyridine and α-picoline were dried over sodium hydroxide pellets for several days and distilled through a three foot column packed with berl saddles. The middle fractions were collected in both cases. The pyridine distilled at 114-115° and the α-picoline came over at 128°. Both were clear, colorless liquids and were stored in dark bottles capped with drying tubes containing potassium hydroxide.

Chloroform was stored over anhydrous calcium chloride for a period of two to three weeks and was distilled before each experiment.

Skellysolve-A was also stored over anhydrous calcium chloride and the necessary quantity was distilled and collected when it was required.

B. Preparation of the Silver Salts

The organic acid was dissolved in alcohol, with heating if necessary. To the alcoholic solution aqueous sodium carbonate was added until the solution turned just alkaline to litmus. The resulting solution was then made just acidic by the addition of dilute nitric acid. Any precipitated acid was removed by filtration.

To the clear, filtered solution there was added an amount of silver nitrate solution slightly in excess of that required for the complete precipitation of the acid. Cooling in an ice bath was found to give better yields of the silver salt. To further increase the yields the volumes were always kept small and the solutions concentrated.

The precipitate of silver salt was separated by filtration and washed with distilled water until a negative test for silver ion was obtained. The salt was then washed with alcohol and dried at 70° for at least twenty-four hours before use.

C. Method of Analysis of the Positive Iodine Compounds

Samples of 0.3 to 0.5 gram were weighed and treated with an excess of acidified 20% potassium iodide solution. The iodine released as a result of the following reaction

$$IPy^{+} + I^{-} \rightarrow I_2 + Py$$

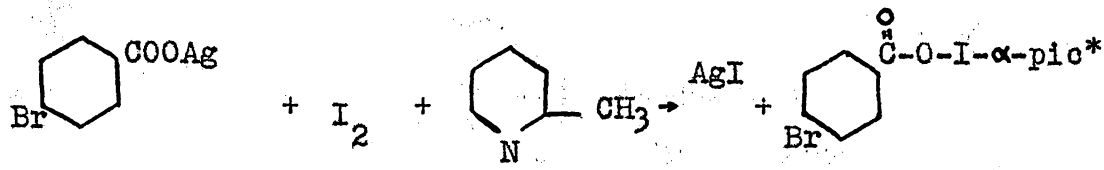
was treated with an excess of standard 0.05N sodium thiosulfate solution and then back-titrated with standard iodine solution using starch indicator.

D. Mono-α-picoline iodine (I) p-bromobenzoate

To a suspension of 155.6 grams (0.5 mole) of silver p-bromobenzoate contained in a 2-liter, 2-necked flask fitted with a mechanical stirrer, 125 grams (approximately 0.5 mole) of iodine crystals were added with efficient stirring. A large portion of the iodine reacted as was evident from the formation of silver iodide. Then 50 grams (0.53 mole) of α-picoline was added in small portions.

As the reaction proceeded, the addition of another 150 cc. of chloroform was necessary due to the formation of a very thick suspension. After twenty minutes of stirring, all the amine was added and the reaction appeared to be completed. The precipitate of silver iodide was removed by filtration and to the chloroform filtrate, contained in a four liter beaker, a liter of Skellysolve-A was added. A large amount of colorless precipitate, which was separated by filtration through a porous glass filter, separated. The precipitate was washed with Skellysolve-A and dry ether. After drying *in vacuo* over sulfuric acid for twenty-four hours, 156g. (0.37 mole) or 75% of mono-α-picoline iodine (I) p-bromobenzoate was obtained. The crystals decomposed at 119-121°.

Anal. Calc'd. for $C_{13}H_{11}O_2NIBr$: I,30.2, Found: I,30.2, 30.1.



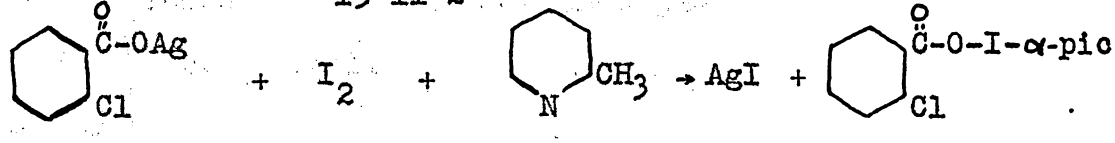
155.6 g.	125 g.	50 g.	156 g., 75 %
(0.5 mole)	(0.49 mole)	(0.53 mole)	(0.37 mole)

*pic will be used as an abbreviation for picoline throughout this report.

E. Mono-α-picoline iodine (I) o-chlorobenzoate

Fifty-five g. (0.21 mole) of silver o-chlorobenzoate was suspended in 500 ml. of chloroform. Fifty g. (0.20 mole) of iodine and 20 g. of (0.21 mole) of α-picoline were then added to this suspension. The mixture was stirred mechanically for 30 minutes after which time all the iodine had been consumed. Silver iodide was filtered off and the clear, chloroform filtrate was treated with two volumes of Skellysolve-A in a large Ehrlenmeyer flask and the flask was placed in the dry ice chest for 24 hours. A crop of pale yellow needles was formed; these were washed with dry ether and dried in vacuo over sulfuric acid. The dried material started to melt at 102° and was completely decomposed at 165°. The weight of the crystals was 34 g. (0.094 mole), corresponding to a yield of 45% of mono-α-picoline iodine (I) o-chlorobenzoate.

Anal. Calcd. for $C_{13}H_{11}O_2NICl$: I,33.8, Found: I,33.8

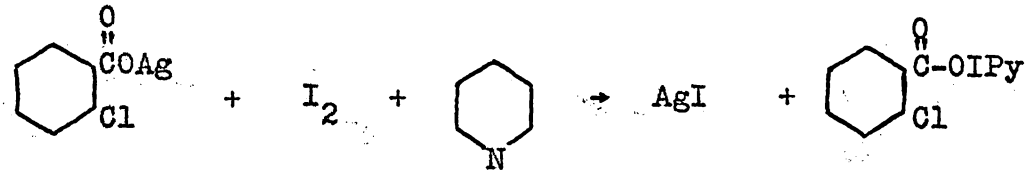


55.1 g.	50 g.	20 g.	34 g., 45%
(0.21 mole)	(0.20 mole)	(0.21 mole)	(0.094 mole)

F. Monopyridine iodine (I) o-chlorobenzoate

To a suspension of 221 g. (0.81 mole) of silver o-chlorobenzoate in one liter of chloroform were added 220 g. (0.80 mole) of iodine crystals and 80 g. (1.0 mole) of pyridine. The mixture was stirred by means of a stirring motor. The reaction proceeded rather slowly with the precipitation of silver iodide and considerable evolution of heat. When the color of the solution started to turn brown due to the dissolution of excess iodine, the mixture was filtered. The chloroform filtrate was treated with an equal volume of Skellysolve-A and placed in a Dry Ice chest for 48 hours. A deposit of orange crystals was formed which became almost colorless when washed with Skellysolve and dry ether. The product was dried in vacuo over sulfuric acid for twenty-four hours; the resulting material decomposed over a range of 91-95°. The yield of monopyridine iodine (I) o-chlorobenzoate was 129 g. (0.36 mole) or 45% of theoretical.

Anal. Calcd. for $C_{12}H_9O_2NICl$: I,35.1, Found: I,35.3, 35.1

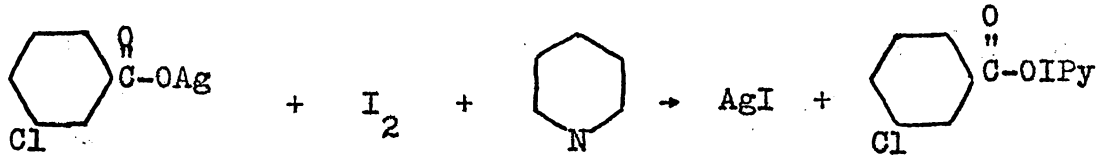


221 g.	220 g.	80 g.	129 g., 45%
(0.81 mole)	(0.80 mole)	(1.0 mole)	(0.36 mole)

G. Monopyridine iodine (I) m-chlorobenzoate

Two hundred twenty one grams (0.81 mole) of silver m-chlorobenzoate was added to a liter of chloroform and the suspension formed was stirred rapidly in order to make the suspension as homogeneous as possible. To the rapidly stirred mixture 220 grams (0.80 mole) of crystalline iodine and 80 grams (1 mole) of pyridine was added. The reaction proceeded rapidly and no large evolution of heat was noted, although some warming occurred. After some time, the solution started to turn brown and the mixture was filtered. The clear filtrate was treated with slightly more than an equal volume of Skellysolve-A and placed in a Dry Ice chest for forty-eight hours. A large deposit of a colorless crystalline solid was formed which was washed with Skellysolve-A and dry ether. The crystals were dried in vacuo over sulfuric acid for twenty-four hours; the yield of monopyridine iodine (I) m-chlorobenzoate, decomposing at 94-97° was 148 g. (0.41 mole) or 51%.

Anal. Calcd. for $C_{12}H_9O_2NICl$: I,35.1, Found: I,35.1, 35.0.

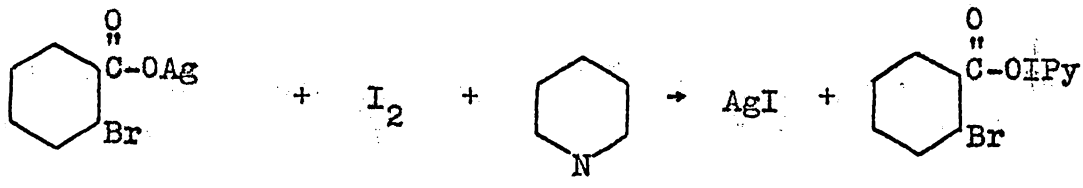


221 g.	220 g.	80 g.	148 g., 51%
(0.81 mole)	(0.80 mole)	(1.0 mole)	(0.41 mole)

H. Monopyridine iodine (I) o-bromobenzoate

In a two liter, two necked flask equipped with an automatic stirrer, 138 g. (0.44 mole) of silver o-bromobenzoate was suspended in one liter of chloroform. To the suspension 101 g. (0.40 mole) of iodine, and 40 g. (0.50 mole) of pyridine was added. The iodine was rapidly and completely consumed. The precipitated silver iodide was removed by filtration and the clear chloroform filtrate was diluted with two volumes of Skellysolve-A and allowed to remain in a Dry Ice chest for twenty-four hours. A pale yellow crystalline solid which was sashed with dry ether and dried *in vacuo* over sulfuric acid was deposited. The yield of monopyridine iodine o-bromobenzoate was 111 g. (0.30 mole) or 68%. The compound decomposed from 101-106°.

