

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

A Spectrophotometric Study of Iodine Chloride in Various Solvents<sup>1</sup>

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RECEIVED JULY 13, 1953

A spectrophotometric investigation of iodine chloride and of quaternary ammonium dichloroiodides in various solvents has been carried out. The equilibrium constant for the formation of a 1:1 complex between iodine chloride and propionitrile has been estimated to be  $153 \pm 13$ . In all cases of such 1:1 complexes with electron-donating solvents the absorption spectrum peak of iodine chloride was shifted from around  $460 \text{ m}\mu$  (characteristic of solutions in non-complexing solvents) to around  $350 \text{ m}\mu$ . This latter wave length was very close to the peak absorption of the dichloroiodide ion around  $340 \text{ m}\mu$  in all solvents. Also evident in the spectra of iodine chloride in nitriles and alcohols was the peak around  $230 \text{ m}\mu$  which is characteristic of the dichloroiodide ion but not of iodine chloride, itself. The height of this peak increased with time in the case of acetonitrile, propionitrile and *t*-butyl alcohol as solvents. The results in acetonitrile and propionitrile as solvents were especially consistent with the view that the complexed iodine chloride underwent a reaction with the solvent or an electron-donating impurity to yield dichloroiodide ion and some easily decomposed source of unipositive iodine. Only the latter type of product can account for the observation that the addition of excess chloride ion to the very dilute solutions of iodine chloride, including those which had undergone this ion-formation reaction to the extent of 85–90%, resulted in yields of about 96% of dichloroiodide ion based on the amounts of iodine chloride initially present in the solutions. Similar results were obtained with *t*-butyl alcohol. The solutions in ethyl alcohol were too unstable for such a quantitative demonstration. The extent of dissociation of dichloroiodide ion, itself, in various solvents was also estimated. In general dissociation was enhanced in polar solvents capable of complexing with the molecular halogen, but in trifluoroacetic acid, a non-complexing polar solvent, virtually complete dissociation was observed, and in acetonitrile and propionitrile, complexing polar solvents, unusually little dissociation was observed.

The 1:1 complexes of halogens with electron donors have been investigated fairly extensively in recent years.<sup>2</sup> Evidence for ion formation associated with such complexing has been presented in a number of cases—particularly electrical conductance studies of iodine in pyridine,<sup>3</sup> of bromine with substituted tetraphenylethylenes,<sup>4</sup> of iodine chloride and iodine bromide in various electron donating, polar solvents,<sup>5</sup> and of liquid iodine chloride.<sup>5a,6</sup> Also spectrophotometric evidence of trihalide ion formation has been reported for solutions of iodine in pyridine<sup>7</sup> and for solutions of iodine, bromine and chlorine in hydroxylic solvents.<sup>8</sup>

The present investigation has involved a spectrophotometric study of iodine chloride and of quaternary ammonium dichloroiodides in various solvents—particularly those in which the formation of dichloroiodide ion from iodine chloride was observed.

## Results and Discussion

The characteristic shift in the absorption spectrum peak of iodine chloride caused by its complexing with an electron-donating solvent is illustrated in Fig. 1 for the case of propionitrile. From such absorption spectra data it has been possible to

(1) Work carried out under Contract No. AT(11-1)-72, Project No. 7 with the U. S. Atomic Energy Commission. Abstracted from the Ph.D. thesis of Jack F. Mills. Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Chicago, Ill., September, 1953.

(2) References are given in (a) R. S. Mulliken, *THIS JOURNAL*, **74**, 811 (1952); (b) R. E. Buckles and J. F. Mills, *ibid.*, **75**, 552 (1953).

(3) L. F. Audrieth and E. J. Birr, *ibid.*, **55**, 668 (1933); G. Kortum and H. Wiiski, *Z. physik Chem.*, **202**, 35 (1953).

(4) R. E. Buckles and N. A. Meinhardt, *THIS JOURNAL*, **74**, 1171 (1952).

(5) (a) N. N. Greenwood and H. J. Emeleus, *J. Chem. Soc.*, 987 (1950); (b) Ya. A. Fialkov and I. D. Muzyka, *Zhur. Obschei Khim.*, **18**, 802, 1205 (1948); (c) J. W. Bennett and A. G. Sharpe, *J. Chem. Soc.*, 1383 (1950).

(6) Ya. A. Fialkov and D. I. Shor, *Zhur. Obschei Khim.*, **18**, 14 (1948).

(7) R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, *THIS JOURNAL*, **73**, 88 (1951); J. Kleinberg, E. Cotton, J. Sattizahn and C. A. VanderWerf, *ibid.*, **75**, 442 (1953).

