

(CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS)

Evidence for the Existence of Unipositive Iodine Ion in Solutions of Iodine in Pyridine

BY RALPH A. ZINGARO, CALVIN A. VANDERWERF AND JACOB KLEINBERG

There has been a recent revival of interest in the nature of solutions of iodine in various solvents.¹ Those solvents which contain an atom possessing a free electron pair have been designated as "active" solvents. All such solvents form brown solutions with iodine, and the reactivity of the iodine is considerably greater than it is in violet solutions. By virtue of the free electron pair on the ring nitrogen, pyridine acts as an "active" solvent toward iodine. Audrieth and Birr,² on the basis of extensive conductivity studies, postulated that the conductance of iodine-pyridine solutions can be explained in large measure by the assumption of the dissociation of dissolved iodine into positive IPy^+ and negative I_3^- ions. This study was undertaken for the purpose of comparing the absorption spectra of pyridine solutions of salts containing the IPy^+ ion³ with those of solutions of iodine in pyridine. Clear evidence demonstrating the validity of the postulates of Audrieth and Birr was obtained and is described in this paper.

Experimental

Absorption Spectra.—All absorption spectra were measured with a Beckman quartz spectrophotometer, model DU. Because of the strong absorption of pyridine, measurements at wave lengths shorter than 305 $\text{m}\mu$ could not be made with this instrument.

The calculated amount of iodine or positive iodine compound was added to a weighed quantity of the solvent contained in a ground-glass stoppered flask. Very dilute solutions were prepared by dilution of the more concentrated ones. The transfer of solvent and solutions was carried out so as to exclude moisture.

Materials.—Resublimed iodine was further purified by two additional sublimations and stored in a desiccator over magnesium perchlorate before use.

The positive iodine compounds were prepared as previously described^{3,4} and their purity was checked by analysis.

J. T. Baker C. P. analyzed pyridine was purified according to the method of Burgess and Kraus.⁵ The final product had a b. p. of 114.8° at 740 mm. and a specific conductivity of 9×10^{-9} ohm⁻¹ at 25°.

Data and Discussion

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 aromatic nitro compounds, all the freshly prepared solutions were characterized by a single band in the region of 315–325 $\text{m}\mu$ as listed in Table I. Since the IPy^+ ion is the only ion common to all these compounds, the band in the region of 320 $\text{m}\mu$ ⁶ can logically be attrib-

uted to this ion. On the other hand, the possibility that this single band may be due to the undissociated $\text{IPy}\cdot\text{OOCR}$ complex must be considered. However, the existence of the single band at 319 $\text{m}\mu$ in the case of the $\text{IPy}\cdot\text{NO}_3$ complex, in which the anion portion of the molecule differs radically from those of the $\text{IPy}\cdot\text{OOCR}$ compounds, together with evidence³ that $\text{IPy}\cdot\text{NO}_3$ undergoes considerable dissociation in methanol solutions containing pyridine, strongly supports the conclusion that the characteristic band is due to the IPy^+ ion.

TABLE I

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

| Salt, concn. 0.01 <i>m</i> | $\lambda_{\text{max.}}$, $\text{m}\mu$ | Transmission, % at $\lambda_{\text{max.}}$ |
|---|---|--|
| <i>p</i> -Toluate | 325 | 3.57 |
| <i>p</i> -Chlorobenzoate ^a | 325 | 2.93 |
| <i>p</i> -Bromobenzoate | 325 | 3.36 |
| <i>p</i> -Bromobenzoate (5×10^{-4} <i>m</i>) | 315 | 50.8 |
| <i>p</i> -Iodobenzoate | 330 ^b | 2.99 |
| <i>m</i> -Iodobenzoate | 325 | 3.62 |
| <i>o</i> -Nitrobenzoate | 340–370 | 3.15 ^c |
| <i>m</i> -Nitrobenzoate | 350 | 3.02 ^c |
| <i>p</i> -Nitrobenzoate | 340–375 | 3.24 ^c |
| Nitrate (3.3×10^{-3} <i>m</i>) | 319 | 35.4 |

^a The decomposition point (152–160°) differs from that observed previously,⁴ but the compound analyzed correctly. ^b Was not measured at 325 $\text{m}\mu$. ^c Values at 325 $\text{m}\mu$.