Anal. Calcd. for $C_{12}H_9O_2NIBr$: I,31.2, Found: I,31.2, 31.2



138 g.	101 g.	40 g.	111 g., 68%
(0.44 mole)	(0.40 mole)	(0.50 mole)	(0.30 mole)

II. The Decomposition Reactions of Positive Iodine Compounds

A. To a suspension of 237 g. (0.9 mole) of silver m-chlorobenzoate in 1200 cc. of chloroform contained in a 3-liter, one-necked flask there was added, with vigorour stirring, 223 g. (slightly less than 0.9 mole) of iodine. An immediate precipitation of yellow silver iodide was noted. Pyridine, 83 ml. (approximately 1 mole) was then added. After the mixture had been stirred mechanically for one hour, the precipitate was filtered off and the chloroform filtrate collected and distilled, while the pot temperature was held below 65°. To the residue remaining in the flask after removal of the chloroform, there was added 200 ml. of ether and the mixture refluxed for seventy two hours. The mixture was then thoroughly shaken and filtered. A tarry residue remained which was extracted with an additional 100 ml. of ether, filtered, and the ether extracts combined.

The ethereal solution was extracted with a 20% solution of sodium thiosulfate until further extraction caused no further change in the yellow color of the ether solution. This was followed by a series of extractions with 5% sodium carbonate solution and then with water. The ether solution was finally treated with five 20 ml. portions of 20% hydrochloric acid. The two phases were separated and the ether solution (II-A-1) dried over

sodium sulfate.

The acid extract was evaporated to one fifth of its original volume on a steam bath and the concentrated solution was cooled in an ice bath. Ammonia gas was bubbled through the cold solution until the solution turned alkaline to litmus. Along with the strong odor of pyridine, a brown precipitate was noted. This precipitate was separated by filtration and was found to sublime readily to give 1.2 g. of colorless needles, extremely volatile and possessing a strong, unpleasant odor. The crystals melted sharply at 52.8-53.2°. When chlorine was bubbled through an ice cold chloroform solution of these crystals, a bright yellow precipitate was formed melting at 127.3-129.1°. The melting point of 3-iodopyridine is given as 53.5° and of the iodochloride as 128-130°. The yield of 3-iodopyridine corresponds to 0.63%.

Evaporation of II-A-1 yielded 12 ml. of a pleasant smelling liquid which on cooling in ice yielded a deposit of crystals that were separated by suction filtration and recrystallized from ligroin until they gave a constant melting point of 172-172.8°. Passage of hydrogen chloride gas through an ether solution of these

crystals yielded the hydrochloride, m.p. 193.9-194.7°. The melting point of 3,5-diiodopyridine is given as 171.5° and that of the hydrochloride is given as 195-196° (26).

Anal. Calcd. for $C_5H_3NI_2$: C, 18.14, H, 0.91, I, 76.70; Found: C, 18.61, H, 1.28, I, 76.21.

The yield of 3,5-diiodopyridine was 0.9 g. or 0.3%.

The liquid portion of II-A-1 was subjected to a careful vacuum distillation. A great deal of difficulty was experienced due to the presence of some iodine containing impurity which decomposed to give free iodine and thus contaminated the sample. After several successive distillations, a stable, colorless sample was obtained which came over at 74-75° at 0.5 mm. of Hg pressure. A portion was analyzed and the remainder was subjected to chemical tests. The liquid contained chlorine, but no iodine, and boiled at 242-244° at atmospheric pressure (744 mm.). The density was 1.19 and the refractive index 1.520. Hydrolysis with diethylene glycol and potassium hydroxide gave m-chlorobenzoic acid; which was easily isolated and identified from the residue. Distillation of the hydrolyzed material gave about 2 ml. of clear liquid which came over below 100° and which when placed over potassium

carbonate separated into two layers. The upper layer was separated and dried over potassium carbonate. The dried liquid reacted with acetyl chloride to give the definite odor of ethyl acetate and formed a solid derivative with 3,5-dinitro benzoyl chloride melting at 92-92.5°. The melting point of ethyl 3,5-dinitrobenzoate is 93°. The conclusion to be drawn from these observations is that the product is ethyl m-chlorobenzoate. A comparison of the physical constants reported for ethyl m-chlorobenzoate and those observed for the product isolated follow.

	Reported for ethyl m-chlorobenzoate	Found
Boiling Point	245	242-244
Density	1.22	1.19
Refractive Index	1.521	1.520
Analysis	C, 58.5	C, 57.1
	H, 4.9	H, 4.7
	Cl, 19.2	Cl, 19.1

The evidence for the product being ethyl m-chlorobenzoate is good, but not conclusive due to the low carbon analysis.

The experiment was repeated several times, and although the neutral fraction was always easily isolated, a pure sample could never be obtained due to continued contamination of the material by iodine which was

released even on gentle heating. If the liquid was redissolved in ether and warmed with Norite, a decolorized solution was obtained, but upon standing for just a few minutes the solution became colored. The presence of some unstable iodine compound is beyond doubt.

B. To 500 ml. of dry ether contained in a one-liter flask equipped with an efficient condenser, there was added 77.5 g. (0.21 mole) of monopyridine iodine (I)-o-chlorobenzoate and the mixture was refluxed for seventy two hours. At the end of this time, the ether extract was filtered off and treated exactly in the same manner as described for II-A-1.

In this manner, there was isolated and purified from the reaction mixture 1.2 g. (2.3%) of 3-iodopyridine which was identified in the manner previously described. No diiodopyridine was isolated.

The quantity of neutral fraction obtained was 1.5 ml. A pure sample could not be prepared, but hydrolysis of the sample showed that both o-chlorobenzoic acid and ethyl alcohol were contained in the original molecule.

C. In 500 ml. of chloroform there was suspended 127 g. (0.48 mole) of silver m-chlorobenzoate to which was added 101 g. (0.4 mole) of iodine and 46.5 g. (0.5 mole) of α-picoline. The mixture was stirred mechanically

for ½ hour until the iodine was consumed. The precipitated silver iodide was removed by filtration and the filtrate was distilled to remove the chloroform. The pot temperature was not permitted to go above 65°. The residue in the flask consisted of yellow crystals contaminated with a heavy brown liquid. To the residue 500 ml. of ether was added and the mixture was refluxed for seventy two hours. After this time, the ether was filtered off and extracted in the manner described in section II-A.

The acid fraction was evaporated to a small volume over a steam bath and ammonia gas was passed through the concentrated acid solution which had been cooled in an ice bath. A strong odor of α-picoline was present and in addition, a heavy brown oil separated out. This oil was separated by decantation and distilled at atmospheric pressure. The distillate came over at 210° and 1.7 g. of a pale yellow oil which was found to be easily soluble in 5% hydrochloric acid was collected. A portion of the oil was easily converted into the yellow picrate which on recrystallization from alcohol melted at 149°. Plazek and Rodewald (21) reported the boiling point of 5-iodo-2-methylpyridine as 205-215° and the melting point of the picrate as 150°. Thus, a yield of 1.7% of 5-iodo-2-methylpyridine was realized in this reaction.

D. Traces of 3-iodopyridine were isolated in the following runs, but the amounts were only sufficient for the purposes of identification: decomposition of monopyridine iodine (I) m-chlorobenzoate in ether; reaction of silver salts of o-iodobenzoic, o-toluic and m-toluic acids with iodine in the presence of pyridine.

Since it was found that monopyridine iodine(I) m-nitrobenzoate was not decomposed by refluxing in diethyl ether, dibutyl ether was used in order to provide a higher temperature for decomposition.

When 27.3 g. of monopyridine iodine(I) m-nitrobenzoate was refluxed with 200 ml. of dibutyl ether, no release of iodine was observed. Immediately upon cooling, 9.5 g. of colorless needles formed. These melted sharply at 122.9-123.5° and the melting point was not changed by recrystallization from alcohol-water mixtures. The crystals did not contain iodine.

Heating the crystals to 100° gave a strong odor of pyridine. When 5 g. of the crystals was heated in a distilling flask, one ml. of pyridine was collected. To establish definitely the fact that the liquid was pyridine, the picrate was prepared and found to melt at 166°. The literature gives 167° as the melting point of pyridinium picrate. The residue in the distilling

flask melted at 141-143° and gave a mixed melting point of 142-143° with an authentic sample of m-nitrobenzoic acid.

On the basis of the data, it is concluded that the crystalline compound formed when monopyridine iodine(I) m-nitrobenzoate is decomposed in butyl ether is pyridinium m-nitrobenzoate. The source of the hydrogen was not established.

DISCUSSION OF PARTS I AND II

The preparation of certain positive iodine compounds which previously could not be made (7) is dependent to a large degree upon solubility factors. By the simple process of crystallizing out the product at low temperatures, several of the compounds which could not be salted out at room temperature have been obtained in good to excellent yields.

A general, but very definite observation which was made and which should be mentioned is that all the o- and m-halo substituted derivatives were relatively unstable. It was found that these compounds turned yellow after a few days and after several weeks a deposit of iodine formed around the inside of the container. At the same time, all the p-halo substituted derivatives, as well as all the nitro compounds, which were prepared as white crystalline solids, showed absolutely no decomposition, even after standing in a desiccator for a period of six months. This indicates that the stability and ease of formation of the positive iodine compound is intimately related to the nature and position of the ring substituents.

It has already been reported (7) that the positive iodine complexes of amino, hydroxy and methoxy benzoic

acids cannot be prepared, but that decomposition products are obtained. The more extensive studies carried out in this investigation have shown that while the o and m-chloro and bromobenzoic acid positive iodine derivatives can be prepared, attempts to prepare the corresponding iodo or methyl derivatives were unsuccessful. Thus we see that there is a gradual transition in stability, i.e., the extreme stability of all the nitro and p-halo compounds, the absolute instability of the amino, hydroxy and methoxy and o- and m-iodo and methyl compounds and the intermediate stability of the o- and m-chloro and bromo compounds. This, of course, indicates that the stability of a positive iodine compound depends on the electron withdrawing power of the ring substituent. This is shown by the relative stability of the compounds just described. Perhaps, the most convincing evidence in favor of this conclusion is the ease of preparation and stability of the o- and m-chloro and bromo derivatives as compared with the iodo- and methyl derivatives. Here, in going from one group to another which is just slightly more electropositive, we come to a sort of "transition point" between stability and instability.

The reason for this behavior is probably due to the strong oxidizing power of the IPy^+ ion. In the case of

a strongly electron withdrawing group, like the nitro group, the cationic iodine is probably best satisfied by coordination with pyridine, i.e., this state best satisfies the electron seeking tendency of the electron-deficient iodine. On the other hand, when the substituent group is strongly electron donating, as in the case of the amino and hydroxy groups, the stability of the IPy^+ ion is substantially reduced, (because of the competition with the electron pair of the ring nitrogen) which arises from the "enriching" of ring positions due to resonance. Thus, in the latter case, the positive iodine has considerable opportunity to satiate its appetite for electrons by ring substitution or oxidation of the ring, rather than through coordination with pyridine.

The isolation of iodopyridine has shed some light on the mechanism of free acid formation which was observed in another investigation (7). A brief outline of the experimental procedure for obtaining this material is given in the following diagram.

