[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Studies on the Chemistry of Halogens and of Polyhalides. X. The Reactions of Iodine Monochloride with Pyridine and with 2,2'-Bipyridine[1]

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The preparation and the isolation of addition compounds of pyridine and of 2,2'-bipyridine and ICl and with $HICl_2$ is described. Absorption spectra of these compounds in acetonitrile solutions have been determined. It is shown that both the 2,2'-bipyridine and the pyridine complexes with iodine monochloride dissociate according to $BP \cdot 2ICl \rightleftarrows BPI^+ + ICl_2^-$ and $2PyICl \rightleftarrows Py_2I^+ + ICl_2^-$.

Introduction

The addition complex of pyridine with iodine monochloride has been described in the literature by several investigators.[2] The most recent work on this compound is that of Fialkov and Muzika,[3] who report the preparation of two addition compounds, $Py \cdot ICl$ and $Py \cdot 2ICl$. From electrolysis and ion transfer studies in nitrobenzene solutions, these authors postulate that the structures of these compounds are, respectively, $(PyI)^+Cl^-$ and $(PyI)^+(ICl_2)^-$.

It is, of course, to be expected that iodine monochloride will form addition compounds with other heterocyclic amines, in particular with the polypyridines. Of these, 2,2'-bipyridine seemed to be particularly interesting since this compound, although it acts as a bidentate ligand with metal ions, coördinates with only one proton in solutions with $pH \geq 1$.[4] The most plausible explanation seems to be that while in crystalline state or in benzene solutions the molecule exists in the *trans* configuration,[5,6] the two rings rotate about the C–C bond and, upon addition of a proton, are stabilized in the *cis* configuration by hydrogen bonding. Although one would expect that 2,2'-bipyridine would form an addition complex with two molecules of iodine monochloride, the possibility of coördination of the positive iodine with both nitrogens in the *cis* form could not be excluded. This investigation was undertaken to compare the reactions of pyridine and of 2,2'-bipyridine with iodine monochloride, and to study spectrophotometrically the ionic or molecular species present in solutions of these complexes.

Experimental Part

Reagents.—The 2,2'-bipyridine (designated below as BP) was obtained from the G. F. Smith Chemical Company and was purified by repeated recrystallizations from hexane; the m.p. was 70.0°, literature values are 69.5[6]-70.0°.[7] Iodine monochloride was prepared and purified by a previously described method.[8] Pyridine was C.P. Merck product; it was shaken up with potassium hydroxide pellets and distilled. Coleman and Bell acetonitrile was purified by the standard methods[8] and its purity was checked by the measurement of specific conductance, which was $0.6\text{-}3 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$.

Spectrophotometric Measurements.—Most of the spectrophotometric measurements were done on a Cary recording spectrophotometer, Model 11, using silica cells of 1.00 or 5.00 cm. in path length.

In some cases where narrow path lengths were needed, the measurements were carried out on a Beckman D.U. spectrophotometer with 1.00 cm. silica cells and 0.9 cm. silica spacers. All measurements were made at room temperature of approximately 25°

Addition Complex of BP with Iodine Monochloride.—Equimolar solutions ($\sim 0.1\ M$) of iodine monochloride and of BP were prepared in carbon tetrachloride and the iodine monochloride then was added slowly to the BP solution from a buret. During the addition, the BP solution was stirred vigorously with an electrical stirrer. The dense yellow precipitate obtained was filtered on a sintered glass crucible, washed with carbon tetrachloride and dried in an oven at 70°. *Anal.* Calcd. for $BP \cdot 2ICl$: C, 24.97; H, 1.66; N, 5.82; iodometric equiv., 120.2. Found: C, 25.40; H, 1.60; N, 6.3; iodometric equiv., 121. The yield was 97–98%.

The compound is quite stable in air and does not seem to undergo hydrolysis with atmospheric moisture as is often the case with other polyhalogen complexes. It is insoluble in water at room temperature but decomposes in boiling water with evolution of iodine; it is readily soluble in organic solvents with the exception of carbon tetrachloride. The compound does not have a sharp melting point, but begins to decompose at approximately 95°.

Alternate Method of Preparation of $BP \cdot 2ICl$.—Approximately 0.2 g. of BP was weighed in a weighing boat and placed in a vacuum desiccator. About 0.5–0.8 g. of iodine monochloride was placed in a crucible at the bottom of the desiccator which was then evacuated. Iodine monochloride vapors reacted rapidly with the BP crystals and, after 24 hours, a black viscous liquid was formed in the weighing boat. The desiccator was then evacuated for several days and gradually the liquid solidified into a brown solid which, upon further evacuation, turned to yellow powder which analyzed as $BP \cdot 2ICl$.