A typical absorption curve for a 0.01 *m* solution of a positive iodine compound is shown in curve A of Fig. 1. On standing for three or four hours, the color of all the solutions changed from a golden yellow to amber and, as is observed in curve B of Fig. 1, a marked change in the absorption spectrum occurred. By simple dilution, curve B was resolved into a curve having distinct peaks at 375 and 320 $\text{m}\mu$, as shown in curve C. This behavior was noted in the solutions of all positive iodine compounds, including the nitro compounds.

The absorption spectrum of a freshly prepared solution of iodine in pyridine is shown in curve A of Fig. 2. Two peaks are noted, at 390 and at 320 $\text{m}\mu$, respectively. The latter undoubtedly corresponds to that observed for the compounds containing the IPy^+ ion. On standing, just as in the case of the positive iodine compounds, a marked increase in absorption occurred (curve B). Dilution of the aged solution again restored the two distinct peaks at 375 $\text{m}\mu$ and 320 $\text{m}\mu$ (curve C). The peak at 375 $\text{m}\mu$ is due to the presence of the I_3^- ion as indicated by the fact that a solution of 0.1 ml. of aqueous I_3^- solution (0.091 *N*) in 29.3 g. of pyridine showed two distinct peaks of 380 $\text{m}\mu$ and at 325 $\text{m}\mu$.⁷ The latter peak corresponds to that ob-

(7) Brode, THIS JOURNAL, **48**, 1877 (1926), reported maxima at 333 and 287 $\text{m}\mu$ for aqueous solutions of iodine in excess potassium iodide.

(1) See Kleinberg and Davidson, *Chem. Revs.*, **42**, 601 (1948), for a review of this subject.

(2) Audrieth and Birr, THIS JOURNAL, **55**, 668 (1933).

(3) Carlsohn, "Über eine neue Klasse von Verbindungen des positiv einwertigen Jods," Verlag von S. Hirzel, Leipzig, 1932.

(4) Zingaro, Kleinberg, Goodrich and VanderWerf, THIS JOURNAL, **71**, 575 (1949).

(5) Burgess and Kraus, *ibid.*, **70**, 706 (1948).

(6) The discrepancy in the case of the nitro compounds is probably due to the strongly absorbing nitro group. As is seen in Table I, however, the nitro compounds show approximately the same per cent. of transmission at 325 $\text{m}\mu$ as do the other salts.

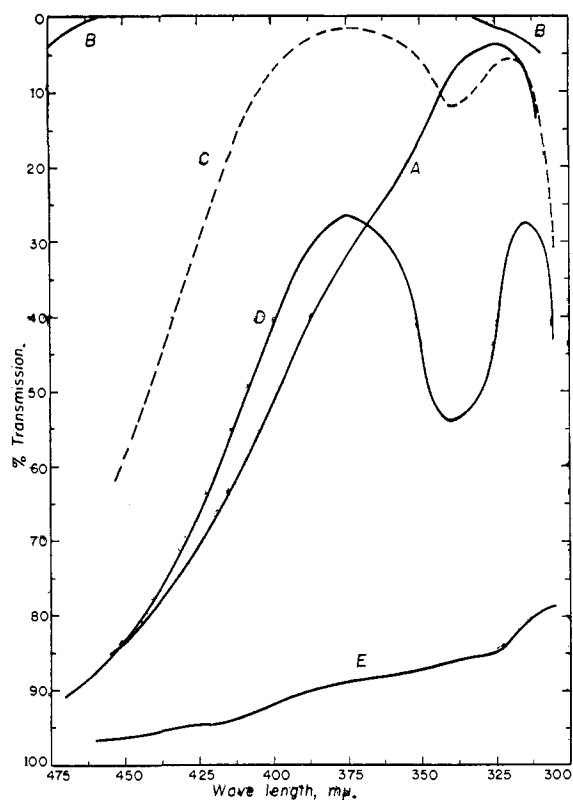
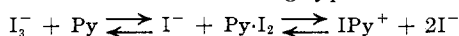


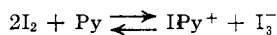
Fig. 1.—Absorption spectra in pyridine: curve A, freshly prepared solution of 0.01 *m* monopyrindine iodine (I) *p*-toluate; curve B, same solution after 4 hours; curve C, after dilution of (B) to 4.6×10^{-4} *m*; curve D, one-day old solution of iodine, 5×10^{-5} *m*; curve E, same solution after five days.

served for the IPy⁺ ion, which may here arise from an equilibrium⁸ of the following type



On the other hand, absorption at this wave length may be due in part directly to the I₃⁻ ion, but the formation of this ion in solutions of iodine in pyridine necessitates the concomitant formation of cationic iodine.

