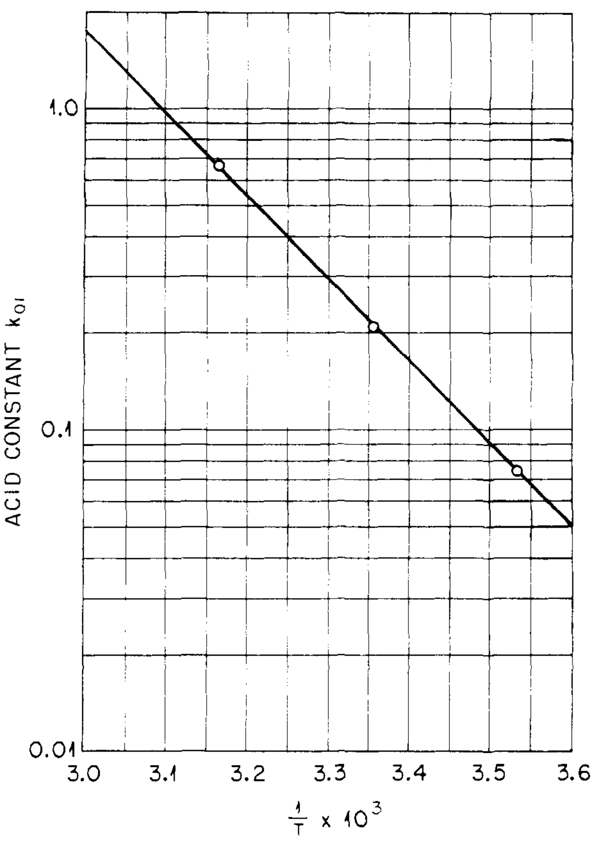

Fig. 1.—Temperature dependence of the U(IV) acid constant.

the entropy difference between U^{+4} and U^{+3} after correction for the entropy of hydrogen ($S^\circ_{U^{+3}}$ = −30 e.u., $S^\circ_{1/2H_2}$ = 15.6 e.u.[5]) the entropy change for reaction (1) readily can be accounted for.

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Studies on the Chemistry of Halogens and of Polyhalides. IV. On the Behavior of Iodine and of Iodine Halides in Acetonitrile[1,2]

By Alexander I. Popov and Norman E. Skelly[3]

Received March 28, 1955

Spectrophotometric investigations of the solutions of iodine monochloride[4] in acetonitrile have shown that this compound undergoes an ionic dissociation.

$$2ICl \rightleftarrows I^+ + ICl_2^-$$

It was observed, however, that the absorption spectrum of iodine chloride in acetonitrile changed with time. The ultraviolet peak at 227 mμ which is due to the ICl_2^- ion[5] slowly increased in intensity, without, however, showing a quantitative conversion of iodine monochloride to the iododichloride ion[6] even after periods of several weeks.

Although it is well known that iodine monochloride and iodine bromide conduct electric current in certain solvents and in the molten state,[7] very little quantitative work has, as yet, been done either upon their conductances in dilute solutions or on the mechanism of such conductance. It was thought that such study may be of interest to the understanding of the behavior of interhalogen compounds in acetonitrile solutions.

Experimental Part

Conductance Measurements.—The conductivity bridge, and the measurement conditions were described in a previous communication.[2] The temperature was maintained at 25 ± 0.003°.

Spectrophotometric Measurements.—All spectrophotometric measurements were done on a Cary recording spectrophotometer model 11. Stoppered silica cells of path length 1.00 ± 0.01 cm. were used. Measurements were made at the room temperature of approximately 25°.

Solvents.—Acetonitrile obtained from the Matheson, Coleman and Bell Co. was purified by the method already described.[2] It is interesting to note that different batches of the solvent seemed to differ considerably in the amount of impurities present, and in some cases required several additional distillations over phosphorus pentoxide before solvent of sufficient purity was obtained.

Iodine.—C.P. iodine (J. T. Baker) was purified by sublimation from a mixture of calcium oxide and potassium iodide.

Iodine Monochloride.—Iodine monochloride was prepared by the method of Cornog and Karges.[8] It was repeatedly purified by fractional crystallization *in vacuo*. The melting point was 27.2° which is identical with the literature value.

Iodine Cyanide.—Iodine cyanide was prepared and purified by the method of Bak and Hillebert.[9] The melting point in a sealed tube was 146–147°, identical with the value reported.

