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

Studies on the Chemistry of Halogens and of Polyhalides. XI. Molecular Complexes of Pyridine, 2-Picoline and 2,6-Lutidine with Iodine and Iodine Halides[1]

BY ALEXANDER I. POPOV AND RALPH H. RYGG

RECEIVED APRIL 5, 1957

Molecular compounds of pyridine, 2-picoline and 2,6-lutidine were prepared with iodine, iodine monochloride and iodine bromide. The dissociation constants of the nine resulting compounds were determined spectrophotometrically in carbon tetrachloride solutions. The order of stability for the halogen series was found to be $ICl > IBr > I_2$, which is in agreement with the acidic strength of the halogens. Comparison within the amine series shows the stability order to be Pic > Py > Lut. The low stability of the lutidine complexes can be ascribed to steric effects.

Introduction

The preceding paper of this series[2] described the molecular complexes of pyridine and of 2,2-bipyridine with iodine monochloride. In continuing the study of the molecular complexes of heterocyclic amines with iodine and iodine halides it was decided to investigate the influence of substituent groups on the pyridine ring upon the dissociation constants of such compounds. It is well known that the addition of methyl groups to pyridine increases the basicity of the nitrogen and therefore should increase the stability of the polyhalogen complexes. In this work complexes of iodine, iodine monochloride and iodine bromide with pyridine, 2-picoline and 2,6-lutidine were prepared and studied.

Experimental Part

Iodine and Iodine Halides.—The methods of preparation and the purification of these reagents have been described in a previous publication.[3] The m.p.'s of the products were in agreement with previously determined values.[3]

Pyridine.—Mallinckrodt A.R. pyridine was purified by drying it with barium oxide for 24 hours and then fractionally distilling it from fresh barium oxide. The final distillate had a b.p. of 113–113.5° (uncor., 731 mm.); reported value[4] 115.6° at 760 mm. The product was stored in brown glass bottles.

2-Picoline.—Fisher purified 2-picoline was stored in the dark for several weeks over sodium hydroxide pellets and then distilled twice through a one meter, helices-packed column. Only the middle fraction of each run was collected. The observed b.p. of 128.5° (at 742 mm.) checked satisfactorily with the literature value of 128.1° (at 740 mm.).[5]

2,6-Lutidine.—The initial method used to purify this compound made use of the low solubility of the lutidine–mercuric chloride complex.[6] This procedure was found to be too time consuming and did not yield a satisfactory product, consequently, a slight modification of the method described by Cathcart and Reynolds[7] was used. Two hundred grams of commercial 2,6-lutidine was mixed with 40 g. of ethyl benzenesulfonate, the mixture was refluxed for one hour, cooled, and the upper layer separated and distilled. The distillate was refluxed over barium oxide and distilled again through a one meter helices packed column. The middle fraction of this distillate was used for subsequent work. The b.p. was 143° (uncor.); reported[7] 146°.

Carbon Tetrachloride and Acetonitrile.—These solvents were purified by previously described methods.[3,8]

Preparation of Molecular Complexes.—These compounds were all prepared by the following general procedure: the desired amount of organic base ($\sim$10 ml.) was dissolved in 50 ml. of carbon tetrachloride; a stoichiometric amount of the corresponding halogen was likewise dissolved in the same volume of the solvent and was added dropwise to the amine solution which was stirred with a magnetic stirrer. The precipitate began to form after approximately $^1/_4$ of the halogen solution was added. The precipitates, in the form of yellow or orange microcrystalline powder, were washed thoroughly with pure solvent, air-dried with suction for several minutes and then placed in a vacuum desiccator over barium oxide. The yields were on the order of 70%. The list of compounds and the analytical data are given in Table I. Of the compounds listed in Table I, the 2-picoline and 2,6-lutidine complexes do not seem to have been reported previously. Attempts to prepare the corresponding iodine complexes in crystalline state were unsuccessful. This was not unexpected in view of the great instability of the iodine–pyridine complex previously reported.[9] All of the prepared compounds were found to be quite stable to atmospheric moisture.