Residue obtained by 1. reaction of a silver salt with iodine in the presence of pyridine (or α-picoline) after removal of silver iodide and evaporation of chloroform solvent, or 2. positive iodine compound, is refluxed with ether for seventy two hours and ether

filtered off from residue.

Extract ether with sodium thiosulfate to remove iodine. This is followed by washing with distilled water and then with dilute sodium carbonate to remove acid. Ether layer washed again with water and then with small portions of 20% hydrochloric acid.

Aqueous acid extract

Evaporate to small volume, pass ammonia through concentrated solution

Precipitate

Sublime

Colorless needles of 3-iodopyridine, melting point 53-54°.

Ice cooled solution of 3-iodopyridine in chloroform; pass chlorine gas.

Yellow precipitate of iodochloride, melting point 127-129°

Ether layer

Dry over sodium sulfate, filter and evaporate.

Pleasant smelling liquid which may yield precipate on standing

Separate by filtration.

Precipitate

Recrystallize from ligroin.

Colorless needles of 3,5-diiodopyridine, melting point 172-172.8°

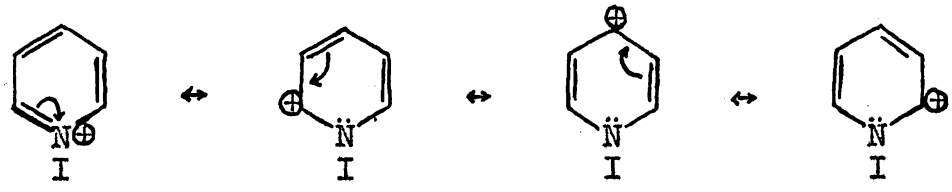
Pass dry hydrogen chloride through ether solution

Colorless precipitate, melting point 193.9-194.7°.

Liquid; may be ethyl ester of acid.

While the yields of 3-iodopyridine were very low, and in many cases, none of the product was obtained, or only in traces, it is possible that the low yields may be explained in part by the extreme volatility of the compound. For example, a full gram of 3-iodopyridine, when allowed to remain overnight on a porous plate, had completely evaporated. The greatest loss probably occurs during the evaporation of the chloroform or during the actual refluxing time. The type of reaction which brings about the formation of free acid may be described in the following equation:

The fact that iodination occurs exclusively in the three and five positions of the pyridine ring and the five position in α-picoline is good evidence for the following resonance in the IPy^+ ion which gives rise to activation in those positions.



This fact also suggests that the formation of 3-iodopyridine in the vapor phase iodination of pyridine may

involve a positive iodine mechanism.

As a result of the experiments performed, there has been obtained good, but inconclusive evidence for the formation of the ethyl ester of the acid, probably through splitting of the ether. It is apparent that the neutral fraction is contaminated with an unstable iodine compound inasmuch as a steady release of iodine is observed, even after the solution has been washed with thiosulfate. This factor presents the major difficulty in the ultimate identification of the neutral fraction.

The case of the decomposition of monopyridine iodine(I) m-nitrobenzoate in dibutyl ether is extremely interesting because there is no release of iodine observed. The good yields of pyridinium m-nitrobenzoate require the release of hydrogen. The hydrogen is most probably released as a result of the iodination of the ether.

Gomberg (24) and Birckenbach and Goubeau (25) have reported that perchloric acid is the main product of the reaction between equivalent quantities of silver perchlorate and iodine in ether as a solvent. They suggest that the ether is iodinated in the alpha position and the resulting product enters into reaction

with the silver salt to form the perchlorate ether. This is very easily decomposed and sensitive to light and moisture. In this work, it is possible that unstable iodination products were formed involving either the solvent and the amine, or both. In many cases, it was noted that the theoretical amount of iodine was not taken up, and often, after the filtrate was separated from the silver iodide, although the solution came through pale amber in color, a rapid and considerable release of iodine was noted.

Thus, the formation of free acid in the reaction of silver salts of carboxylic acids with iodine in the presence of tertiary amines, may arise from the formation of unstable iodination products as well as from the formation of iodopyridines.

III. Some Reactions of Silver Carboxylates With One Equivalent of Bromine

These reactions were carried out in an attempt to prepare an organic pseudohalogen of the hypothetical structure $(RCOO)_n$. While no evidence for the existence of such a compound has been obtained, several interesting observations were made which certainly warrant further investigation.

In order to maintain completely anhydrous conditions, the reaction was always run in an atmosphere of dry nitrogen. Bromine was dried by storage under concentrated sulfuric acid and was distilled directly into the reaction flask. Before the addition of bromine to the reaction mixture, dry nitrogen was passed through the suspension of the already thoroughly dried silver salt in carbon tetrachloride.

A. Reaction of silver p-nitrobenzoate with one equivalent of bromine in carbon tetrachloride.

A suspension of 3.0 g. (0.01 mole) of silver p-nitrobenzoate in 100 ml. of carbon tetrachloride was prepared in the reaction flask. After the system was flushed with dry nitrogen for thirty minutes, 0.25 ml. (slightly less than 0.01 mole) of bromine was distilled into the reaction mixture. The orange color

of the bromine-carbon tetrachloride solution remained practically unchanged after a half hour. Samples of the filtrate gave negative tests with alcoholic solutions of potassium iodide and silver nitrate. After five days, there was some indication of disappearance of the bromine, but this may have been due to evaporation. The suspension was finally filtered and evaporated. The only evidence of any reaction was a small amount of nitrobenzene which was probably formed by a decarboxylation.

In the case of m-nitrobenzoic acid, the identical behavior was observed. Silver p-aminobenzoate also gave absolutely no indication of any reaction.

It is interesting to note that the addition of small amounts of alcohol caused a rapid reaction in each case as was evidenced by the rapid disappearance of the bromine.

B. Reaction of silver benzoate with one equivalent of bromine

To a suspension of 9.6 g. (0.04 mole) of silver benzoate in 200 ml. of carbon tetrachloride there was added 1 ml. (0.037 mole) of bromine. The reaction proceeded rapidly with the disappearance of the bromine. After the reaction appeared completed, the colorless

filtrate was tested with silver nitrate and potassium iodide solutions and again no reaction was observed. Evaporation of the remainder of the filtrate in the atmosphere yielded white crystals of benzoic acid and small quantities of bromobenzene.

C. Reaction of silver benzoate with one equivalent of bromine followed by the addition of cylohexene

Into a suspension of 19.6 g. (0.085 mole) of silver benzoate in 200 ml. of carbon tetrachloride, 2 ml. (0.075 mole) of bromine was distilled directly from sulfuric acid and the mixture agitated by means of nitrogen gas. When the color of the bromine had disappeared, 7 g. (0.085 mole) of cyclohexene was added and the liberation of large amounts of heat was noted. The suspension was filtered, and the filtrate evaporated on a steam bath. When the carbon tetrachloride had evaporated, a light brown solid of the consistency of a soft wax remained. This material was easily soluble in every organic solvent tested: ether, alcohol, acetone, chloroform, carbon tetrachloride and ligroin. It was completely insoluble in water. Thus, recrystallization was virtually impossible. Each time it was recovered from a solvent, the physical state remained unchanged, the solid maintaining its soft, waxy

consistency. Attempts to distill, even at pressures as low as 0.005 mm. of mercury were wholly unsuccessful.

The physical properties of the compound corresponded to none of those reported for either the cis or trans forms of 1, 2-dibromocyclohexane, 1-bromo, 2-benzoyloxycyclohexane, or 1, 2-dibenzoyloxycyclohexane. A positive test for bromine was obtained, but in view of the fact that the material was undoubtedly impure, this observation is not too significant. After the material had stood for ten days, on reattempted recrystallization from ligroin, some sharp melting, colorless needles were obtained, but these were identified by a mixed melting point as benzoic acid. These may also have been present as an impurity or resulted from some reaction other than addition to cyclohexene. Although the original material seemed to possess some definite crystalline form, sublimation also failed.

Absolutely no definite information concerning the structure of this compound was obtained. The product was obtained in good yields in other runs, but no additional information of its structure was obtained.

D. Reaction of benzoyl peroxide with carbon tetrachloride

In an attempt to obtain some information concerning the compound described in III-C, 2.4 g. (0.01 mole) of benzoyl peroxide and 1.6 g. (0.02 mole) of cyclohexene were refluxed in 25 ml. of carbon tetrachloride over a steam bath for forty-eight hours. The carbon tetrachloride was then distilled off leaving a heavy brown residue. On standing for several hours, this residue started to solidify and emit a strong, camphor-like odor. Since the possibility that the material might be hexachloroethane was considered, the brown residue was subjected to a sublimation and a good sample of colorless needles were obtained which melted at 186-188° in a sealed tube. The melting point of hexachloroethane is given as 186.9-187.4°.

The experiment was rerun in the absence of cyclohexene and again, hexachloroethane was isolated and identified. If the crystals could be more easily separated from the residue, it appeared that a fairly good yield of hexachloroethane might be realized. The formation of hexachloroethane is quite interesting and warrants further investigation.

IV. The Electrical Conductivity of Positive Iodine Compounds in Pyridine Solution

A. The electrolysis of monopyridine iodine(I) m-nitrobenzoate in pyridine.

The purpose of this experiment was to determine whether silver iodide could be made to plate out quantitatively at a silver cathode by electrolysis of a positive iodine compound. It was believed that the deposition might take place in accordance with Faraday's laws.

A solution of 1.6 g. of monopyridine iodine(I) m-nitrobenzoate in 80 ml. of pyridine was electrolyzed for three hours in a divided cell. The anode was of platinum foil, 1 x 2½ cm. and the cathode was of silver foil, 1½ x 6 cm. A direct current potential of 110 volts was applied between the electrodes; the cell was connected in series with an ammeter and silver coulometer. The ammeter reading was 0.002 amperes, and little change in this value occurred during the time of passage of the current. The anode compartment showed no change, the original yellow color of the solution remained the same. The cathode compartment, however, turned almost brown and a deposit of colorless crystalline material was noted at the base of this

compartment. The coulometer showed an increase in weight of 0.0295 g. of silver. The cathode itself, in spite of the fact that a precipitate of yellow silver iodide had been formed at the surface, showed a loss in weight of 0.1744 g. It should be emphasized that no deposition of any kind was observed in the anode compartment.

The crystals that deposited in the cathode chamber were removed and were found to decompose into a yellow powder on heating. Heating the yellow powder in an open flame caused it to emit purple fumes. These were believed to be iodine. The original colorless crystals were unaffected by water, but upon the addition of a mineral acid or alcohol, the yellow powder formed at once. On the assumption that the crystals were silver iodide solvated with pyridine, the following experiments were performed.

A quantity of silver iodide was continously shaken with excess pyridine for two hours. None of the original yellow solid remained, but a colorless crystalline solid was formed which was removed by filtration. The crystals behaved exactly as those isolated from the cathode; silver iodide was formed on heating, treatment with nitric acid or washing with

alcohol.