Iodine Bromide.—Iodine bromide was prepared by the addition of 88 g. (0.55 mole) of bromine to 127 (0.50 mole) of iodine. The mixture was warmed on a water-bath until the iodine completely dissolved. When the mixture was cooled, solid iodine bromide crystallized out. The product was purified by repeatedly melting and cooling the crystals and discarding each time approximately 20% of the liquid melt. This procedure was repeated until the same melting point was obtained on two successive recrystallizations. The melting point was found to be 41.5° as compared with the value of 42° reported in the literature.[10]

Solutions.—Stock solutions were prepared by dissolving a weighed amount of the solute in purified acetonitrile. The exact concentrations were determined by iodometric titrations. Aliquots of stock solutions were then diluted to required concentration. All the solutions were at first prepared in a dry-box and the absorption cells and the conductance cells were likewise filled there. Since, as shall be described below, the absorption spectra as well as the specific conductance of the solutions showed a pronounced change with time, a special all-glass apparatus was designed which permitted the carrying out of the purification of the solvent, preparation of solutions at various known concentrations, and the measurement of the electrical conductance without any exposure to the atmosphere.[11]

Results

Iodine Monochloride.—Absorption spectra of iodine monochloride in acetonitrile have been re-

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(1) Abstracted in part from the Ph.D. thesis of Norman E. Skelly, State University of Iowa, 1955.

(2) Previous paper of this series, This Journal, **76**, 5309 (1954).

(3) Du Pont Postgraduate Fellow, 1953–1954.

(4) R. E. Buckles and J. F. Mills, This Journal, **76**, 4845 (1954).

(5) A. I. Popov and J. N. Jessup, *ibid.*, **74**, 6127 (1952).

(6) The ICl_2^- ion has often been called the dichloroiodide. However, since it is produced by the addition of the chloride ion to iodine monochloride it seems more correct to call it iododichloride.

(7) (a) L. Bruner and A. Galecki, *Z. physik. Chem.*, **84**, 513 (1913); (b) N. N. Greenwood and H. J. Emeleus, *J. Chem. Soc.*, 987 (1950).

(8) J. Cornog and R. A. Karges, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 165.

(9) B. Bak and A. Hillebert, *Org. Syntheses*, **32**, 29 (1952).

(10) A. E. Gillam, *Trans. Faraday Soc.*, **29**, 1132 (1933).

(11) A. I. Popov, N. E. Skelly and R. Rygg, to be published.

ported previously. Both maxima, the one at 358 mμ which is due to the iodine monochloride, and the one at 227 mμ, due to the ICl_2^- ion showed increase in absorption with time (Table I). The rate of the reaction appears to be strongly dependent on the total concentration of iodine monochloride. In 4×10^{-5} *M* solution of iodine monochloride after 17 days the reaction apparently goes to 95% completion (since the molar absorbancy index of ICl_2^- at 227 mμ is 53400). On the other hand the 5×10^{-4} *M* solution showed only approximately 13% conversion after 29 days. It is interesting to note that in two cases the absorption spectra indicate the formation of the triiodide ion.

TABLE I

MOLAR ABSORBANCY INDICES AT 227 mμ FOR IODINE MONOCHLORIDE IN ACETONITRILE AT 25°

Time, days	Molar concn. × 10⁵ 500	50	10	8	4
0	334	1080	4020	4762	14450
4	514	1350	5020	6890	15100
7	720	1482	7700	8938	16890
10	Off scale	1984	10900	12380	21000
17		3480	*a*	*a*	25000
25		3140			25000
29		3496			25000
38					25000

[a] Appearance of I_3^-.

The electrical conductances of iodine monochloride solutions in acetonitrile were found to be quite low, especially in the more dilute solutions. The molar conductances rose rapidly with dilution typifying the usual behavior of weak electrolytes. There was no possibility of obtaining the conductance at infinite dilution by either the usual extrapolation methods, or by the method of Fuoss and Kraus.[12]

The measurements of the conductance were further complicated by the fact that it increased with time. Specific conductance of a 1.52×10^{-2} *M* iodine monochloride solution prepared in the dry-box increased from 2.01×10^{-5} ohm⁻¹ cm.⁻¹ to 11.36×10^{-5} ohm⁻¹ cm.⁻¹ in 82.5 hours. The increase, however, was much slower when the conductance was measured in an enclosed apparatus mentioned above. A solution of 3.65×10^{-2} *M* increased only from 1.18×10^{-5} to 4.52×10^{-5} ohm⁻¹ cm.⁻¹ in 210 hours (Fig. 1).

Iodine Bromide and Iodine.—The behavior of the iodine bromide and of iodine in acetonitrile were similar to that of iodine monochloride. Both compounds showed an increase in conductance with time and failed to follow Beer's law in the ultraviolet region of the spectrum. In this region iodine bromide and iodine had absorption spectra indicative of the dibromoiodide and triiodide ions, respectively. The change in the conductance for iodine solutions was much less pronounced than that for the iodine halides. An increase of 6% in the conductance was observed for 0.158 *M* iodine solution within a 24-hour period. The change in electrical conductance with time for iodine bromide is given in Fig. 1. Some values for the molar conductances of iodine, iodine monochloride and iodine bromide are given in Table II. The values were obtained in each case by the extrapolation of a series of measurements to zero time.