Solutions.—All solutions of the solid complexes were prepared by dissolving weighed amounts of crystals in the appropriate volume of solvents. Unstable iodine complexes were prepared by mixing equimolar solutions of iodine and of the corresponding amine. Solutions of halogens were prepared by dissolving an approximate amount of halogen in the solvent, determining its concentration iodometrically and diluting to the required concentration. Standard solutions of pyridine, 2-picoline and 2,6-lutidine were prepared by the addition of desired amounts of the respective amines from a weight buret, to a known volume of the solvent.

Spectrophotometric Measurements.—Spectrophotometric measurements were made at room temperature of approximately 25° on a Cary recording spectrophotometer with silica cells of 1.00 and 5.00 cm. path lengths.

Results

Preliminary Spectrophotometric Measurements.—The absorption spectra of the three halogen compounds and of the three amines in carbon tetrachloride solutions were determined in the 290–550 mμ spectral regions. The spectra of iodine and of iodine halides showed good agreement with the results obtained by earlier investigators.[11] The absorption of the amines was found to be negligible.

A series of studies were then made on solutions of halogens to which an increasing amount of a particular amine has been added. In all cases the

---

[1] From the Ph.D. Thesis presented by Ralph H. Rygg to the Graduate College, State University of Iowa, June, 1957.

[2] A. I. Popov and R. T. Pflaum, THIS JOURNAL, **79**, 570 (1957).

[3] A. I. Popov and N. E. Skelly, *ibid.*, **77**, 3722 (1955).

[4] A. Weissberger, E. Proskauer, J. Riddick and E. E. Toops, Jr., "Organic Solvents," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1955, p. 243.

[5] K. R. Hoffman and C. A. Vanderwerf, THIS JOURNAL, **68**, 997 (1946).

[6] J. G. Heap, W. J. Jones and J. B. Speakman, *ibid.*, **43**, 1936 (1921).

[7] J. A. Cathcart and D. D. Reynolds, *ibid.*, **73**, 3504 (1951).

[8] A. I. Popov, D. H. Geske and N. C. Baenziger, *ibid.*, **78**, 1793 (1956).

[9] M. Chatelet, *Compt. rend.*, **196**, 1421 (1933).

[10] Ya. A. Fialkov and I. D. Muzyka, *Zhur. Obshchei. Khim.*, **18**, 1205 (1948).

[11] A. E. Gillam, *Trans. Faraday Soc.*, **29**, 1132 (1933); A. I. Popov, K. Brinker, L. Campanaro and R. Rinehart, THIS JOURNAL, **73**, 514 (1951); H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 2832 (1948); **71**, 2703 (1949).

TABLE I

MOLECULAR COMPLEXES OF PYRIDINE WITH IODINE HALIDES

Compound	M.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Iodometric equiv. Calcd.	Iodometric equiv. Found
PyICl	133 (lit.[10] 132)	...	...	..	..	120.8	121.4
PyIBr	114.5 (lit.[10] 115)	...	...	..	..	142.9	143.8
2-Pic·ICl[a]	77.5	28.19	28.60	2.74	2 79	127.8	128.1
2-Pic·IBr[a]	67–68	24.02	24.04	2.35	2.05	150.0	150.8
2,6-Lut·ICl[a]	112–113	31.18	31.52	3.36	3.36	134.2	134.4
2,6-Lut·IBr[a]	106–108	27.59	27.59	2.92	2.99	157.0	158.4

[a] Previously unreported compounds.

absorption curves of the halogen were altered with the absorption maximum shifting to shorter wave lengths. A clearly defined isosbestic point was found in each case. The addition of the amines was continued until no further change in the absorption spectrum was observed. At this point it was assumed that the curve was that of the amine–halogen complex. Table II summarizes the results of this study.