As final proof of the fate of the silver cathode, a few thin strips of metallic silver were allowed to remain in contact with a 0.1 molar solution of monopyridine iodine(I) m-nitrobenzoate in pyridine. After forty-eight hours the metallic silver disappeared completely and the white crystalline material was formed which behaved just as that previously described. It seems probable that the IPY^+ ion acts as an oxidizing agent towards silver to form silver iodide.

B. The conductivities of various positive iodine compounds in pyridine.

1. Preparation of pure pyridine

Pyridine obtained by the method to be described was that used for both conductivity studies and measurements of absorption spectra. The method used, except for the preliminary drying over potassium hydroxide, was that described by Burgess and Kraus (15). The starting product was Baker's analyzed pyridine. This was stored over potassium hydroxide for two days and fractionated through a four foot column packed with berl saddles. A middle fraction boiling at 114.2-114.6° was collected and treated with aluminum chloride to eliminate any traces of alcohol. The aluminum

chloride had to be added in very small portions due to the formation of a crystalline complex which was accompanied by the liberation of a large quantity of heat. After twenty-four hours, the material was again fractionated and a middle fraction boiling at 114.2-114.9^{o} was collected over aluminum oxide. This was refluxed, distilled and again collected over alumina. The final product was distilled in an atmosphere free of carbon dioxide and moisture. The column was flushed for an hour with nitrogen which had been passed through potassium hydroxide and sulfuric acid. The final product came over at 114.8^{o} and was collected and stored in a brown bottle stoppered with a ground-glass, potassium hydroxide filled stopper. The final product had a conductivity of not greater than 5×10^{-9} ohms^{-1} at 25°.

2. Conductivity measurements

All measurements were made on a Henry type bridge employing a 1000 cycle audiophone AC circuit. Due to the high values for the resistance, a parallel resistance had to be used, as well as a condenser having a variable capacitance of up to 6000 microfarads. The purpose of the latter was to compensate for errors arising from the polarization of the electrodes. Approximate values for the resistance were first obtained on a portable

conductivity bridge so that the amount of parallel resistance which would give the most accurate values could be calculated.

The cell used was of the Henry type with polished platinum electrodes. The cell constant was found to be 0.1458 from calibration with standard potassium chloride solution at 25°. Previous independent calibrations gave values of 0.1457 and 0.1459 for this cell. The solutions were prepared by adding a weighed amount of the positive iodine salt to a weighed amount of pyridine contained in a glass stoppered flask. The transfer of solution from the flask to the cell was accomplished so as to exclude air and moisture as much as possible. A pipette to which a stopcock was fused was filled by automatic suction; a drying tower connecting the pipette and the pump. The stem of the pipette was inserted through one of the openings of a two-hole rubber stopper which fit securely into the opening of either the flask or the cell. The second opening of the stopper, which provided an air inlet, was connected by means of a rubber tube to a potassium hydroxide drying tower. Before any measurements were made, the cell was rinsed at least ten times with the solution whose resistance was to be measured. All

TABLE I

CONDUCTIVITIES OF SOME POSITIVE IODINE SALTS AT 25°

IN PYRIDINE SOLVENT

Derivative of Monopyridine Iodine(I)	Concentration Molal	Specific Conductivity x 10^7	Molar Conductance
o-nitrobenzoate	0.01026	99.5	0.969
m-nitrobenzoate	0.01026	48.1	0.469
p-nitrobenzoate	0.01026	54.3	0.529
o-chlorobenzoate	0.01026	42	0.41
m-chlorobenzoate	0.01026	34	0.33
p-chlorobenzoate	0.01026	17	0.16
o-bromobenzoate	0.01026	40	0.39
m-bromobenzoate	0.01026	50	0.49
p-bromobenzoate	0.01026	41	0.39
m-iodobenzoate	0.01026	33	0.32
p-iodobenzoate	0.01026	16	0.16
p-toluate	0.01026	219	2.13
nitrate	0.0033	580	5.65

No significant interpretation can be attached to these results. Such a discussion would require the calculation of the individual dissociation constants for the various compounds, as well as the determination of the individual ionic conductivities. Such work would compromise an extensive research project in itself. A few qualitative observations are self evident, however. The nitrate, as would be expected, shows a conductivity considerably greater than that of any of the organic compounds. This is undoubtedly due to the fact that the nitrate is not nearly as good a coordinator as the organic ions and hence forms a much more ionic salt. The greater salt-like nature of the nitrate is further emphasized by the fact that the solution was considerably more dilute, and still showed a considerably greater conductance than did the organic derivatives. The high value for the conductivity of the p-toluate derivative can be attributed to several factors. Perhaps, the toluate has a much greater mobility than do the other anions. This may arise from a lesser degree of solvation in solution. If an ion has to carry along with it a lesser number of solvent molecules, its velocity will be proportionally greater. Again, such a conclusion would have to be

tested experimentally by determining the relative degree of solvation of these ions as well as their mobilities.

C. The effect of time on the conductivity of positive iodine salts in pyridine.

This study was undertaken in conjunction with a more extended study of the absorption spectra of these compounds. The values obtained for a 0.0100 molal solution of monopyridine iodine(I) p-bromobenzoate in pyridine are given in Table II.

TABLE II

VARIATION OF THE CONDUCTIVITY OF A 0.01 m SOLUTION OF MONOPYRIDINE IODINE (I) p-BROMOBENZOATE IN PYRIDINE AT 25°.

Time	Specific Conductance x 10^7
4 minutes	39.3
12 "	39.3
17 "	39.3
42 "	39.3
55 "	39.4
91 "	39.5
140 "	41.3
260 "	41.9
18 hours	48.7
20 "	48.9
22 "	50.1
25 "	51.8
48 "	55.1
69 "	56.7
92 "	58.5
116 "	60.5
138 "	62.0
163 "	68.4

Table II, Cont'd.

Time	Specific Conductance x 10^7
12 days	269
13 "	295
14 "	331
15 "	430
16 "	550
18 "	574
19 "	595

The measurements were not carried out further because it was concluded from spectroscopic evidence that the release of iodine created a new situation with the iodine forming the predominant conducting species. The data presented are in agreement with the spectroscopic data and will be discussed in the next section which deals with the spectra of pyridine solutions of iodine and positive iodine compounds.

V. Absorption Spectra of Positive Iodine Salts and Iodine in Pyridine and the Absorption Spectrum of Iodine in Water.

A. 1. Preparation of materials

The pyridine used in these studies was purified in the same manner as that used for the conductivity studies (see Section IV-B), and possessed the same specific conductance. The importance of the purity of the solvent in these studies cannot be overemphasized and it should be pointed out that the method of purification used eliminated any traces of alcohol and water which may have been present. The water used was first distilled from potassium permanganate in order to eliminate any traces of organic materials and then distilled from a quartz vessel through a tin condenser. The final product was collected in a Pyrex bottle that had been thoroughly steamed for several days and rinsed with conductivity water. No effort was made to eliminate carbon dioxide as it was assumed that it would not interfere.

The iodine was Merck's c.p. grade and it was subjected to two further resublimations, after which it was stored in a desiccator over magnesium perchlorate.

The positive iodine compounds were prepared as

described previously (5, 7). Their purity was checked by analysis.

The solutions were prepared by adding the calculated amount of solute to a weighed quantity of the solvent contained in a ground-glass stoppered flask. The very dilute solutions were prepared by dilution of the more concentrated ones. The method of transfer of solvent and solutions is described in Section IV-B.

2. Methods and apparatus

All absorption spectra were measured with a Beckman Quartz spectrophotometer, Model DU. A pair of 1 cm. silica cells were used, one of which always contained the blank. Wavelengths from 700 to 320 mμ were obtained by means of tungsten lamp; below the latter wavelength, in the ultraviolet region, a hydrogen discharge lamp was used. In the case of the measurements in pyridine, absorption below 305 mμ could not be measured because of the strong absorption of pyridine in this region. In water, measurements were carried out to 265 mμ. The slit widths varied from about 0.01 mm. in the region of 600-700 mμ to the maximum width of 2mm. at the shortest wavelengths.

B. Absorption spectra of some positive iodine compounds in pyridine

All the positive iodine compounds, which are themselves colorless, were found to be readily soluble in pyridine with the formation of golden yellow solutions. Except in the case of the nitro compounds, all the freshly prepared solutions were characterized by a single band in the region of 315-325 mμ and these are listed in Table III.

TABLE III

ABSORPTION OF SOME FRESHLY PREPARED SOLUTIONS OF DERIVATIVES OF MONOPYRIDINE IODINE(I) IN PYRIDINE

Salt (conc. 0.01 m)	Max., mμ	% Transmission at λ max.
p-Toluate	325	3.57
p-Chlorobenzoate [a]	325	2.93
p-Bromobenzoate	325	3.36
p-Bromobenzoate ($5x10^{-4}$m)	315	50.8
p-Iodobenzoate	330 [b]	2.99
m-Iodobenzoate	325	3.62
o- Nitrobenzoate	340-370	3.15 [c]
m-Nitrobenzoate	350	3.02 [c]
p-Nitrobenzoate	340-375	3.24 [c]
Nitrate ($3.3x10^{-5}$m)	319	35.4

[a] The decomposition point (152-160°) differs from that observed previously (7), but the compound analyzed correctly.

[b] Was not measured at 325 mμ.

[c] Values at 325 mμ.

In making the measurements, readings were taken at intervals of 10 mμ in the case of the first solution studied (p-iodobenzoate), and this accounts for the 330 mμ peak observed. When measurements were carried out on other solutions, readings were taken at intervals of 5 mμ in the region 20 mμ on either side of the maximum and at 1 mμ on the immediate sides of the maximum.

