plex in which an electron has been transferred from the donor to the acceptor.

The energy (E) associated with eq. 7 from the variation method is given by eq. 8

$$(E_0 - E)(E_1 - E) = (H_{01} - ES_{01})^2 \qquad (8)$$

where $E_0 = \int \psi_0 H \psi_0 \, d\tau$, $E_1 = \int \psi_1 H \psi_1 \, d\tau$, $H_{01} = \int \psi_0 H \psi_1 \, d\tau$, $S_{01} = \int \psi_0 \psi_1 \, d\tau$, H = total exact Hamiltonian for the entire system, E_0 = ground-state energy after electrostatic interactions, and E_1 = charge-transfer excited state energy before mixing with ground state. The integral H_{01} is the resonance energy due to the mixing of ψ_0 and ψ_1.

$$E_0 - E = (H_{01} - ES_{01})^2/(E_1 - E) \qquad (8a)$$

$$E = E_0 - (H_{01} - ES_{01})^2/(E_1 - E) \qquad (8b)$$

There are two solutions for E. One corresponds to the final ground state (E_G) and one to the final excited state (E_E). Because the energy of interaction between acids and bases is in general small, and $E_1 - E$ is very large, $E_G \sim E_0$. Substitution of E_0 for E in the right-hand side and $E = E_G$ in the left-hand side of eq. 8b gives eq. 9.

$$E_G = E_0 - (H_{01} - E_0S_{01})^2/(E_1 - E_0) \qquad (9)$$

It can be seen from this last equation that the energy of the ground state E_G has contributions from electrostatic interactions E_0 and a second term that is principally due to covalency. The energetics is schematically illustrated in Figure 1.

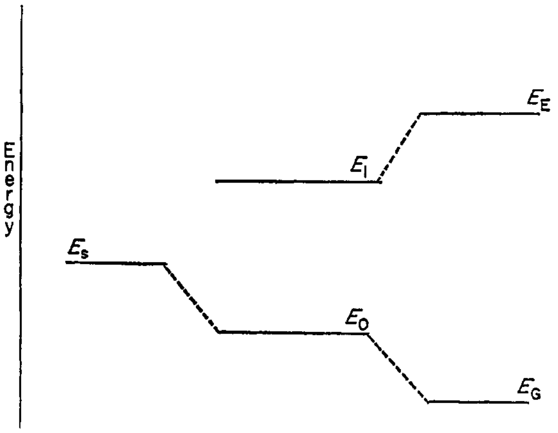

Figure 1. Diagram of bonding terms in an acid–base interaction: E_s is the energy of the infinitely separated acid and base; $E_s - E_0$ = stabilization energy due to classical electrostatic interactions; and $E_0 - E_G$ = stabilization energy due to electron delocalization.

In summary, a large number of systems have been correlated by this approach. The parameters assigned agree with qualitative chemical intuition regarding the acid–base interactions and also with semiquantitative estimates regarding the amount of covalency. In view of the arbitrary assignment of $E_A = C_A = 1$ for iodine, large numbers are obtained for the C_B parameters compared to E_B. The arbitrariness of this assumption disappears when the product E_AE_B is compared to C_AC_B. This assumption permits comparison of C_A values with other C_A values. It will be essential to collect more thermodynamic data to ascertain the limits of this correlation. In this connection, acids and bases which undergo large changes in geometry upon coordination should be examined. It will also be interesting to obtain data on systems where the enthalpy of adduct formation is much larger than those reported here. Such systems will indicate whether the parameters reported remain constant when a large perturbation is made on the acids and bases by coordination.

Acknowledgment. The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758. We also wish to acknowledge a helpful discussion with Professor Z. Hugus, Jr., on this problem.

Studies on the Chemistry of Halogens and of Polyhalides. XXIV. The Behavior of Iodine Monochloride Complexes with 2,2'-Bipyridines in 1,2-Dichloroethane Solutions[1]

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Iodine monochloride complexes of 2,2'-bipyridines were prepared, and their behavior in 1,2-dichloroethane was investigated spectrophotometrically. It is shown that in this solvent the complex BP·2ICl readily dissociates into its component molecules and that BP·HICl$_2$ is then gradually formed. This reaction is evidently due to catalytic dehydrochlorination of 1,2-dichloroethane which leads to formation of hydrochloric acid and vinyl chloride. The former reacts with iodine monochloride to form HICl$_2$, while vinyl chloride either undergoes polymerization or reacts with an excess of iodine monochloride to give 2,2-dichloro-1-iodoethane.