TABLE II

ABSORPTION CHARACTERISTICS OF THE HALOGENS AND OF THE AMINE-HALOGEN COMPLEXES

Compound	Max., wave length, mμ	a_m	Isosbestic point, mμ
ICl	459	156	..
IBr	492	400	..
I_2	517	920	..
Py·ICl	..[a]	..	387
2-Pic·ICl	..[a]	..	387
2,6-Lut·ICl	320	325	388
Py·IBr	357	650	426[b]
2-Pic·IBr	359	636	425[b]
2,6-Lut·IBr	365	590	429[b]
Py·I_2	406[c]	1600	473
2-Pic·I_2	414[c]	1600	473
2,6-Lut·I_2	423[c]	1460	479

[a] No maximum, but a distinct change in the absorption spectra with ICl curve disappearing. [b] Isosbestic point shifted with high concentrations of amines, but the complex absorption peak remained constant. [c] Over 1000-fold excess of the amines was necessary to obtain these values.

Mole Ratio Method.—The molar absorbancy indexes of the complexes were calculated at several wave lengths from the curves obtained in the previous experiments, and were plotted against the mole ratios of amine/halogen. The wave lengths at which the measurements were made were selected so as to include the absorption maxima of the respective halide and of the halide–amine complex. Figure 1 shows the curve for the picoline series. The results in the other two series are entirely analogous.

When the molar absorbancy index reached a constant value, that is, when further increase in the concentration of the amine did not produce any change in absorbance of the system, it was assumed that all of the halogen had been converted to the complex, and since, as mentioned above, the excess amine had no absorption in the regions studied, the extrapolated molar absorbancy index should be that of the corresponding complex. In this manner the molar absorbancy for the nine complexes was determined at several wave lengths.

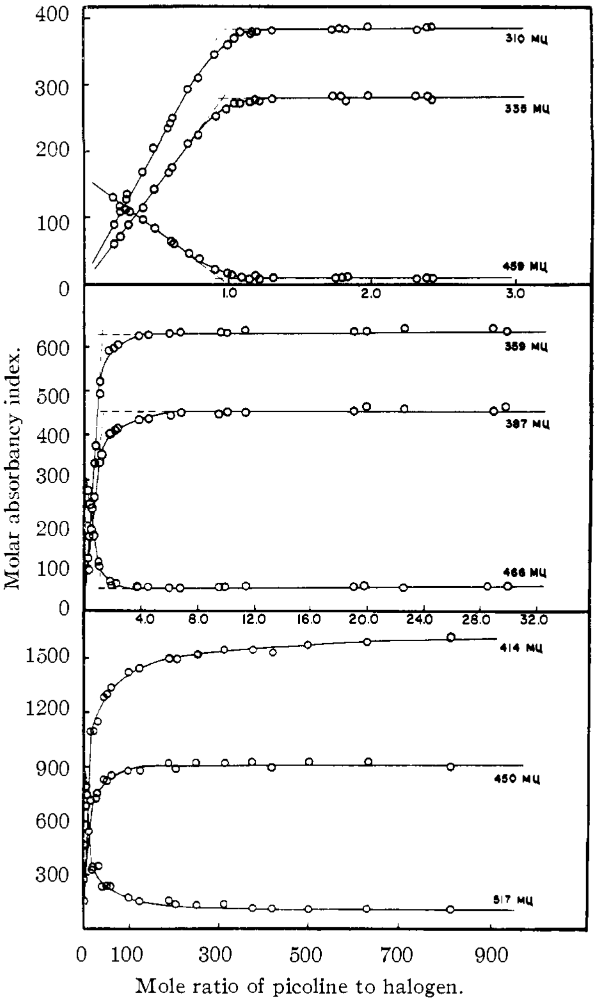

Fig. 1.—Mole ratio study of picoline-halogen complexes: upper curves, ICl complex; middle curves, IBr complex; lower curves, I_2 complex.