A typical absorption curve for solution of a positive iodine compound is typified by curve A of Figure 1 which illustrates the experimental values obtained for a 0.01 m solution of monopyridine iodine(I) p-toluate in pyridine. On standing for from three to four hours, the color of all the solutions changed from a golden yellow to amber, and as is shown in curve B of Fig. 1, this was accompanied by a marked increase in absorption. By simple dilution, the resulting curve could be resolved into a curve having distinct peaks at 375 mμ and 320 mμ, as is shown in Curve C. In every case, including the solutions of the nitro compounds, the identical behavior was observed. It is of considerable importance, as will be shown in the discussion of these observations, to mention that the 375 mμ band was always more intense than the

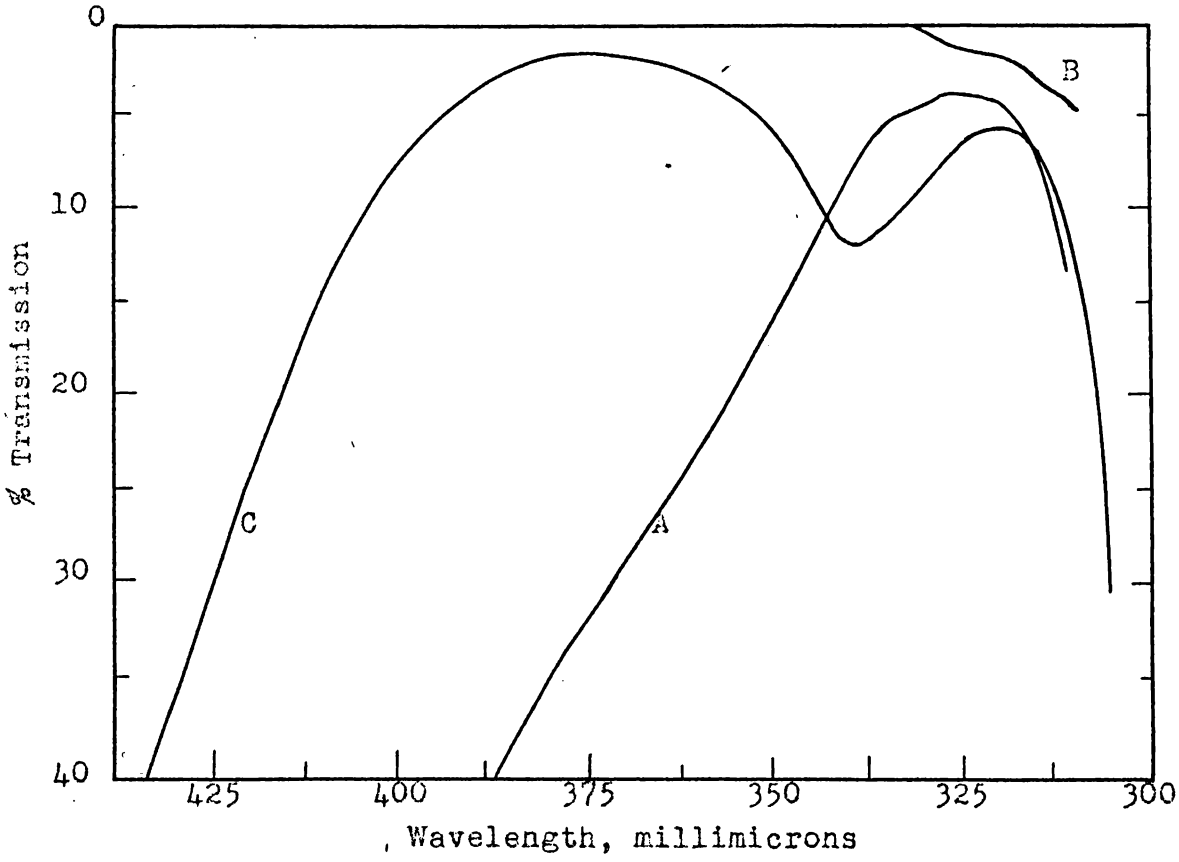


Fig. 1. Absorption spectrum of monopyridine iodine(I) p-toluate in pyridine. Curve A: freshly prepared solution, conc. 0.01 m; curve B: same solution after four hours; curve C: same as B, but diluted in pyridine to conc. 5 x 10^{-5} m.

320 mμ band. In Table IV are listed the values for the intensities of the absorption bands of some solutions of positive iodine compounds after aging and dilution.

TABLE IV

EFFECT OF AGING AND DILUTION ON THE ABSORPTION OF MONOPYRIDINE IODINE (I) DERIVATIVES

Salt* (Conc. ca. 5×10^{-5}m)	$\lambda_1$max.,	$\lambda_2$max., mμ	% Transmission at $\lambda_1$max-	at $\lambda_2$max.
p-Toluate	375	320	1.78	5.30
p-Iodobenzoate	375	320	0.58	4.59
p-Nitrobenzoate	375	320	0.19	1.77
m-Iodobenzoate	375	320	0.02	1.51

*All these solutions were approximately one day old.

C. Absorption spectrum of iodine in pyridine

The absorption spectrum for a freshly prepared solution of iodine in pyridine is shown in curve A of Fig. 2. The curve shows two absorption bands; one broad band in the region of 390 mμ and another narrower band at 320 mμ. On standing, just as in case of the positive iodine compounds, a marked increase in absorption occurs, as is seen in curve B. Dilution of the aged solution again shows the presence of two

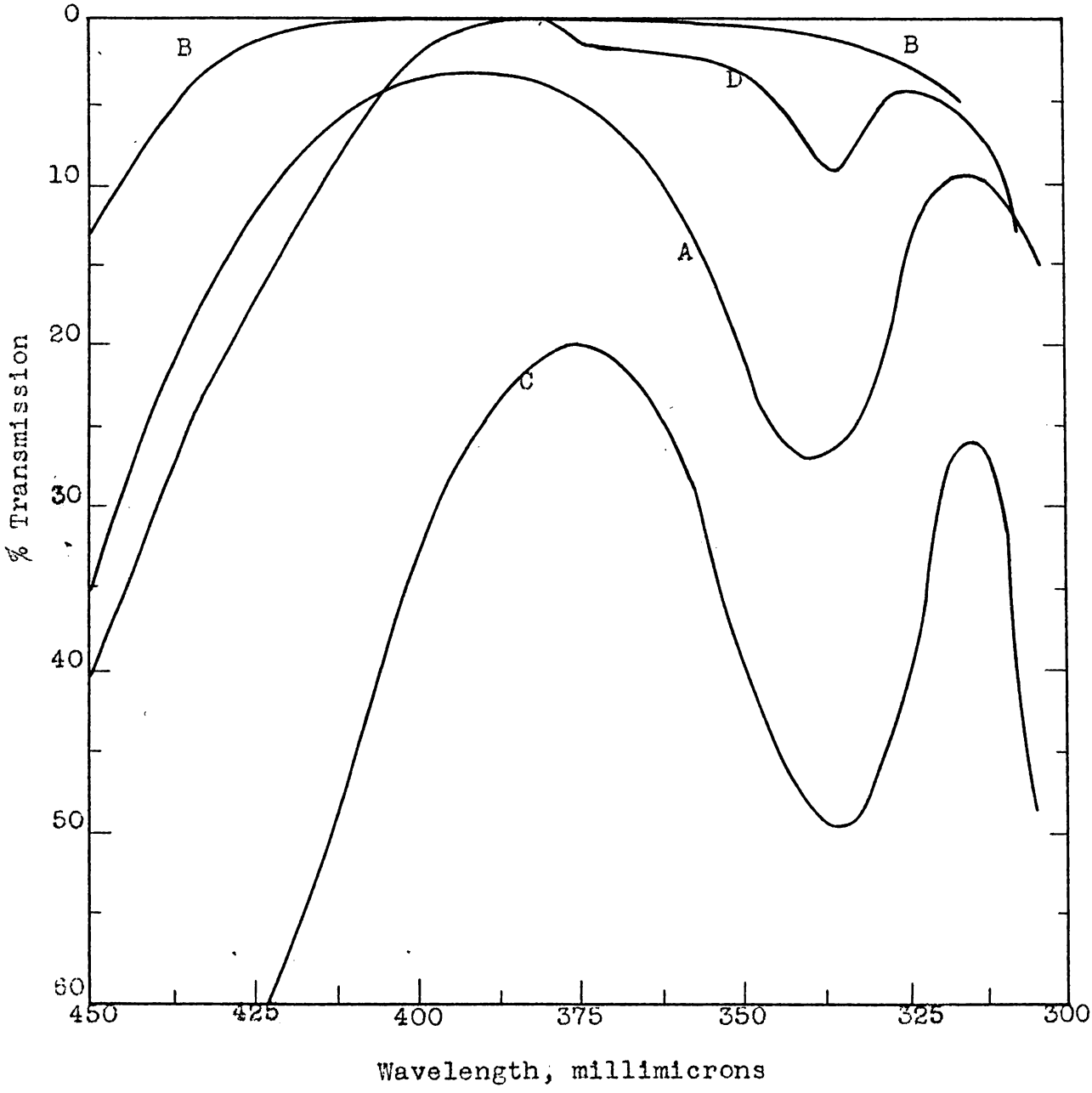


Fig. 2. Absorption spectrum of iodine in pyridine. Curve A: freshly prepared solution, conc. 0.0005 m; curve B: same solution after four hours; curve C: same as B, but diluted in pyridine to conc. 0.0001 m; curve D: solution of 0.0003 N triiodide in pyridine.

absorption bands at 375 mμ and 320 mμ, respectively (curve C).

In curve D of Fig. 2, there is shown the absorption spectrum measured for a solution of 0.1 ml. of an aqueous solution of iodine in excess potassium iodide (0.091 N) in 29.3 g. of pyridine. Two sharp absorption bands are observed at 380 mμ and 325 mμ, respectively. These correspond almost exactly with those observed for solutions of iodine in the same solvent.

Attention is now called to curve A of Fig. 3 where the absorption spectrum for a very dilute solution of iodine in pyridine prepared by dilution of a more concentrated, day-old solution is shown. After five days, the solution became almost colorless, and as is seen in curve B, both peaks have completely disappeared. Addition of a drop of freshly prepared iodine solution caused immediate restoration of the two original peaks. In Table V, some data observed for another dilute solution of iodine in pyridine is given.