Introduction

Studies of halogen complexes in nonaqueous solvents are very frequently plagued with slow reactions which are accompanied by corresponding changes in the ab-

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[1] Paper XXIII in this series: *J. Inorg. Nucl. Chem.*, **26**, 2027 (1964).

sorption spectra and in the electrical conductances of the solutions.[2–4]

In many cases the time reaction is simply due to the hydrolysis of the halogen by small amounts of water present in the nonaqueous solvent, or to the halogenation of the solvent and/or the donor molecule. In other cases, where the above reasons can be eliminated, they have been attributed to a slow transition from an "outer" complex to a "inner" complex[2,3] as defined by Mulliken[5] or to a possible interaction between 1:1 and 2:1 complexes.[4]

Preliminary studies of the iodine monochloride–bipyridine and iodine monochloride–biquinoline complexes in 1,2-dichloroethane[6] have indicated that the system is unstable and that there is a gradual change of absorbance with time. This study was undertaken to investigate the mechanism of the reaction and to determine the nature of chemical species present in iodine monochloride–bipyridine mixtures in 1,2-dichloroethane.

Experimental

Reagents. Iodine monochloride was prepared and purified by previously described techniques.[7] The melting point of the recrystallized product was 27.2°, identical with the literature value.[7]

The 2,2′-bipyridine (abbreviated as BP) and 4,4′-dimethyl-2,2′-bipyridine were obtained from the G. F. Smith Chemical Co. They were used without further purification. The melting points were 70.5° (lit.[8] m.p. 69.5–70.0°) and 172° (lit.[9] m.p. 171–172°), respectively.

Purification procedures for 1,2-dichloroethane and carbon tetrachloride have been described previously.[10] The purity of these solvents was checked by vapor phase chromatography. There was no indication of any extraneous peaks.

Preparation of Halogen Complexes. BP·2ICl. The addition complex of BP with iodine monochloride was precipitated out of carbon tetrachloride solution as shown in a previous paper.[2] It was also obtained by mixing the components in 1,2-dichloroethane and then diluting the resulting mixture with carbon tetrachloride. In both cases the yields were quantitative. The purification was easily carried out as follows: 3.0 g. of the crude product was dissolved into 50 ml. of 1,2-dichloroethane containing a few drops of iodine monochloride at about 50°, and the resulting solution was diluted with 70 ml. of carbon tetrachloride at the same temperature. Upon cooling, fine, clear yellow needles (2.4 g.) were obtained. The compound begins to decompose at approximately 100° and completely melts at around 140°. An attempt to prepare the 1:1 complex (BP·ICl) in the presence of an excess of BP in 1,2-dichloroethane was unsuccessful. *Anal.* Calcd. for $C_{10}H_8N_2I_2Cl_2$: C, 24.97; H, 1.68; N, 5.82; iodometric equiv., 120.3. Found: C, 25.03; H, 1.64; N, 5.88; iodometric equiv., 121.0.

Dimethyl-BP·2ICl. This complex was prepared by the same methods as described for BP·2ICl. The yield was 94.1%. In the purification procedure, 1.5 g. of the product was dissolved in 120 ml. of dichloroethane containing a few drops of iodine monochloride, filtered, and diluted with 200 ml. of carbon tetrachloride. About 1.0 g. of fine yellow needles was obtained. The complex does not have a definite melting point, but it decomposes gradually at approximately 130 to 140°. *Anal.* Calcd. for $C_{12}H_{12}N_2I_2Cl_2$: C, 28.31; H, 2.38; N, 5.50; iodometric equiv., 127.2. Found: C, 28.40; H, 2.48; N, 5.48; iodometric equiv., 128.6.