In the case of iodine monochloride this constant value is reached with a very small excess of the three amines, and the break in the curve is reached at 1:1 mole ratio. The constancy of absorbance is reached at considerably larger amine/halogen mole ratios in the iodine bromide series, although the break in the curve still indicates a 1:1 complex and the molar absorbancy index does not reach a constant value for the iodine series until a several hundred-fold excess of the amine is present. The above results give a good qualitative indication that the relative strengths of the complexes decrease in going from iodine monochloride to iodine bromide to iodine.

Method of Continuous Variation.—Job's method of continuous variation was tried on pyridine–IBr, picoline–IBr, lutidine–IBr, pyridine–ICl, picoline–ICl and lutidine–ICl in carbon tetrachloride solutions. In all cases sharp maxima or minima (depending on the wave length) were obtained at 1:1 mole ratio of the reacting species. It was found to be impossible to make this study for the iodine series. Even ninefold excess of amine is insufficient to give any appreciable change in the absorption spectrum. This correlates well with the instability of the complex as revealed by the mole ratio study.

Determination of the Formation Constant of the Complexes.—In a 1:1 mixture of the reacting components in carbon tetrachloride we have the reaction

$$BX_2 \rightleftarrows B + X_2$$

and the total absorbance at a given wave length is equal to

$$As_{total} = a_{m(B)}bC_B + a_{m(X_2)}\,bC_{X_2} + a_{mBX_2}bc_{\,BX_2} \quad (1)$$

If C_X represents the maximum possible concentration of the complex in an equimolar mixture of a halogen and an amine, and α its degree of dissociation, we have

$$As_{total} = a_{mB}b\alpha C_X + a_{m(X_2)}b\alpha C_X + a_{mBX_2}b(1-\alpha)C_X \quad (2)$$

Knowing $a_{m(X_2)}$ from a separate measurement on the halogen solution, and $a_{m(BX_2)}$ from the mole ratio study, and since $a_{m(B)} = 0$, it is possible to calculate α from eq. 2, and then, obviously, the dissociation constant using Ostwald's dilution law.

The measurements were made at several wave lengths and at several concentrations. In general good reproducible results were obtained. Typical data for solutions at two different concentrations are given in Table III.

TABLE III

DEGREES OF DISSOCIATION AND DISSOCIATION CONSTANTS OF AMINE–HALOGEN COMPLEXES IN CARBON TETRACHLORIDE SOLUTION AT 25°

	$C = 1 \times 10^{-3}\,M$		$C = 4 \times 10^{-4}\,M$		
Complex	α	K	α	K	K av.
Py·ICl	0.044	2.03×10^{-6}	0.070	2.11×10^{-6}	2.07×10^{-6}
2-Pic·ICl	.029	8.66×10^{-7}	.057	1.37×10^{-6}	1.12×10^{-6}
2,6-Lut·ICl	.104	1.13×10^{-5}	.154	1.12×10^{-5}	1.12×10^{-5}
Py·IBr	.242	7.72×10^{-5}	.354	7.75×10^{-5}	7.73×10^{-5}
2-Pic·IBr	.175	3.71×10^{-5}	.291	4.78×10^{-5}	4.25×10^{-5}
2,6-Lut·IBr	.402	2.70×10^{-4}	.547	2.64×10^{-4}	2.67×10^{-4}
Py·I_2	.918	1.03×10^{-2}	.961	9.47×10^{-3}	9.88×10^{-3}
2-Pic·I_2	.882	6.59×10^{-3}	.947	6.77×10^{-3}	6.68×10^{-3}
2,6-Lut·I_2	.955	2.03×10^{-2}	.980	1.92×10^{-2}	1.97×10^{-2}

Absorption Spectra in Acetonitrile Solutions.—The six solid complexes obtained in the investigation (ICl and IBr series) were all readily soluble in acetonitrile. The absorption curves of the solutions were determined and are shown in Fig. 2. It is seen that the iodine monochloride complexes all show the characteristic absorption maximum of the ICl_2^- ion at 227 mμ[12]; the corresponding iodine bromide complexes show the 256 mμ peak of IBr_2^- ion.[12] The low peak at 267 mμ for the 2,6-Lut·ICl complex corresponds to the absorption peak of lutidine itself. The spectra, of course, include the absorption due to the solvated iodine cation $[B_2I]^+$; however, it has been shown earlier[2] that the molar absorbancy indexes of these species are considerably lower than those of the polyhalide ions, and do not influence the position of the polyhalide absorption maximum.