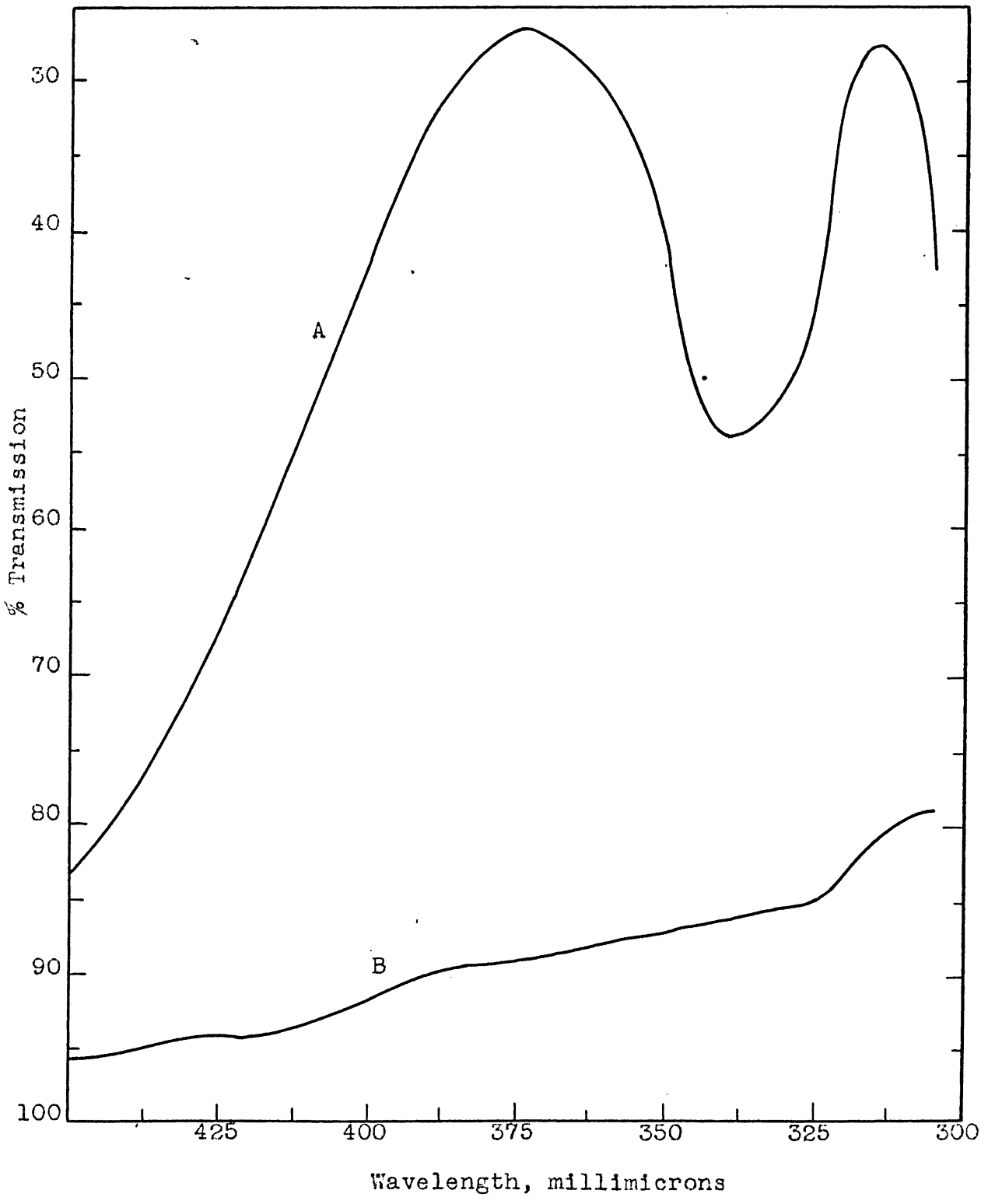


Fig. 3. Effect of aging on a solution of iodine in pyridine. Curve A: one day old solution of iodine in pyridine, conc. 0.00005 m; curve B: same solution after five days.

TABLE V

EFFECT OF AGING ON THE ABSORPTION SPECTRUM OF A DILUTE SOLUTION OF IODINE IN PYRIDINE Conc. 2×10^{-5}m

Time	% Transmission at 375 mμ	% Transmission at 320 mμ
a. 0	35.6	41.1
b. 2 hr.	38.6	47.5
c. 3½ hr.	39.8	43.2
d. 22 hr.	44.8	47.7
e. 26 hr.	45.9	48.8
f. 48 hr.	53.8	54.0
g. 95 hrs.	68.8	65.8
h. 12 days	67.7	62.9

After the lapse of twelve days the measurements were discontinued. The fact that the intensity of both bands falls off rather rapidly shows definitely that these solutions undergo a drastic change and that the dissolved species which give rise to these bands are being used up. Perhaps, the most interesting observation is the fluctuation in the magnitude of the values for the band intensities. Thus, while a general decrease in absorption is observed, the values occasionally increase. For instance, in the case of the 320 mμ band, there is

an increase in absorption from b to c and from g to h, and in the case of the 375 mμ band there is an increase from g to h. Also of interest, is the increase in intensity in the band of shorter wavelength on standing. Thus, while it has been emphasized that the 375 mμ band is less intense than the 320 mμ band, the last two measurements in Table V show that the 320 mμ band has become more intense than the 375 mμ band as a result of aging.

D. Titration of a solution of iodine in pyridine

This study was undertaken in order to supplement the data of section C. A dilute solution of iodine in pyridine was prepared and 5 ml. portions were withdrawn at intervals and pipetted into 20 ml. of 20% potassium iodide solution acidified with hydrochloric acid. The solution was titrated with standard sodium thiosulfate solution to a starch end-point. The data obtained on a run is given in Table VI.

TABLE VI

TITRATION OF A SOLUTION OF IODINE IN PYRIDINE OVER AN EXTENDED PERIOD OF TIME

Time	ml. of 0.0088 N Sodium Thiosulfate
3 min.	4.95
15 "	4.65
30 "	4.00
52 "	2.88
71 "	4.31
87 "	4.81
1 hr. 52 min.	5.21
2 " 25 "	4.71
4 " 8 "	4.70
26 hr.	3.18
48 hr.	3.44
48 hr. 7 min.	4.56
49 hr. 39 "	4.60

The tremendous variation in these values, especially the variation encountered with samples withdrawn within a few minutes of each other gives no information, but only tends to further confuse the situation. One very definite conclusion which can be reached is that such a method of titration is wholly unsatisfactory if one

wishes to determine the normality of a solution of iodine in pyridine. Whether a similar behavior is shown by iodine in other "active" solvents requires further investigation. The possible significance of this data as well as that obtained for the measurements of the absorption spectra will be discussed at the end of part V.

E. Absorption spectra of iodine in water and in potassium iodide solution

The absorption spectra for a series of four solutions of iodine in water were measured. All were found to possess three distinct absorption bands: The first, in the visible at 495 mμ showed the strongest optical density; the second, at 368 mμ absorbed most weakly, and the third, in the ultraviolet at 294 mμ, showed intermediate absorption.

In Table VII are given the values of the optical densities at the maxima observed for the solutions studied.

TABLE VII

ABSORPTION OF SOME FRESHLY PREPARED SOLUTIONS OF IODINE IN WATER

Conc., moles/liter	λ_1	D^*_1	λ_2	D_2	λ_3	D_3
a. 1.51×10^{-3}	495	0.895	368	0.304	294	0.525
b. 7.55×10^{-4}	495	0.433	370	0.227	294	0.382
c. 3.78×10^{-4}	495	0.208	365	0.123	294	0.204
d. 1.89×10^{-4}	495	0.105	365	0.042	294	0.071

*D signifies optical density

These solutions were quite stable, i.e., they showed little change in absorption over a period of several days. After a period of two weeks, however, considerable change had occurred. For instance, in solution a, the optical density corresponding to the first maximum at 495 mμ had decreased to 0.820 while the values at the maxima at 368 mμ and 294 mμ showed increases to 0.496 and 0.809, respectively. Here the markedly greater intensity of the band at 294 mμ in contrast with the intensity of 368 mμ band should be noted. A similar observation was noted for solution b, in which the value for the first maximum at 495 mμ showed a decrease to 0.393 and the bands at 370 mμ

and 294 mμ had increased to 0.306 and 0.499, respectively. The data given in Table VII is plotted in Fig. 4.

When the solutions were added to an excess of potassium iodide solution, the color changed from amber to a clear, golden yellow and this was accompanied by a marked change in the absorption spectrum. This is clearly illustrated in Fig. 5. It can be seen that the band at 495 mμ is completely suppressed while the intensities of absorption of the bands at 365 mμ and 294 mμ are strongly increased. In the case of solutions a, b and c, the solutions formed by dissolution in an equal volume of 0.3 M potassium iodide, gave rise to such strong absorption at the shorter wavelengths that they were beyond the range of the instrument. The data plotted in Fig. 5 was obtained by dissolving 10 ml. of solution d in 20 ml. of 0.3 M potassium iodide solution. The blank was prepared from 20 ml. of the same potassium iodide solution and 10 ml. of water. The purpose of employing this blank was to compensate for absorption due to the iodide ion. On the other hand, the concentration of the iodide ion in the blank may have been so much greater than in the solution studied because of the formation of triiodide ion in the experimental solution, that a

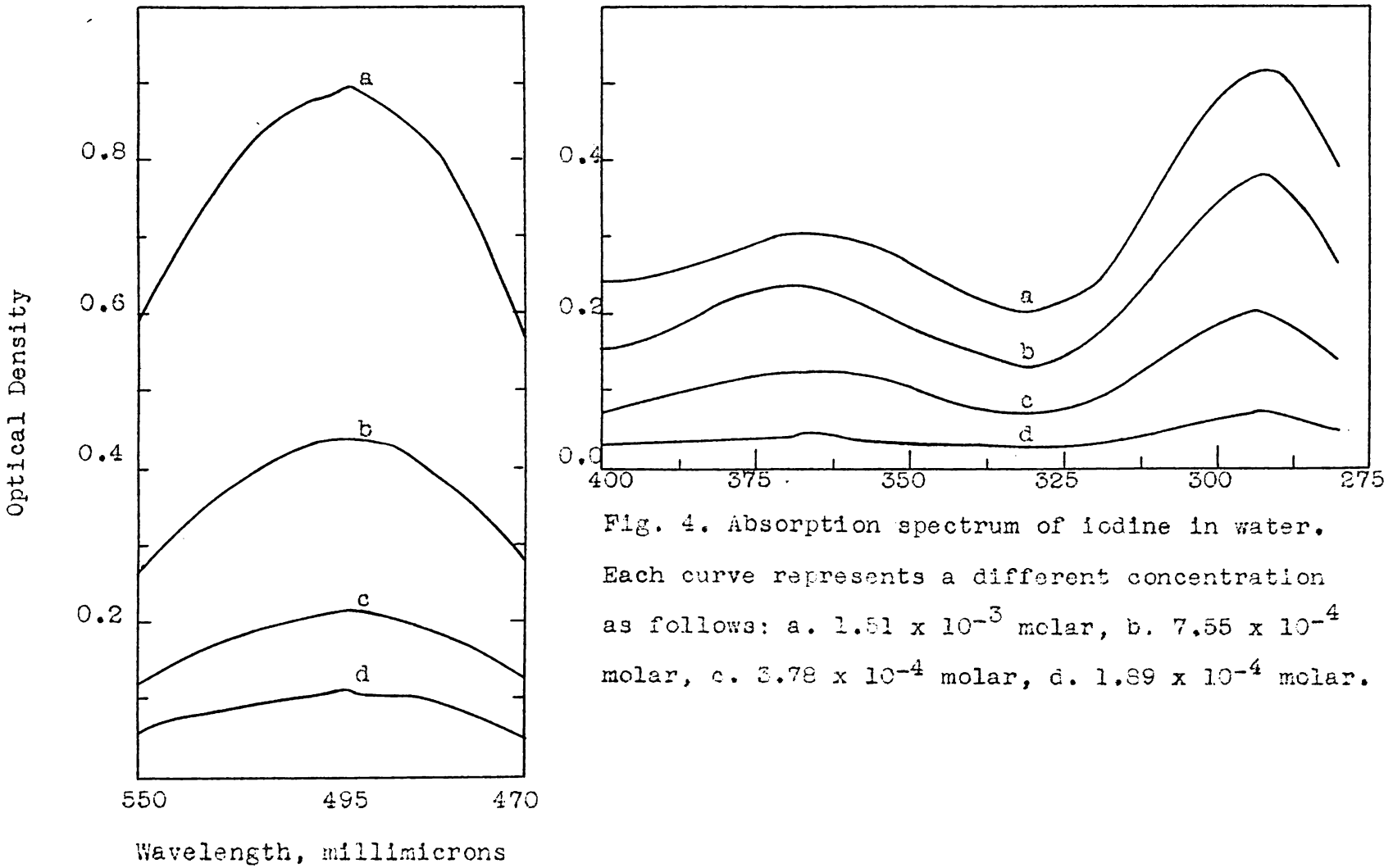


Fig. 4. Absorption spectrum of iodine in water. Each curve represents a different concentration as follows: a. 1.51×10^{-3} molar, b. 7.55×10^{-4} molar, c. 3.78×10^{-4} molar, d. 1.89×10^{-4} molar.