BP·HICl₂. This compound was prepared by recrystallization of 2.0 g. of BP·2ICl in 90 ml. of chloroform previously shaken with a few milliliters of concentrated hydrochloric acid. The product was obtained in the form of yellow needles which were purified by the method indicated above. About 1.4 g. of orange-yellow needles was obtained by the purification procedure, m.p. 140°. *Anal.* Calcd. for $C_{10}H_9N_2ICl_2$: C, 33.82; H, 2.56; N, 7.89; Cl, 19.99; I, 35.74; iodometric equiv., 177.6. Found: C, 33.95; H, 2.59; N, 8.48; Cl, 19.38; I, 35.59; iodometric equiv., 179.5.

Dimethyl-BP·HICl₂. This compound was prepared in the same way as the BP·$HICl_2$. About 2.7 g. of yellow needles which melt at 153° was obtained from 4.0 g. of dimethyl-BP·2ICl. *Anal.* Calcd. for $C_{12}H_{13}N_2ICl_2$: C, 37.61; H, 3.42; N, 7.31; Cl, 18.53; I, 33.12; iodometric equiv., 191.6. Found: C, 37.19; H, 3.41; N, 7.01; Cl, 18.80; I, 32.75; iodometric equiv., 190.3.

Stability of ICl Solutions in 1,2-Dichloroethane. Iodine monochloride dissolved in 1,2-dichloroethane showed an absorption spectrum with a maximum at 428 mμ and molar absorptivity of 133. The solutions were stable for periods of several weeks if contact with atmospheric moisture was precluded.

Spectrophotometric Measurements. All the solutions of the solid complexes were prepared by dissolving weighed amounts of crystals in the appropriate volume of the solvent. The mixed solutions of the bases and iodine monochloride were prepared by diluting the stock solutions of the components. The stock solutions of iodine monochloride were prepared by dissolving an approximate amount in the solvent and their concentrations were determined iodometrically. In order to obtain the spectrum of the BPH^+ ion, bipyridine was dissolved in 1,2-dichloroethane which was saturated with hydrochloric acid.

Spectrophotometric measurements were made at room temperature on a Cary 14 recording spectrophotometer with silica cells of 1.00-, 2.00-, and 10.00-cm. path lengths. The infrared measurements were made on a Beckman IR 5A recording spectrophotometer.

Isolation of BP·HICl₂ from the Aged Solutions. A solution of BP and iodine monochloride in 1,2-dichloroethane was prepared in a 1000-ml. volumetric flask. The concentrations of the components were: BP, 1.00 $\times 10^{-3}$ *M;* ICl, 2.32 $\times 10^{-3}$ *M.* The reaction leading to the formation of $HICl_2$ was followed spectrophotometrically. When the reaction reached equilibrium state, as shown by the constancy of the absorption

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(2) A. I. Popov and R. T. Pflaum, *J. Am. Chem. Soc.*, **79**, 570 (1957).

(3) A. I. Popov and W. A. Deskin, *ibid.*, **80**, 2976 (1958).

(4) C. D. Schmulbach and D. M. Hart, *ibid.*, **86**, 2347 (1964).

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(8) P. Krumholz, *Anais Acad. brasil cienc.*, **22**, 263 (1950).

(9) F. H. Case, *J. Am. Chem. Soc.*, **68**, 2574 (1946).

(10) (a) A. I. Popov and R. F. Swensen, *ibid.*, **77**, 3724 (1955); (b) A. I. Popov, D. H. Geske, and N. C. Baenziger, *ibid.*, **78**, 1793 (1956).

spectrum, the solution was gradually evaporated in dry nitrogen atmosphere, at first at reduced pressure and then at ordinary pressure. The orange-yellow needles obtained by this procedure were dried *in vacuo*. The yield was 0.350 g. (98.5% of theory), m.p. 136°. *Anal.* Found: C, 33.70; H, 2.54; N, 7.98; Cl, 19.69; I, 35.91; iodometric equiv., 178.0; which corresponds to the composition of BP·$HICl_2$ as shown above.