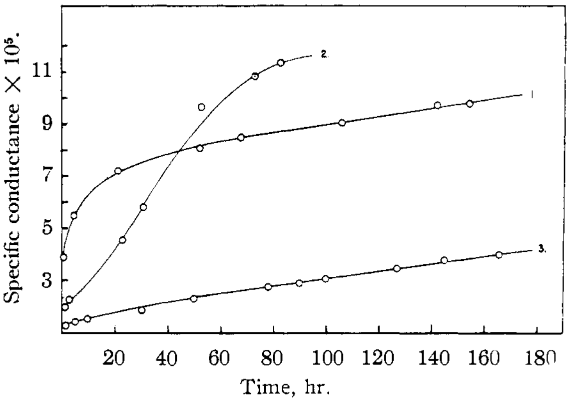

Fig. 1.—Variation of specific conductance with time: 1, iodine bromide solution 5.95×10^{-3} *M*; 2, iodine monochloride solution 1.54×10^{-2} *M*; 3, iodine monochloride solution in enclosed apparatus 3.65×10^{-2} *M*. Divide ordinate values by 10 for curve 1.

TABLE II

MOLAR CONDUCTANCE OF IODINE AND OF IODINE HALIDES IN ACETONITRILE

Iodine $C \times 10^2$	Λ_m	Iodine monochloride $C \times 10^2$	Λ_m	Iodine bromide $C \times 10^2$	Λ_m	Iodine cyanide $C \times 10^2$	Λ_m
15.80	0.0349	3.14	0.325	4.50	0.229	44.8	7.0×10^{-3}
7.74	.0512	3.65	.312	2.24	.247	..	....
4.10	.0920	3.75	.237	0.90	.973	..	....
1.90	.132	..	...	0.45	.787	..	....
0.50	.245	..	...	0.27	1.12	..	....
0.10	.553	..	...	..	...	..	....

It is interesting to note that although acetonitrile has a much higher dielectric constant than pyridine (36.5 *vs.* 12.3 at 25°), yet the iodine exhibits a much smaller conductance in the former solvent. The difference in behavior is very likely due to the fact that pyridine is a much stronger electron donor than the acetonitrile and therefore in the $Py \cdot I_2$ complex iodine is much more strongly polarized than in $CH_3CN \cdot I_2$.

Iodine Cyanide.—Iodine cyanide solutions in acetonitrile were extremely weak conductors, and a 0.448 *M* solution showed conductance of only 3.15×10^{-6} ohm⁻¹ cm.⁻¹ which increased to 3.38×10^{-6} ohm⁻¹ cm.⁻¹ after 81.6 hours. Because of the high concentration of the solute and the high resistance obtained even with the cells with smallest constant (0.0406) it was thought impractical to carry out measurements at greater dilutions since then the conductance of the solvent becomes an important factor.

Discussion and Conclusions

Iodine and iodine halides are notorious for undergoing some sort of a slow reaction in non-aqueous solvents, as was shown by both the electrical conductance and the spectrophotometric measure-

[12] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933).

ments, especially for the case of iodine–pyridine solutions.[13]

The reasons for the slow reactions have been attributed either to a gradual halogenation of the solvent[13b,c] or to a reaction with traces of moisture and/or other impurities.[13e] In a recent work of Buckles and Mills[4] the authors report that they have found no evidence for a reaction of iodine monochloride with the solvent. It seems from the data obtained in this investigation that the evidence favors a slow reaction with the moisture because of the drastic change in the rate of increase of electrical conductance when the measurements were made in an enclosed system. It is evident, however, that a considerable amount of further work is needed to elucidate completely the behavior of interhalogen compounds in various solvents.

Acknowledgment.—The authors gratefully acknowledge the support of a part of this project by the Research Corporation. They also wish to express their appreciation to Dr. Robert E. Buckles of this Laboratory for many helpful discussions on this problem.

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[13] (a) L. F. Audrieth and E. J. Birr, This Journal, **56**, 668 (1933); (b) G. Kortum and H. Wilski, *Z. physik. Chem.*, **202**, 35 (1953); (c) R. Zingaro, C. A. VanderWerf and J. Kleinberg, This Journal, **73**, 88 (1951); (d) J. Kleinberg, E. Colton, J. Sattizahn and C. A. VanderWerf, *ibid.*, **75**, 447 (1953); (e) C. Reed and R. S. Mulliken, *ibid.*, **76**, 3869 (1954).