The polyhalide ion maxima showed variations of absorbance with time which is characteristic of the iodine halide solutions in acetonitrile.[2] This makes it difficult, if not impossible, to determine precisely the dissociation constants of the complexes.

Discussion

The agreement between the two sets of equilibrium constants shown in Table III can be considered satisfactory except for the picoline·ICl and picoline·IBr complexes. The difference in the dissociation constants of those complexes at the two concentrations is reproducible and cannot be ascribed to an experimental error. It is possible that the difference is due to the formation of a higher complex of the type 2Pic·IX at higher concentrations.

The order of stabilities of the complexes with respect to halogens parallels very well their acid strength,[13] ICl > IBr > I_2. The same parallel does not hold for the basic strength of the amines, the basic dissociation constants for pyridine, 2-picoline and 2,6-lutidine being, respectively, 2×10^{-9}, 1×10^{-8} and 4×10^{-8}.[14] If the complex forming ability of the amines depended only on their basic strength the stability of the halogen complexes should be in the order Lut· > Pic· > Py. The actually observed order is Pic· > Py· > Lut. This inversion is not particularly surprising since it has been shown that because of the steric hindrance of the two methyl groups of the 2,6-lutidine, this compound forms weaker complexes with sizable ligands than does pyridine. Thus pyridine forms a stronger complex with boron trifluoride than lutidine.[15] It seems that the methyl groups of the lutidine offer steric hindrance to the coördination of the iodine atom (or the iodine cation I^+) with the nitrogen of the amine. This results in the corresponding decrease in the stability of the com-

---

[12] A. I. Popov and R. F. Swensen, THIS JOURNAL, **77**, 3724 (1955).

[13] R. L. Scott, *ibid.*, **75**, 1550 (1953).

[14] F. L. Hahn and R. Klockmann, *Z. physik. Chem.*, **146**, 389 (1930); G. Barrow, *J. Biol. Chem.*, **121**, 310 (1937); R. J. Bruhlman and F. H. Verhoek, THIS JOURNAL, **70**, 1401 (1948).

[15] H. C. Brown, H. I. Schlesinger and S. Z. Cardon, *ibid.*, **64**, 325 (1942).

plex. On the other hand, the hindrance which one methyl group of the 2-picoline offers does not interfere sterically with the complex formation and since this amine is a stronger base than pyridine, correspondingly stronger complexes are formed with the iodine halides.

In a polar solvent, such as acetonitrile, the complexes undergo an ionic dissociation

$$2B{\cdot}IX \longrightarrow B_2I^+ + IX_2^-$$

while in non-polar carbon tetrachloride we have

$$B{\cdot}IX \longrightarrow B + IX{\cdot}$$

This difference in the mode of dissociation of the polyhalogen complexes depending on the polarity of the solvent has been observed previously in the case of phosphorus polyhalides PCl_6I and PBr_6I.[16]

Acknowledgment.—The authors are indebted to the Research Corporation for the support of this work.