Recovery of 1,2-Dichloroethane from the Aged Solutions. The solvent recovered in the above procedure was treated with aqueous potassium iodide and then with aqueous sodium thiosulfate solutions. After azeotropic removal of water, it was dried and distilled as described in the previous paper.[10a]

Preparation of 2,2-Dichloro-1-iodoethane. Iodine monochloride (0.3 mole) was dissolved in 300 ml. of carbon tetrachloride. Gaseous vinyl chloride was then gradually introduced to the solution which was vigorously stirred. The passage of vinyl chloride was continued for 5 hr. at room temperature. After standing overnight, the reaction mixture was treated with a dilute aqueous solution of potassium iodide and sodium thiosulfate. The carbon tetrachloride layer was separated and dried by adding anhydrous sodium sulfate. The solution was then fractionally distilled through a 20-cm. fractionating column packed with helices. After distilling off carbon tetrachloride, about 40 g. of a fraction boiling at 168–171° was collected. It was further treated with a dilute aqueous solution of potassium iodide and sodium thiosulfate and vacuum distilled below 60°. Its specific gravity was 2.1982 at 23° (lit.[11] 2.2187, the measured temperature not being described) and $n^{20}D$ 1.5774. *Anal.* Calcd. for $C_2H_3Cl_2I$: C, 10.67; H, 1.33; Cl, 31.57; I, 56.43. Found: C, 10.68; H, 1.49; Cl, 31.19; I, 57.64.

Results

The spectroscopic behavior of the mixed solution of 2,2′-BP and iodine monochloride in 1,2-dichloroethane is shown in Figure 1. At first the spectrum is essentially that of free 2,2′-bipyridine although the shorter wave length peaks are submerged in the high intensity absorption due to iodine monochloride. However, a weak inflection originally observed at 310 mμ gradually increases in intensity and forms a peak which eventually reaches a constant height. Repeated investigations of this phenomenon showed that the change of the absorption spectrum is reproducible and that the rate of the change is considerably enhanced by the increase of the molar ratio of iodine monochloride to 2,2′-BP. Table I illustrates the relation between the molar ratio of the reactants and the reaction time, as indicated by the constancy of the absorption peak at 310 mμ.

Table I. Effect of Molar Ratio of Iodine Monochloride on the Rate of the Reaction

Concn. of BP, 10^5 M	4.68	4.68	4.68	4.68
Mole ratio ICl/BP	1.63	2.58	3.60	30.0
Time, hr.	500	180	60	10

The spectrum of the solid complex, BP·2ICl, dissolved in 1,2-dichloroethane showed similar behavior as

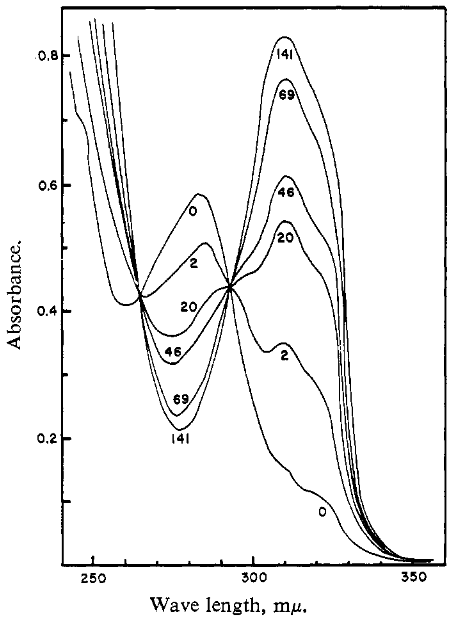

Figure 1. Spectrophotometric change of the mixed solution of 2,2′-bipyridine and iodine monochloride: BP, 4.68 × 10^{-5} M; ICl, 12.10 × 10^{-5} M; figures on the curves, elapsed time in hours.

illustrated in Figure 2. In the visible region there is a weak absorption peak at about 427 mμ characteristic of free iodine monochloride. The rate of the intensity decrease of the visible absorption peak is in good agreement with the rate of the intensity increase at 310 mμ.

The series of spectra in Figures 1 and 2 have distinct isosbestic points, except for a slight shift in the visible spectra shown in Figure 2. Similar coincidental changes between the visible and the ultraviolet absorption spectra were also found in the spectra of the 2,2′-bipyridine–iodine monochloride mixed system in 1,2-dichloroethane as shown in Figure 3.