Recrystallizations.—Attempts were made to recrystallize this substance from acetone, ethylene dichloride, ether, ethanol, methanol, ethyl acetate and chloroform. The last solvent gave the best results but only when the yellow powder was dissolved in carefully purified chloroform[9] with subsequent evaporation of the solvent under reduced pressure. Shiny, transparent, yellow crystals were obtained which analyzed to $BP \cdot 2ICl$.

It was observed that when chloroform was not rigorously purified before use, a small quantity of yellow needle-like crystals, quite different in appearance from those of $BP \cdot 2ICl$, were obtained. These crystals were identified as $BP \cdot HICl_2$. *Anal.* Calcd. for $BP \cdot HICl_2$: C, 33.8; H, 2.54; N, 7.89; iodometric equiv., 177.5. Found: C, 35.0; H, 2.81; N, 8.34; iodometric equiv., 177. This compound can be prepared easily by recrystallization of the $BP \cdot 2ICl$ complex from chloroform previously shaken up with a few ml. of concentrated hydrochloric acid. It is stable in air, soluble in polar solvents, and melts sharply and reversibly at 139°.

Pyridine–ICl Complex.—The complex was prepared by a method analogous to that used in the preparation of $BP \cdot 2ICl$. It was obtained in the form of a bright yellow microcrystalline powder, iodometric equivalent of which was

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(1) Paper presented before the Physical–Inorganic Division at the 128th meeting of the American Chemical Society, September 10, 1955, Minneapolis, Minnesota.

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(9) P. Walden, *Z. physik. Chem.*, **147**, 1 (1930).

found to be 120.6, calculated weight for Py·ICl is 120.7. Attempts to prepare Py·2ICl described in the literature[3] were unsuccessful.

Pyridinium Iododichloride.—This compound was prepared by the adding of hydrochloric acid to Py·ICl in chloroform solution and recrystallizing. Iodometric equivalent was found to be 138, calculated for $Py\cdot HICl_2$, 139.

Dipyridinoiodine(I) Perchlorate.—The perchlorate was prepared by the reaction of $Py_2\cdot AgClO_4$ with iodine in chloroform solution.[10] It was obtained as greyish-white powder. Iodometric equivalent was found to be 194, calcd. for $Py_2\cdot ICIO_4$, 192.

Pyridinium Perchlorate.—Pyridinium perchlorate was obtained by the addition of 70% perchloric acid to a solution of pyridine in acetic acid. The white microcrystalline precipitate was filtered, washed and dried. The melting point of the compound was 287°; literature[11] value 288°.

Results and Discussion

The absorption spectra of BP, BPH^+ (obtained by the addition of a slight excess of hydrochloric acid to a BP solution), $BP\cdot HICl_2$ and BP·2ICl in acetonitrile solution are shown in Fig. 1. The spectra of BP and BPH^+ in this solvent are similar to those in aqueous solutions.[12]

The absorption spectra of BP·2ICl and of $BP\cdot HICl_2$ yield some interesting information. It is seen that at longer wave lengths the absorption curve of the second compound practically coincides with that for $BP\cdot H^+$. However, beyond 260 mμ, the characteristic absorption maximum of the ICl_2^- ion[13] at 227 mμ is observed. The molar absorptivity at this wave length is 57,500. The molar absorptivity of BPH^+, calculated from the absorption curve of BPHCl, is 5,000. This leaves 52,500 for the absorbance of the ICl_2^- which is close to the value of 54,500 obtained from solutions of tetramethylammonium iododichloride in the same solvent[13] after suppression of the slight dissociation of the ICl_2^- ion by an excess of the chloride ion. This peak did not show any change with time, and appears to obey Beer's law.

The BP·2ICl curve also gives the characteristic ICl_2^- absorption maximum at 227 mμ. The molar absorptivity varied between 39,000 and 62,000 depending on the concentration and the age of the solution, the aged and the more dilute solutions showing a higher molar absorptivity. The concentration range of the solutions measured varied between 2×10^{-4} and 8×10^{-6} *M*.