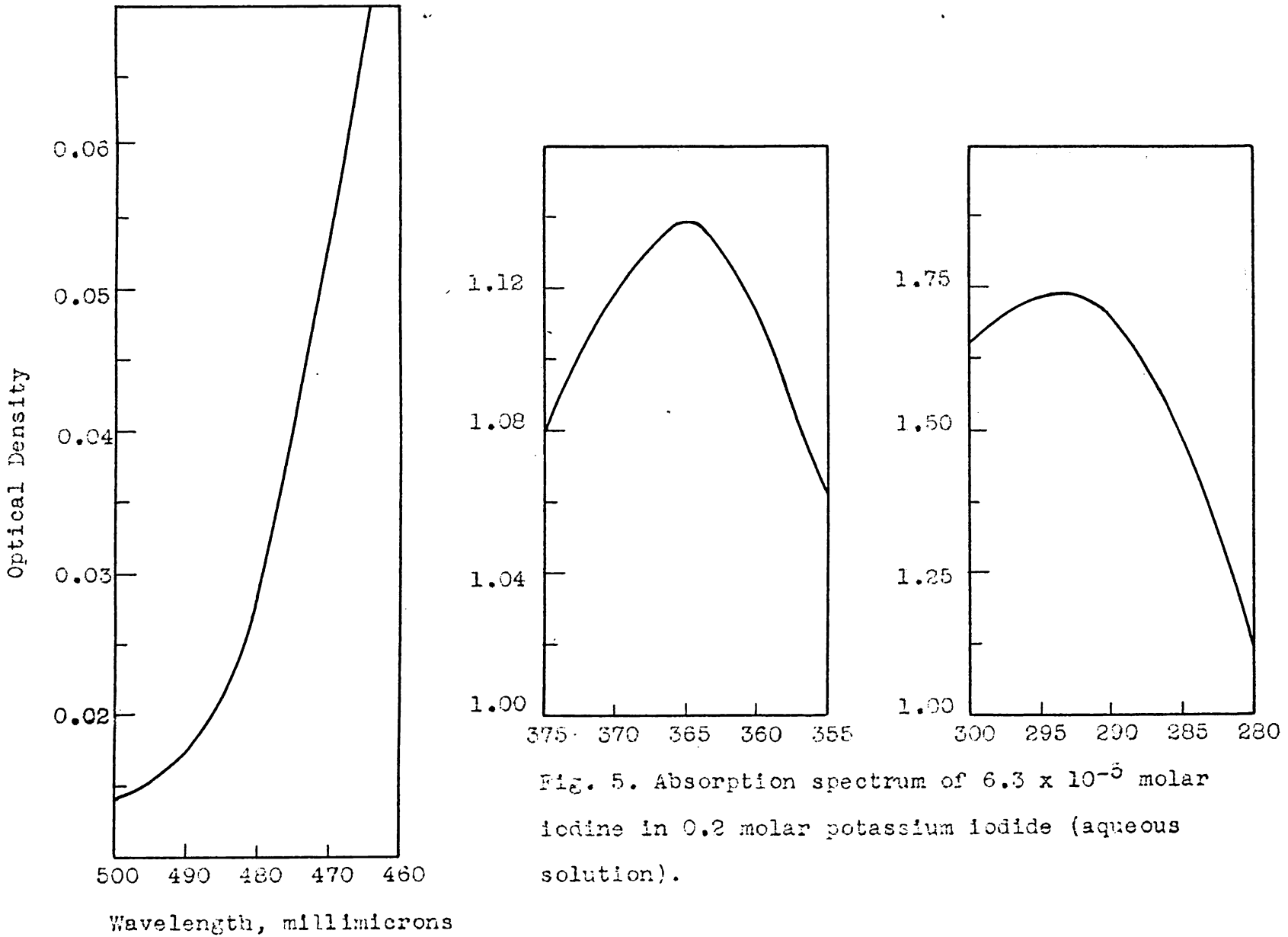


Fig. 5. Absorption spectrum of 6.3 x 10^{-5} molar iodine in 0.2 molar potassium iodide (aqueous solution).

greater error may have been introduced. Once more, the optical density of the 294 mμ band was much greater than the 365 mμ band, 1.74 and 1.14, respectively.

DISCUSSION OF PART V

Since all the positive iodine compounds, which are colorless in the solid state, dissolve in pyridine to give light golden yellow solutions characterized by a single absorption band in the region of 315-325 mμ (except the aromatic nitro derivatives), it seems logical to attribute this absorption to the common IPy^+ ion. On the other hand, the possibility that this single absorption band may be due to the undissociated IPy·OOCR complex cannot be immediately dismissed. The evidence for the former conclusion is twofold. First, the existence of the single band at 319 mμ in the case of the $IPy \cdot NO_3$ complex, if it were due to molecular absorption, would not be expected to fall in the same region as for the other complexes in view of the considerable difference in the anionic portion of the molecule. Furthermore, it has been shown by conductivity measurements both in pyridine (Table I, section IV-B) and in methanol-pyridine mixtures (5) that $IPy \cdot NO_3$ undergoes considerable dissociation. The second argument arises from the fact that all these solutions are yellow when dissolved in pyridine. If the color were due to the molecule, then it would be expected that the solid should be

colored similarly, and this is not the case. The formation of the same colored solution in every case is again best explained by dissociation into the common IPy^+ ion. This evidence strongly supports the conclusion that the characteristic band is due to the IPy^+ ion.

The reason for the discrepancy in the case of the o, m and p-nitro derivatives has not been established, and only tentative explanations can be advanced. It appears that the maxima observed for these compounds in the region of 350 mμ, is probably due to the aromatic portion of the molecule which is greatly influenced by the presence of the nitro group. The possibility of compound formation between pyridine and the nitrobenzoate also suggests itself and is extremely likely in view of the strong electropositive centers which would be present in the nitro benzoate group. It is seen in Table III, however, that nitro compounds show approximately the same percent of transmission at 325 mμ as do the other salts.

The change in color of these solutions on aging with the subsequent formation of a new peak in the region of 375 mμ will be discussed in connection with the spectrum of iodine in pyridine which follows.

The absorption spectrum of solutions of iodine in pyridine is characterized by two bands, the first and more strongly absorbing band occurs at 375 mμ, and the second more weakly absorbing band occurs at 320-325 mμ. A solution of triiodide ion in pyridine gives an identical spectrum. The latter peak corresponds to that observed for the IPy^+ ion and it may arise from an equilibrium of the following type:

$$I_3^- + Py \rightleftharpoons I^- + Py \cdot I_2 \rightleftharpoons IPy^+ + 2I^-$$

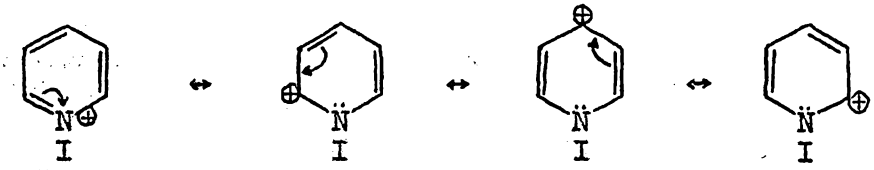
The band at 375 mμ may be identified with the 353 mμ band reported by Brode (16) and found at 368 mμ in this report (see section V-E) for the triiodide ion. It must be mentioned that a second and considerably more strongly absorbing band in the neighborhood of 290 mμ was found for aqueous solutions containing the triiodide ion in both this investigation, and that of other investigators as shown in Table VIII. It thus seems reasonable to argue that the 320 mμ band found in iodine-pyridine solutions may also arise from the polyiodide ion. This, however, does not appear to be the case for the following reasons. The identity of this band with that found for IPy^+ derivatives has already been mentioned; in addition, spectroscopic studies of triiodide ion in alcohol (17) reveal the

presence of two bands at 363 and 297 mμ, while in acetone, Benesi and Hildebrand (18) report a single band at 363 mμ. It appears unlikely, therefore, that the second band should be shifted to 320 mμ in pyridine and remain practically unchanged in alcohol. Furthermore, both the results of this project, as well as the work of Brode (16) have revealed that the second band is considerably more intense than the first 368 mμ band. In the case of pyridine, however, the 320 mμ band has been found to be a weaker band than the 375 mμ band. It seems probable that if the shorter ultraviolet band in both aqueous and pyridine solutions of iodine were due to the same electronic transition in the triiodide ion, then it should show the same relative absorption with respect to the longer wavelength band in each solvent and we know that this is not the case. Another indirect, but very logical line of reasoning is that if triiodide ion is formed almost immediately on dissolution of iodine in pyridine, the concomitant formation of a cation is necessitated and it has been shown that cationic iodine coordinated with pyridine is extremely stable. The evidence presented appears to be most reasonably explained by the following equilibrium.

$$2\,I_2 + Py \rightleftharpoons IPy^+ + I_3^-$$

This study reveals an obvious disagreement with the data of Getman (11), who reported a single maximum at 480 mμ for solutions of iodine in pyridine. In these studies, the observations were reproducable on repeated attempts and no indication of a maximum at 480 mμ was ever noted. Benesi and Hildebrand (18) reported a similar disagreement in their studies of solutions of iodine in acetone. They attributed the single maximum at 363 mμ to I_3^- ion formed in a rapid chemical reaction in which the authors postulated the formation of iodoacetone. While such a reaction is probable in acetone and other "active" solvents such as alcohol, it would be exceedingly more difficult to replace a hydrogen in the pyridine nucleus. The chemical studies on the decomposition of positive iodine complexes discussed in the second part of this report show that the iodination of the pyridine ring proceeds with great difficulty, if at all. In the case of pyridine, coordination of cationic iodine with the ring nitrogen has been shown to result in the formation of a stable species. In the case of other "active" solvents, especially those containing oxygen, a corresponding oxonium ion would be expected to be

more reactive, since stabilization of the resulting cation is not possible through resonance. Furthermore, reaction of the oxonium ion with the solvent is much more probable than is the case in pyridine. Thus, we may very well consider the stability of the monopyridine iodine(I) structure to be considerably enhanced by resonance among the following structures.