Spectral changes were very markedly accelerated by irradiation. In order to study this effect, two solutions were prepared containing 2.00 × 10^{-5} M BP + 5.00 × 10^{-5} M ICl and 1.00 × 10^{-4} M BP + 2.50 × 10^{-4} M ICl. Each solution was divided into two parts, one of which was exposed to light and the other, in amber flasks, was stored in the dark. The absorption spectra of these solutions were measured as a function of time. As shown in Figure 4, solutions which were exposed to light reached equilibrium after 20 hr., while solutions kept in the dark showed only ~30% conversion from the spectra of BP + ICl to those of BP·$HICl_2$ after 270 hr. When these solutions were exposed to light (indicated by arrows on the graphs), they very rapidly attained equilibrium.

Since the slow reaction leads to the formation of the BP·$HICl_2$ complex, it is evident that there is a slow generation of hydrochloric acid in the solution. This reaction may be due to one of the following mechanisms: (a) halogenation of the BP nucleus, (b) halogenation of the solvent, (c) decomposition of iodine monochloride by absorption of the atmospheric moisture, (d) dehydrochlorination of 1,2-dichloroethane.

Quantitative recovery of BP as BP·$HICl_2$ argues strongly against the halogenation of the BP nucleus. The effect of the presence of water in the system was also investigated. An equimolar amount of water was

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(11) L. Henry, *Bull. soc. chim. France*, [2] 42, 263 (1884).

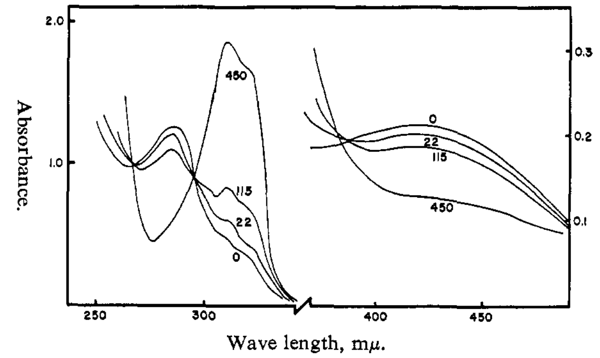

Figure 2. Spectrophotometric change of the solution of BP·2ICl in the ultraviolet and visible region: concentration, 1.10 × 10^{-4} *M;* path lengths of the cells, 1.0 cm. (ultraviolet) and 10.0 cm. (visible); figures on the curves, elapsed time in hours.

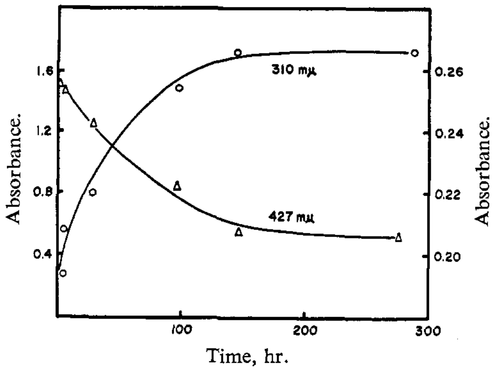

Figure 3. Change of the absorption intensity of the 2,2′-bipyridine–iodine monochloride system: BP, 1.02 × 10^{-4} *M;* ICl, 2.55 × 10^{-4} *M;* intensity at 310 mμ in 1.0-cm. cell, right abscissa; intensity at 472 mμ in 10.0-cm. cell, left abscissa.

added to 4.30 × 10^{-5} *M* solutions of BP·2ICl in 1,2-dichloroethane in one case and a threefold excess of water in another. There was, however, no meaningful difference in the rate of the spectral changes as compared to a run without water. The rate of the spectral variation was actually slightly slower in the presence of water.

In order to test the remaining possibilities, an *equimolar* mixture of BP and of iodine monochloride, 4.5 × 10^{-5} *M* in each component, was prepared in 1,2-dichloroethane and the solution was allowed to come to equilibrium. The equilibrium absorbance value at 310 mμ showed an essentially quantitative formation of BP·$HICl_2$ in the solution. In other words, *all of the iodine monochloride present in the solution is recovered in the complex.* Evidently, hydrogen chloride has to come from some other source. It must come, therefore, from the dehydrochlorination of the solvent. This reaction should lead to the formation of vinyl chloride.