From the evidence presented, the following dissociation is established as the reaction of iodine in pyridine



Attention is called to curve D of Fig. 1, 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 both peaks completely disappeared (E). Addition of a drop of freshly prepared iodine solution caused immediate restoration of the original peaks. In more concentrated solutions, a similar behavior was observed, but even after three weeks the peaks had not completely disappeared.

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

(8) The inference that this type of behavior may be shown by all the so-called "active" solvents is being explored in this Laboratory.

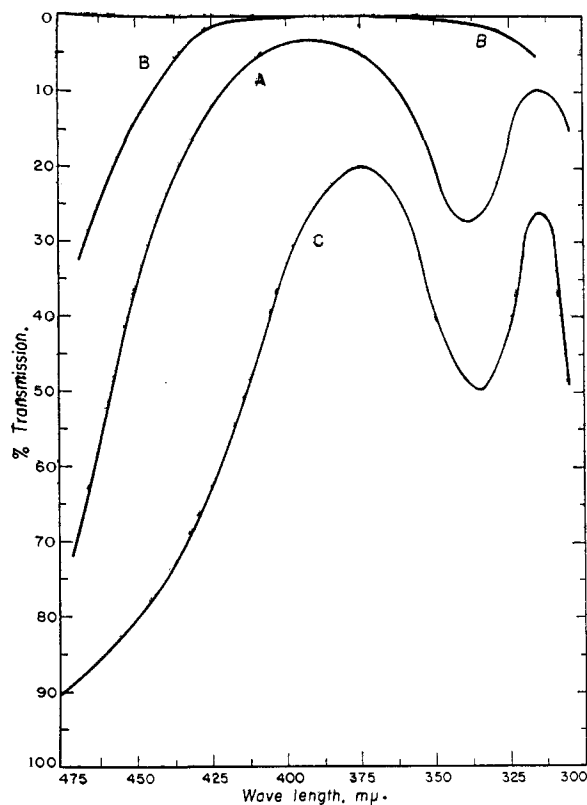


Fig. 2.—Absorption spectra of iodine in pyridine: curve A, freshly prepared solution, 5×10^{-4} *m*; curve B, same solution after 24 hours; curve C, same as B, but diluted to 6.6×10^{-5} *m*.

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 I₃⁻ ion. Conductivity measurements of solutions of the benzoate derivatives in pyridine at concentrations of 0.01 *m* showed a specific conductance of 10^{-7} *ohm*⁻¹ which remained constant for a period of from three to four hours, and then increased steadily to a value of 10^{-6} *ohm*⁻¹ after 15 days. This is of the same order of magnitude as reported for 0.006 *m* solutions of iodine in pyridine.² 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 conductivity reported by Audrieth and Birr,² can be explained by the formation of increasing quantities of the I₃⁻ and IPy⁺ ions.

The values for the absorption maxima for solutions of iodine in pyridine found in this investigation are in disagreement with the data of Getman,⁹ who reported a single maximum at 480 *mμ*. Our observations were reproducible on repeated attempts, and no indication of a maximum at 480 *mμ*

(9) Getman, *THIS JOURNAL*, **50**, 2883 (1928).

was ever noted. Benesi and Hildebrand,¹⁰ in extensive studies on solutions of iodine in acetone, reported a similar disagreement.

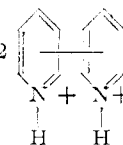
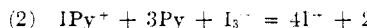
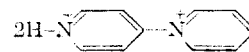
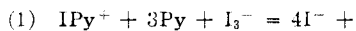
A satisfactory explanation for the behavior of solutions of iodine in pyridine must account for the great increase in conductivity as well as for the disappearance of the original ionic species. In order to account for the fact that the limiting conductance is about twice as great as might be expected on the basis of a simple dissociation of the iodine molecule into a positive and negative ion, Audrieth and Birr² proposed a mechanism involving dissociation into a ternary salt of the formula $\text{Py}^{++}, 2\text{I}^-$. 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 pyridylpyridinium chloride,¹¹ best explained by the postulation of the CIPy^+ ion,¹² the other on the formation of dipyrindyl when pyridine is heated with iodine.¹³ The equations for the reactions are

(10) Benesi and Hildebrand, *THIS JOURNAL*, **71**, 2703 (1949).