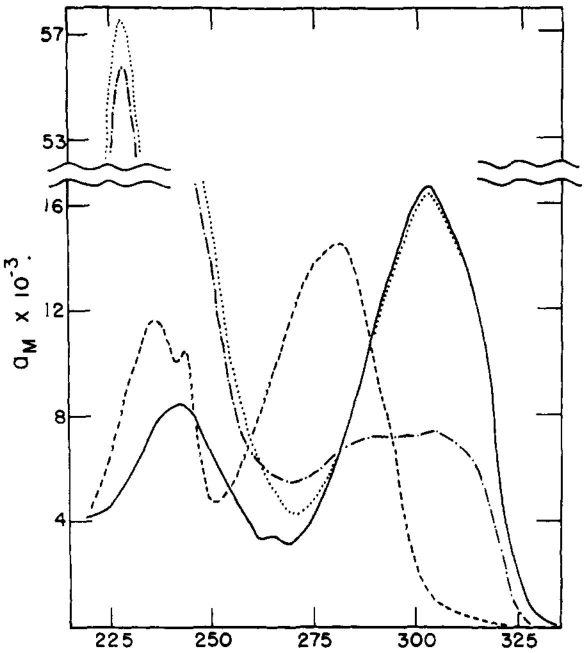

Fig. 1.—Absorption spectra of 2,2'-bipyridine and of 2,2'-bipyridine compounds in acetonitrile: - - - -, 2,2'-bipyridine; ———, BP·HCl; . . . ., $BP\cdot HICl_2$; - · - · -, BP·2ICl.

The presence of the ICl_2^- ion shows that the compound undergoes dissociation

$$BP\cdot 2ICl \rightleftarrows BPI^+ + ICl_2^- \qquad (1)$$

However, the situation seems to be more complex because of the variation in the intensity of the absorption maximum with time, which is indicative of the presence of free iodine monochloride.[8] However, the molar absorptivity of a fresh 1.0×10^{-4} *M* solution of ICl is only 8,000 (calculated on the basis of ICl_2^-). Since the lowest value obtained on this investigation for 2×10^{-4} *M* solution was 39,000, it is evident that the maximum cannot be attributed to a simple dissociation of iodine monochloride. It seems quite likely that, as BP·2ICl is dissolved in acetonitrile, it undergoes the following series of reactions

$$BP\cdot 2ICl \rightleftarrows BP\cdot ICl + ICl \qquad (2)$$

$$BP\cdot ICl \rightleftarrows BP\cdot I^+ + Cl^- \qquad (3)$$

$$ICl + Cl^- \rightleftarrows ICl_2^- \qquad (4)$$

The over-all reaction is given by eq. 1.

It has been established that the equilibrium constant for reaction 3 in acetonitrile is of the order of 1.0×10^7.[14] Equilibria constants for reactions 1 and 2 cannot be determined at the present time because of uncertainty in the absorption values of BP·ICl and of $BP\cdot I^+$. (An attempt was made to prepare $BP\cdot ClO_4$ and $BP\cdot INO_3$ by the method used for the pyridine analogs but it was unsuccessful.) A rough estimation can be made of the degree to which reaction 4 occurs from the intensity of the ICl_2^- peak at 227 mμ which, as was mentioned above, reaches 62,000 in 8×10^{-6} *M* solutions. This value is nearly 9,000 units higher than that for the ICl_2^- ion itself. Since it is doubtful that the absorption of BPI^+ ion would be much higher than 10,000 at this wave length, and since 62,000 seems to be a limiting value for the BP·2ICl absorption at this wave length, it can be concluded that in 10^{-5} *M* solution reaction 4 occurs to the extent of $\geqslant 90\%$.

The study of the pyridine system gives additional support to the above ideas. The absorption curves of Py·ICl, $Py\cdot HICl_2$, $Py\cdot HClO_4$, $Py_2\cdot ClO_4$ and pyridine are given in Fig. 2. Again, in the first two cases, we have the characteristic ICl_2^- peaks at 227 mμ. Subtracting the molar absorptivity of PyH^+ ion from that of $Py\cdot HICl_2$ at this wave length, we get 53,200–1,000 or 52,200 for the molar ab-