Several attempts were made to detect vinyl chloride in the aged solution by infrared measurements and by vapor phase chromatography. However, the attempts were unsuccessful. It should be noted that the solutions were very dilute (10^{-4}–10^{-5} *M*) and thus most of vinyl chloride generated in the solution probably reacts with an excess of iodine monochloride to form 2,2-dichloro-1-iodoethane and/or it could undergo polymerization. Actually, when the mixed solution of 2,2′-BP and iodine monochloride in 1,2-dichloroethane was kept standing for over 1 month, the recovery of BP·$HICl_2$ by the method described above led to a viscous precipitate of BP·$HICl_2$, with the yield being over 100%. This may be attributable to the contamination of the product by polymerized vinyl chloride.

In order to test this hypothesis, a solution of bipyridinium chloride in 1,2-dichloroethane was diluted with the solvent recovered from the aged solution (purified as described above). The absorption spectrum of the resulting solution was not that of BP·H^+ ion but rather was identical with that of BP·$HICl_2$. These results were entirely reproducible. Since all of iodine monochloride was removed from the aged solution by sodium thiosulfate before distillation, it seems reasonable to postulate that the formation of BP·$HICl_2$ is due to the decomposition of 2,2-dichloro-1-iodoethane.

This assumption was confirmed by a direct preparation of 2,2-dichloro-1-iodoethane and its reaction in the investigated system. The procedure described above was carried out using a 1.00 × 10^{-4} *M* solution of 2,2-dichloro-1-iodoethane in 1,2-dichloroethane instead of the recovered solvent. Once again the absorption spectrum unambiguously showed the formation of BP·$HICl_2$.

Iodine monochloride can also be lost by the 2,2-dichloro-1-iodoethane in the presence of BP, although the reaction proceeds much slower. A solution 4.5 × 10^{-5} *M* in BP and 8.0 × 10^{-3} *M* in 2,2-dichloro-1-iodoethane was prepared in 1,2-dichloroethane and allowed to stand for several days. Studies of the absorption spectra showed, once again, a gradual formation of BP·$HICl_2$.

As to the 4,4′-dimethyl-2,2′-BP system, the situation is the same as in the 2,2′-BP system. Absorption spectra are shown in Table II.

Table II. Spectra of 4,4′-Dimethyl-2,2′-BP and of 4,4′-Dimethyl-2,2′-BP·$HICl_2$ in 1,2-Dichloroethane

	λ_1, mμ	ϵ_1 × 10^{-4}	λ_2, mμ	ϵ_2 × 10^{-4}	λ_3, mμ	ϵ_3 × 10^{-4}
Dimethyl-BP	282.0	1.28	250	0.88	242	0.97
Dimethyl-BP·$HICl_2$	307	1.63[a]				

[a] An approximate value could be also estimated from the absorption spectrum of an aged solution of dimethyl-BP·2ICl (concentration, 4.01 × 10^{-5} *M*). The time required to attain the equilibrium was 194 hr.

Discussion

It has been well known that, among many of the commonly used chloro solvents, 1,2-dichloroethane is relatively reactive and under certain conditions undergoes dehydrochlorination to form vinyl chloride and hydrochloric acid.[12] Usually highly chlorinated hydrocarbons are apt to be dehydrochlorinated, and such reaction can be catalyzed by nitrogen bases such as alkylamines and their hydrochloride salts as well as by quinoline, pyridine, etc.[13] However, it was rather unexpected

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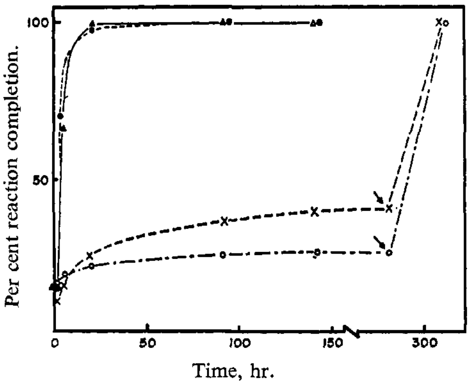

Figure 4. Effect of irradiation on the 2,2'-bipyridine–iodine monochloride system: (a) ---●--- (exposed) and ---×--- (unexposed): BP, 2.00×10^{-5} *M;* ICl, 5.00×10^{-5} *M;* path length of the cell, 2.0 cm.; (b) —△— (exposed) and ---○--- (unexposed): BP, 1.00×10^{-4} *M;* ICl, 2.50×10^{-4} *M;* path length of the cell, 1.0 cm. The arrows designate the start of exposure to room light.

that the relatively weak base such as 2,2'-BP causes the dehydrochlorination of 1,2-dichloroethane in the presence of ICl.