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Studies on the Chemistry of Halogens and of Polyhalides. V. Spectrophotometric Study of Polyhalogen Complexes in Acetonitrile and in Ethylene Dichloride

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Absorption spectra of several polyhalogen complexes have been recently determined in various solvents,[1] but only in the case of the iododichloride and iodotetrachloride ions in acetonitrile, has the investigation been carried out with thoroughness, and the absorption characteristics have been determined. This work was undertaken in order to obtain precise data on the absorption spectra of the more common of the remaining polyhalide anions such as the IBr_2^-, I_2Br^-, $IBrCl^-$, I_2Cl^-, I_3^- and Br_3^-. It was of interest to determine the absorption spectra in polar and non-polar solvents. For the first type, acetonitrile seems to be a good choice because of high dielectric constant (36.5 at 25°), fair resistance to halogenation, and especially its transparency down to 200 mμ. The choice of the second solvent was primarily determined by the limited solubilities of ionic polyhalides in non-polar liquids. The best possibility seems to be ethylene dichloride ($D = 10.2$ at 25°) which can dissolve sufficient amounts of the tetraalkylammonium polyhalides for spectrophotometric measurements and is transparent down to 235 mμ.

Experimental Part

Apparatus.—All spectrophotometric measurements were made on a Cary recording spectrophotometer, model 11, under conditions described in previous publications.[1b]

Solvents.—Acetonitrile was obtained from the Matheson, Coleman and Bell Co., and purified by methods already described.[1b] Ethylene dichloride was obtained from the Union Carbide and Carbon Co. It was purified by shaking it with several portions of sulfuric acid until the acid layer remained clear, washing it with copious amounts of water, followed by washing with a dilute solution of sodium bicarbonate and again with water. Since ethylene dichloride forms an azeotropic mixture with water, the latter was removed by distillation and the last traces of moisture were further removed by refluxing the solvent for several hours over phosphorus pentoxide and then distilling it twice from the same reagent. The boiling point of the solvent was 83.5° at 760 mm.

It was found important to check the purity of ethylene dichloride by the following procedure. A small amount of bromine was added to a couple of hundred milliliters of the solvent and the amount of halogen was titrated iodometrically in an aliquot portion. The titration was repeated the next day and if no change in bromine concentration was observed, the solvent was used for subsequent spectrophotometric work.

Polyhalogen Complexes.—The following polyhalogen complexes were prepared according to the general directions of Chattaway and Hoyle[2]: Tetramethylammonium diiodobromide, tetramethylammonium iododibromide, tetramethylammonium iododichloride, tetramethylammonium iodobromochloride and tetramethylammonium triiodide. The tetrabutylammonium tribromide and the tetrapropylammonium iododibromide were, respectively, furnished by L. Harris and N. E. Skelly of this Laboratory. The purity of preparations was checked by iodometric titrations and by comparison of the melting points with those in the literature,[2] and satisfactory agreements were obtained in each case.

Considerable difficulties were experienced in the preparation of the tetramethylammonium diiodochloride which, to the authors' knowledge, has not been, as yet, described in the literature. The addition of one mole of iodine to tetramethylammonium chloride in methanol solution resulted in the formation of a mixture of the diiodochloride, tetraiodochloride and of pentaiodide ions. Somewhat better results were obtained in using isopropyl alcohol as a solvent. Upon cooling the solution containing a mixture of iodine and tetramethylammonium chloride, first a mixture of the tetraiodochloride and of diiodochloride was obtained, but upon filtering and letting the solution stand overnight, a crop of bronze-red crystals was obtained which analyzed to be the diiodochloride. The crystals had a m.p. of 102°. The compound is rather unstable and slowly gives up iodine. Complete decomposition was observed after several weeks. The absorption spectra of the diiodochloride solutions were determined on freshly prepared samples.

Solutions.—Preliminary experiments have indicated that the solutions of polyhalogen complexes in purified acetonitrile and ethylene dichloride are quite stable for at least 24 hours. The solutions were prepared by dissolving a weighed amount of a salt in a given volume of the solvent and then diluting to required concentrations. All measurements were made on solutions prepared on the same day.

Suppression of Dissociation.—Since it is known that the polyhalide ions dissociate in acetonitrile, and since it was desired to obtain the true molar absorbancy indices for these species, the absorption spectra were determined on solutions containing an excess of the dissociated halide ion in the form of the corresponding tetramethylammonium salt. The halide salt was added until no further change in the absorption spectra was observed. None of the simple halides absorbed appreciably at the wave lengths investigated.

Results and Discussion

The absorption spectra of the polyhalogen complexes in the two solvents are given in Figs. 1 and 2 and the absorption data and the peak maxima are shown in Table I. All of the polyhalogen complexes

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[1] (a) A. I. Popov and E. H. Schmorr, This Journal, **74**, 4672 (1952); (b) A. I. Popov and J. N. Jessup, *ibid.*, **74**, 6127 (1952); (c) R. E. Buckles and J. F. Mills, *ibid.*, **76**, 3116, 4845, 6021 (1954).

[2] F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923).