(11) Koenigs and Greiner, *Ber.*, **64**, 1045 (1931).

(12) Elderfield, "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 413, 427.

(13) Willink and Wibaut, *Rec. trav. chim.*, **54**, 275 (1935).



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

Summary

1. The absorption spectra of solutions of iodine and positive iodine salts in pyridine and their change with time have been studied.

2. Evidence for the existence of the IPy^+ and I_3^- ions in solutions of iodine in pyridine has been presented.

3. Tentative mechanisms have been proposed to explain the increasing conductivity and disappearance of absorption bands in these solutions.

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RECEIVED JUNE 28, 1950

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The Vapor Pressures and Freezing Points of Some Organic Fluorine Compounds^{1,2}

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The measurements reported in this paper were made in connection with a general program of research in this Laboratory concerning the solubility and other physical properties of organic fluorine compounds.

Experimental

Materials.—The three fluorotoluenes were Eastman Kodak Co. best grade. The three chlorobenzotrifluorides were furnished by the Hooker Electrochemical Company. The *p*-bis-(trifluoromethyl)-benzene was made in this Laboratory by Dr. A. R. Gilbert and Mr. J. B. Bond under the direction of Dr. C. K. Bradsher. The materials were dried over Drierite and then distilled at a high reflux ratio through a silvered vacuum-jacketed glass column packed with $\frac{1}{8}$ " glass helices. A two junction copper-constantan thermel was used to measure the still head temperature.

Vapor Pressures.—A modification of the method of Ramsay and Young which has been previously described⁴ was used for pressures below 100–150 mm. For higher pressures a boiling point apparatus similar to that of Rossini and co-workers⁵ was used. The pressure was controlled with a sulfuric acid manostat similar to that used by Huntress and Hershberg.⁶ The pressure was measured with a mercury manometer and a cathetometer. The pressure over the

reference limb of the manometer was reduced to less than 0.01 mm. with a mercury diffusion pump and then checked with a McLeod gage. The temperature was measured with a platinum resistance thermometer, a standard resistor, and a Leeds and Northrup Type K2 potentiometer. The platinum resistance thermometer and the standard resistor were placed in series with a 2-volt battery and a 2000-ohm resistor. The potential drops across the standard resistor and the platinum thermometer were measured with the potentiometer. From the ratio of these two potential drops and the resistance of the standard resistor the resistance of the platinum thermometer could be calculated. The boiling point apparatus, the manometer, the manostat, a rotary oil pump and a controlled air leak operated by the manostat were connected to a surge tank. The rate at which the air was removed from the system by the pump and the rate at which the controlled air leak admitted air to the system were controlled by means of needle valves. In operation, with the liquid boiling in the boiling point apparatus, the pressure in the system was reduced to the desired value and the two needle valves adjusted. After a few minutes the resistance of the platinum thermometer and the pressure were taken. As a check on the method the vapor pressure of water was measured. The mean deviation of the pressure values calculated from the data of Osborne and Meyers⁷ and the experimental values was ± 0.13 mm. for eleven measurements between 180 and 760 mm.

Freezing Points.—The cooling curves of the best fractions from the distillations were determined in a freezing point apparatus patterned after that of Schwab and Wichers.⁸ From the cooling curves the freezing points and the freezing point depressions were obtained graphically by the method of Stull.⁹

Results

Approximately twenty to twenty-five individual

(7) Osborne and Meyers, *J. Research Natl. Bur. Standards*, **13**, 1 (1934).

(8) Schwab and Wichers, *ibid.*, **34**, 333 (1945).

(9) Stull, *Ind. Eng. Chem., Anal. Ed.*, **16**, 234 (1946).

(1) The work reported was carried out under Contract N6ori 107, T. O. II with the Office of Naval Research.

(2) This paper was taken in part from the thesis submitted by John C. Potter to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

(3) Department of Chemistry, North Carolina State College, Raleigh, N. C.

(4) Stuckey and Saylor, *THIS JOURNAL*, **62**, 2922 (1940).

(5) Willingham, Taylor, Pignocco and Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

(6) Huntress and Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **5**, 144 (1933).