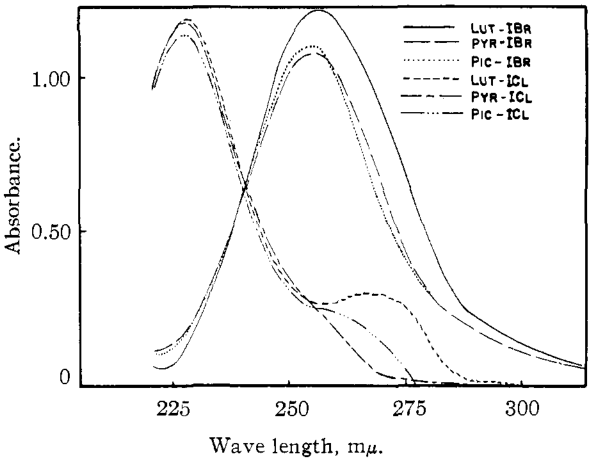

Fig. 2.—Absorption of ICl and IBr complexes in acetonitrile solutions; concn. 4×10^{-5} *M*.

IOWA CITY, IOWA

---

[16] A. I. Popov and E. H. Schmorr, THIS JOURNAL, **74**, 4672 (1952).

[CONTRIBUTION FROM HANFORD LABORATORIES OPERATION, GENERAL ELECTRIC CO.]

The Mechanism of Uranium Extraction by Tributyl Phosphate

BY H. T. HAHN

RECEIVED MARCH 21, 1957

Self-diffusion coefficients of uranium were measured by the capillary cell technique in concentrated aqueous solutions of uranyl nitrate and in hydrocarbon solutions of the uranyl nitrate–tributyl phosphate complex. The slowest diffusion rate observed was that of the complex in a solution of tributyl phosphate and Amsco 125-90W, a kerosene diluent. To determine whether the reaction was controlled by an interfacial barrier or by diffusion in the organic phase, the rate of extraction across a quiet interface was followed photometrically. It was found that the extraction initially proceeded by a combination of diffusion and convection, the convective force arising from the dissipation of reaction energy at the interface. The effect of an interfacial barrier was demonstrated by the addition of a surfactant to the system. The activation energy for diffusion of the uranyl nitrate–tributyl phosphate complex in Amsco was determined to be 5.68 kcal./mole.

Introduction

The rate-controlling step in the extraction of uranyl nitrate by tributyl phosphate may involve diffusion in either phase, complex formation, or elimination of water from the uranyl ion. In order to determine the importance of these factors it is then necessary to determine diffusion coefficients of uranium in concentrated aqueous solutions and in organic media. It is also necessary to follow, in detail, the transfer of uranium across the aqueous–organic interface. From a comparison of the extraction profiles based on the theoretical diffusion equation with experimentally observed profiles, conclusions may be drawn as to the mechanism of transfer.

Theoretical

Determination of the diffusion coefficients was made by the capillary cell method described elsewhere.[1] Briefly, the solution of Fick's equation for the case of diffusion from a capillary open at one end may be stated in terms of the fraction of activity remaining in a tube of length *l*, after time *t*

$$\gamma = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2\pi^2Dt/4l^2] \quad (1)$$

The series is rapidly convergent and for values of $\gamma < 0.5$ may be represented by the first term with less than 0.2% error

$$D = [4l^2/\pi^2t]\ln(8/\pi^2\gamma) \quad (2)$$

Minimum error in D occurs when $\gamma = 0.32$. It was possible to use equation 2 in almost every case described in this paper.

In those experiments in which the progress of extraction was determined as a function of both time and space coördinates, the experimental situation was one of free diffusion in two phases from an initially sharp interface, no changes in concentration being noted at either end of the cell. Let the organic phase be represented by the numeral II, and the aqueous phase by I. The equilibrium distribution between organic and aqueous phases $E_A{}^0$ is assumed to hold for all time at the interface plane $X = 0$. Initially $C = C_0$ for $X < 0$ and $C = 0$ for $X > 0$; alternatively stated, X is positive in the organic phase.

If only diffusion is involved in the transport between phases, Fick's Second Law may be applied to each phase

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2}$$

where $D = D_{\text{I}}$ for $X < 0$ and $D = D_{\text{II}}$ for $X > 0$

---

[1] J. S. Anderson and K. Saddington, *J. Chem. Soc.*, S80, S381 (1949).