The over-all reactions in the system, 2,2'-BP–ICl in 1,2-dichloroethane, are summarized as

$$BP\cdot 2ICl \longrightarrow BP + 2ICl \qquad (1)$$

$$CH_2ClCH_2Cl \longrightarrow CH_2{=}CHCl + H^+ + Cl^- \qquad (2)$$

$$ICl + Cl^- \longrightarrow ICl_2^- \qquad (3)$$

$$BP + H^+ + ICl_2^- \longrightarrow BP\cdot HICl_2 \qquad (4)$$

$$CH_2{=}CHCl + ICl \longrightarrow CH_2ICHCl_2 \qquad (5)$$

Since 1,2-dichloroethane has a dielectric constant of 10.36 at 25°, it is obvious that most of the ions exist as ion pairs.

Although the iodine monochloride complexes are usually quite stable in solutions,[14] BP·2ICl or dimethyl-BP·2ICl are extremely unstable in solvents such as 1,2-dichloroethane and upon dissolution the complexes are eventually completely dissociated.

Since the dehydrochlorination reaction (2) is accelerated by irradiation and by the presence of the amine, its decomposition mechanism is considered to be a halogen-catalyzed chain reaction as Sherman, *et al.*,[15] proposed for the catalytic effect of chlorine on dehydrochlorination.

The spectrum of BP·$HICl_2$ has an intense absorption peak at about 230 mμ with a molar absorptivity of about 52,000. Its exact position and intensity are difficult to estimate more accurately because of the high absorption by the solvent in that spectral region. It seems probable, however, that this peak is due to the absorption by the ICl_2^- ion.[2] No attempt was made to study the rate of the dehydrochlorination reaction, since this is rather far removed from the present research interests of the authors.

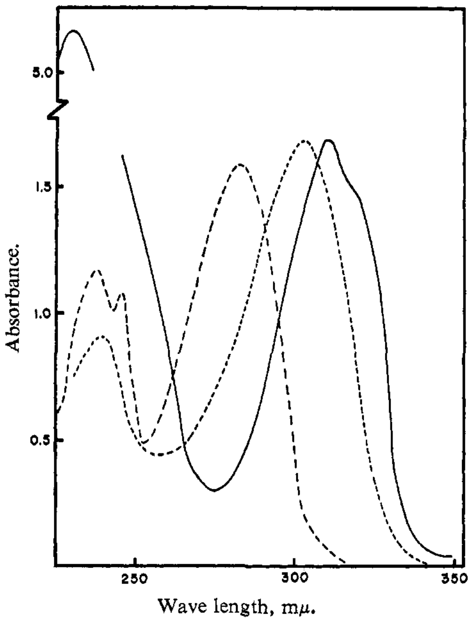

Figure 5. Absorption spectra of 2,2'-bipyridine and 2,2'-bipyridine compounds in 1,2-dichloroethane: --------, 2,2'-BP; ———, 2,2'-BP·$HICl_2$; ......, 2,2'-BP·HCl (qualitative measurement).

It has been previously shown by Nakamoto[16] that 2,2'-BP monohydrochloride has the *cis* configuration with the proton being attached to one of the two nitrogen atoms. Since the main absorption peak of BP·$HICl_2$ is very close to that of the hydrochloride (310 and 303 mμ, respectively), it seems probable that the BP·$HICl_2$ complex also has the cisnoid configuration.

The discovery that 1,2-dichloroethane can undergo dehydrochlorination in the presence of BP and of iodine monochloride was completely unexpected. In the past this solvent has been frequently used by several investigators as an inert medium for the study of halogen charge-transfer complexes. It is seen from the above results, however, that 1,2-dichloroethane is far from being an ideal solvent for such studies and that there is yet another possible mechanism responsible for the instability of halogen complexes in solutions and for the frequently observed "slow reactions" in these systems.

Acknowledgment. The authors gratefully acknowledge the support of this work by the U. S. Army Research Office (Durham).

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