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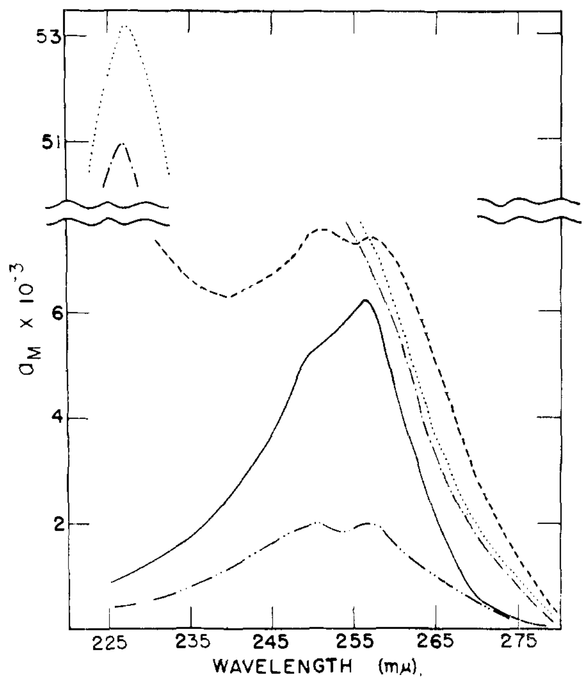

Fig. 2.—Absorption spectra of pyridine and of pyridine compounds in acetonitrile: -·-·-·, pyridine; ———, $PyHClO_4$; - - - -, Py_2IClO_4; . . . ., $PyHICl_2$; -·-·-, PyICl.

sorptivity of ICl_2^-. It is seen that this value agrees closely with that obtained for the $BP\cdot HICl_2$ complex.

On the other hand, the iodine monochloride complex again yields variable molar absorptivities, varying from 45,000 to 51,000 at 227 mμ, but the variations seem to be much less pronounced than in the case of BP. Continuous variation method on the pyridine–iodine monochloride system in the 300–400 mμ region gave a series of sharp maxima at a 1:1 mole ratio of reacting species. Since, in this case, the molar absorptivity of the positive iodine complex with pyridine is known, it is possible to estimate the absorbance due to the ICl_2^- ion alone.

At 227 mμ, the molar absorptivity for a 4.3×10^{-5} *M* solution of Py·ICl is 44,400, calculated on the basis of the ICl_2^- ion. At this wave length, Py_2I^+ has a molar absorptivity of 8,500 which leaves 35,900 for the molar absorptivity of ICl_2^-. These results indicate that we have a dissociation of the Py·ICl complex according to

$$2\text{P}\cdot\text{yICl} \rightleftarrows \text{Py}_2\text{I}^+ + \text{ICl}_2^-$$

and that in 4.3×10^{-5} *M* solution it occurs to the extent of ~ 70%.

Numerous spectrophotometric studies have been done in the past on solutions of iodine in pyridine.[15] Although in some cases evidence was obtained that the triiodide ion was formed in such systems, in general, it was assumed that the absorption was due to the PyI^+ ion. It seems from the results obtained in this investigation that two molecules of pyridine are coördinated to the positive iodine. The fact that positive iodine can have a coördination number of two is confirmed by the existence of such compounds as $Py_2\cdot IClO_4$, $Py_2\cdot INO_3$, etc.[10] Because of the time-dependent change in the absorption spectra of solutions containing iodine monochloride, exact quantitative calculations of the equilibria constants for the reactions described in this report seem to be impossible at the present time. The reasons for this change are now being investigated in this Laboratory.

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Alkylhydrazines. I. Formation of a New Diazo-like Species by the Oxidation of 1,1-Dialkylhydrazines in Solution

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It has been found that 1,1-dialkylhydrazines react with alkali halates and halogens in acidic media to form a new class of diazo-like compounds, $R_2N^+{=}N^-$, which exhibit remarkable stability as their conjugate acids, $R_2N^+{=}NH$, but in neutral or basic solution immediately dimerize to form tetraalkyltetrazenes, $R_2NN{=}NNR_2$. For example, the oxidation of 1,1-dimethylhydrazine with iodine or bromine in neutral or weakly basic solution at 0° involves a two-electron change and produces tetramethyltetrazene in essentially quantitative amounts. In acidic solution at 0° the reaction of 1,1-dimethylhydrazine with potassium iodate or bromate consumes two equivalents of oxidant and forms a diazo-like compound which can be either reconverted quantitatively by stannous chloride to 1,1-dimethylhydrazine or converted quantitatively to tetramethyltetrazene by careful neutralization of the freshly prepared acidic solutions at low temperatures. Evidence for the formation of this class of diazo-like compounds is interpreted on the basis of the present experimental data and related to the previously postulated reactions for the oxidation of hydrazine itself. Application of this species to preparative chemistry is discussed briefly.

Introduction

Although the mechanism for the oxidation of hydrazine in solution has been partially established from experiments with isotopically distinguished nitrogen and kinetic studies,[1,2] no concerted effort has been directed toward the elucidation of the oxi-

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