Such stability is primarily due to the aromaticity of the pyridine ring and is, of course, impossible in the case of all the saturated aliphatic solvents. An immediate dissociation of iodine in "active" solvents is wholly plausible, however, and the formation of an oxonium ion provides a very reasonable mechanism for the observed behavior of iodine in an "active" solvent. For example, the postulated formation of iodoacetone when iodine is dissolved in acetone is given by the following equations.

$$(CH_3)_2C{=}O + I_2 \rightleftharpoons (CH_3)_2C{=}O{\cdot}I_2 \rightleftharpoons (CH_3)_2C{=}\overset{+}{O}I + I^-$$

$$I^- + I_2 \rightleftharpoons I_3^-$$

$$(CH_3)_2C{=}\overset{+}{O}I + CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \rightarrow CH_2I\overset{O}{\overset{\|}{C}}{-}CH_3 + \overset{+}{H}$$

This mechanism satisfactorily explains the immediate formation of triiodide ion, an observation which has been reported for almost all the brown solvents. Furthermore, the iodide ion may further function as a base to facilitate the release of a proton from the α-carbon with the resulting formation of a carbanion which may easily be attacked by the positive iodine to give an α-iodo compound. This mechanism further explains the disappearance of iodine which is reported for many brown solvents, including pyridine-iodine solutions studied in this project.

Since the aliphatic amines also possess a free electron pair and also act as strong bases, they too would be expected to form brown solutions with iodine. In this case too, it seems unlikely that a stable cation would be formed. The behavior of iodine in an aliphatic amine would be expected to be analogous to that in acetone or alcohol.

The possibility of both steric and electronic effects, in determining the behavior of a solvent towards iodine, presents many interesting possibilities. It is possible that certain tertiary amines whose electron pair is hindered sterically, may show very

anomolous behavior. Thus, a very interesting study would be the behavior toward iodine of a series of triphenyl amines containing different ortho substituents. These substituents should be chosen so as to give rise to both effects. As a matter of interest, but of not of surprise, the teriary amine, heptacosafluorotributylamine, $(C_4F_9)_3N$, dissolved iodine only on heating and gave a violet solution. In this case, both the steric hindrance arising from the presence of three alkyl groups surrounding the nitrogen, as well as the tremendously decreased basicity of nitrogen resulting from fluorine saturation, completely altered the behavior of the amine.

The experimental section of this report has already described the slow disappearance of iodine which is observed for very dilute solutions of iodine in pyridine. Since the characteristic peaks can be restored immediately by the addition of fresh iodine, it is proved that the species responsible for these bands undergo a slow chemical reaction. The preliminary increase in absorption in more concentrated solutions must also be explained.

The behavior of solutions of iodine in pyridine is best interpreted as indicating a gradual increasing

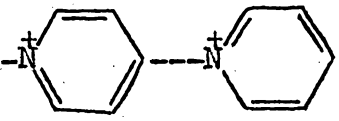
dissociation into ions which gives rise to concentrations of the absorbing species above the range of the instrument. The diminishing absorption must be due to the disappearance of the original ionic species. The latter reaction involved apparently occurs so slowly that it can be observed only in extremely dilute solutions.

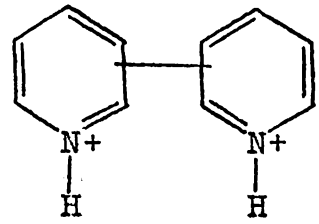
The appearance of the second peak at 375 mμ when solutions of positive iodine salts are allowed to stand (curve C. Fig. 1)indicates the formation of the I_3^- ion. Conductivity measurements of solutions of the benzoate derivatives in pyridine at concentrations of 0.01 m showed a specific conductance of 10^{-7} $ohms^{-1}$, a value which remained constant for a period of from three to four hours, and then increased steadily to a value of 10^{-5} $ohms^{-1}$ after fifteen days (see Tables I and II). This is of the same order of magnitude as reported for 0.006 m solutions of iodine in pyridine (13). The stronger absorption of iodine-pyridine solutions, as well as their greater conductivity as compared with solutions of positive iodine compounds of greater concentration, indicates a considerable dissociation of the former into the ionic species. In either case, the increasing con-

ductivity reported by Audrieth and Birr (13) can be explained by the formation of increasing quantities of the I_3^- and IPy^+ ions.

A satisfactory explanation for the behavior of solutions of iodine in pyridine must account for the great increase in conductivity as well as for the disappearance of the original ionic species. In order to account for the fact that the limiting conductance is about twice as great as might be expected on the basis of a simple dissociation of the iodine molecule into a positive and negative ion, Audrieth and Birr (13) proposed a mechanism involving dissociation into a ternary salt of the formula Py^{++} , $2I^-$. Since evidence has been presented that the ions responsible for the characteristic absorption peaks disappear with time, two alternative reactions may be proposed tentatively; one based on the preparation of pyridyl pyridinium chloride (19) best explained by the postulation of the $ClPy^+$ ion (22) the other on the formation of dipyridyl when pyridine is heated with iodine (23).

The equations for the reactions are:

(1) $Ipy^+ + 3py + I_3^- \rightarrow 4I^- + 2$ 

(2) $Ipy^+ + 3py + I_3^- \rightarrow 4I^- + 2$ 

Attempts to isolate these products from iodine-pyridine mixtures led only to the formation of tarry residues.

The data obtained for solutions of iodine in water do not contribute anything new to the understanding of iodine solutions. The three maxima observed are in good agreement with those reported by other workers (24, 17, 16). The first maximum falls just between the values reported for undissociated iodine in both violet and brown solvents; thus for "active" solvents the maxima reported fall between 460 and 480 mμ and in violet solvents a value of 520 mμ is reported, while in water the first and most intense maximum is found at 495 mμ. No good explanation for this shift has been presented, but it certainly indicates that this band is due to molecular iodine

and that most of the iodine in water exists in this form. The values observed for the second and third maxima are almost identical with those observed for solutions containing the triiodide ion. The values are listed in Table VIII.

TABLE VIII

ABSORPTION BANDS OBSERVED FOR VARIOUS SOLUTIONS CONTAINING THE TRIIODIDE ION

Investigator	Solvent	λ_1, mμ	λ_2, mμ
This investigation	water	368	294
Brode (16)	water	353	289
Hildebrand and Benesi (18)	acetone	363	none reported
Cennano (17)	methanol	360	297
Walls and Ludlam (17)	ethanol	363	282

The addition of potassium iodide solution causes a tremendous increase in the intensity of both the latter bands and complete disappearance of the band in the visible region. This, of course, is due to the complexing of the free iodine and the formation of polyiodide ion. The importance of the fact that the band at 294 mμ absorbs more strongly than the 365 mμ band has already been discussed. It appears that both these bands arise from the triiodide ion, but the

evidence is not conclusive. If the source of the bands of higher frequency were definitely ascertained, such data would contribute greatly to the understanding of the nature of iodine solutions. Most workers appear reluctant to attribute this band to the triiodide ion. Mulliken (17), in discussing the work of Cennano, Walls and Ludlam (17) assigns only the 365 mμ band to the triiodide ion and says that the second band is due to small amounts of iodine complexes arising from aromatic impurities. Similarly, Hildebrand and Benesi (18) are content to establish the presence of triiodide ion in acetone by the presence of a single band at 363 mμ. It appears, however, that both bands are due to this ion, since the addition of excess iodide ion causes a sharp increase in the intensity of both bands.

The subject of the decomposition of molecular iodine in solution, especially into triiodide, remains unanswered. It is generally agreed that molecular iodine, in both brown and violet solvents, reveals but a single band in the visible protion of the spectrum. Batley (20) found that solutions of iodine in alcohol saturated with ozone (to prevent formation of triiodide) gave a single band at 447 mμ. This indicates that the

formation of triiodide in alcohol, as well as in acetone and pyridine, is an immediate and rapid reaction and further strengthens the hypothesis of initial solvent-iodine complex formation. One immediate question which presents itself is this: although, it is admitted that the formation of triiodide is an immediate reaction, why does the visible band disappear almost immediately? It must be admitted that it seems unlikely that all of the molecular iodine, whether it exists as the solvent complex or in the free state, would be expected to disappear immediately. Nevertheless, this is the case in all of the brown solvents except ether and water. A situation like that presented by Batley, in which the solvent is saturated with ozone, while it does prove the point that no maximum except at 447 mμ is present (in ethanol) "if reactions are avoided", does not represent the true picture, since the presence of the oxidizing agent completely changes the behavior of the iodine. What remains to be explained is the nature of the reaction of the iodine with the solvent.

SUGGESTIONS FOR FUTURE WORK

1. The formation of hexachloroethane in the decomposition of benzoyl peroxide in carbon tetrachloride is an interesting reaction and should be further investigated. It probably occurs through a free radical mechanism, but no proof of this has been shown in this project.

2. Quantitative interpretation of the absorption band found at 320 mμ for solutions of positive iodine compounds in pyridine is important. Such a study would require the determination of the dissociation constants of these compounds in pyridine.

3. A series of concurrent spectrophotometric and conductivity measurements of solutions of iodine in a series of amines of decreasing basicity should yield data which should bear out or refute many of the present ideas concerning the nature of iodine solutions. Such a study might well be accompanied by the preparation of a series of positive iodine compounds containing various coordinating amines. It is the opinion of this author, however, that many would be unstable and only some tertiary aromatic amines would be satisfactory coordinating agents.

It is apparent that additional significant data could be obtained by performing a series of concurrent experiments in which a series of amines with sterically hindered nitrogen were used.

4. An interesting theoretical problem would involve the quantum mechanical elucidation of the dissociation of iodine in pyridine, i.e., the stability of the IPy^+ ion and the electronic transitions possible for the I-N bond.

SUMMARY

A modification of the original synthesis of positive iodine compounds, which consists in the crystallization of the salt from chloroform-ligroin solution at dry-ice temperatures is described. Five new compounds which could not be prepared by a former method have now been prepared and it is suggested that the new method be used in all preparations of these compounds.

The decomposition of positive iodine compounds has been found to yield small quantities of 3-iodopyridine, 3, 5-diiodopyridine and 5-iodo, 2-methyl picoline. This reaction explains some of the free acid formation observed in studies on the preparation of these compounds. The halogenation, which occurs exclusively in the three and five positions, strongly supports a positive iodine mechanism.

Benzoyl peroxide has been found to decompose in carbon tetrachloride to give hexachloroethane, and the addition of cyclohexene to the intermediate formed by the reaction of silver benzoate with one equivalent of bromine gives good yields of an unidentified product.

The conductivities and/or absorption spectra

and their change with time have been studied for the following solutions: positive iodine compounds in pyridine; iodine in pyridine; and iodine in water. These studies have revealed the existence of an absorption band in the region of 320 mμ for solutions of iodine in pyridine which can be identified with a similar band observed for solutions of positive iodine compounds, which contain the IPy^+ ion. The existence of triiodide ion in solutions of iodine and pyridine has been proved and the following dissociation of iodine in pyridine is postulated:

$$2\ I_2 + Py \rightleftharpoons I_2 \cdot Py \rightleftharpoons IPy^+ + I_3^-$$

A tentative mechanism to explain the limiting equivalent conductance of solutions of iodine in pyridine has been proposed.

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