(8) (a) L. I. Katzin, *J. Chem. Phys.*, **20**, 1165 (1952); (b) L. I. Katzin, *ibid.*, **21**, 490 (1953). Earlier references for solutions of iodine are given in the latter reference.

estimate the equilibrium constant for the formation of the complex between iodine chloride and propionitrile in cyclohexane as  $153 \pm 13$  at  $25^\circ$  where the measure of the precision sets the 95% confidence limits of the average. The method of calculation used was that described for an earlier investigation<sup>2b</sup> in which the equilibrium constant  $K$  was calculated by use of equation 1

$$A_s = C_a a_c b + (C_a a_x b - A_s) / N_B K \quad (1)^9$$

The maximum value for the molar absorptancy index of the complex ( $a_c$ ) was found to be 150 at  $374 \text{ m}\mu$ , the same wave length as the peak for iodine chloride in cyclohexane containing 10 mole % propionitrile. Thus, it would appear that iodine chloride is virtually completely complexed in this solution.

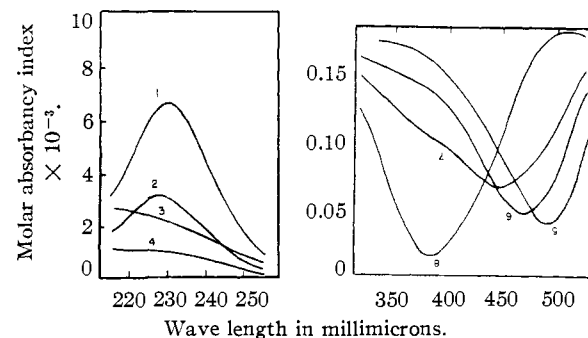


Fig. 1.—Absorption spectra of iodine chloride in cyclohexane-propionitrile mixtures. Molar absorptancy index plotted against wave length in millimicrons: (1) 50; (2) 20; (3) 0; (4) 10 mole % propionitrile each  $9.85 \times 10^{-5} \text{ M}$  in iodine chloride; (5) 100; (6) 5.0; (7) 1.0; (8) 0 mole % propionitrile each  $1.29 \times 10^{-2} \text{ M}$  solution in iodine chloride. A  $1.29 \times 10^{-2} \text{ M}$  solution of iodine chloride in 10 mole % propionitrile solution had virtually the same absorption spectrum as (5) except that the peak was shifted to  $374 \text{ m}\mu$ .

The shift in spectrum which characterizes the

(9)  $A_s$  is the absorbance (optical density) of the solution,  $C_a$  the total concentration of halogen in moles per liter,  $a_c$  the molar absorptancy index (molar extinction coefficient) of the complexed halogen,  $a_x$  the molar absorptancy index of the uncomplexed halogen,  $b$  the thickness of the cell, and  $N_B$  the mole fraction of the propionitrile.

TABLE I  
MOLAR ABSORBANCY INDICES OF IODINE CHLORIDE AND OF THE DICHLOROIODIDE ION IN VARIOUS SOLVENTS

Solvent	$\lambda, m\mu$	ICl		$\lambda, m\mu$	$R_4NCl_2^a$		
		Concn., $M$	$a_m$		Concn., $M$	$a_m$	$a_m^b$
CH <sub>3</sub> CN	359	$8.0 \times 10^{-3}$	137	337	$3.5 \times 10^{-3}$	319	320
	227	$4.0 \times 10^{-3c}$	$2.2 \times 10^4$	227	$6.4 \times 10^{-3}$	$5.3 \times 10^4$	$5.6 \times 10^4$
C <sub>2</sub> H <sub>5</sub> CN	356	$4.5 \times 10^{-3}$	142	338	$5.0 \times 10^{-3}$	328	329
	229	$9.0 \times 10^{-3c}$	$2.4 \times 10^4$	229	$2.0 \times 10^{-3}$	$5.3 \times 10^4$	$5.4 \times 10^4$
C <sub>4</sub> H <sub>9</sub> CN	357	$3.0 \times 10^{-3}$	143	338	$5.5 \times 10^{-3}$	331	...
	232	$3.0 \times 10^{-4}$	$5.1 \times 10^3$	232	$1.4 \times 10^{-5}$	$5.4 \times 10^4$	...
(CH <sub>3</sub> ) <sub>2</sub> COH	346	$6.0 \times 10^{-3}$	188	343	$6.0 \times 10^{-3}$	...	296 <sup>d</sup>
	225	$1.0 \times 10^{-4e}$	$1.3 \times 10^3$	225	$4.0 \times 10^{-5}$	...	$5.4 \times 10^{4de}$
C <sub>2</sub> H <sub>5</sub> OH	343	$7.2 \times 10^{-3}$	181	343	$6.1 \times 10^{-3}$	262	303
	227	$2.5 \times 10^{-4}$	$7.4 \times 10^3$	227	$2.5 \times 10^{-4}$	$1.4 \times 10^4$	...
CH <sub>3</sub> OH	344	$1.5 \times 10^{-2}$	189	343	$5.8 \times 10^{-3}$	235	283
CH <sub>3</sub> COOH	362	$5.5 \times 10^{-3}$	138	340	$1.6 \times 10^{-3}$	239	302
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	426	$4.3 \times 10^{-3}$	132	340	$3.1 \times 10^{-3}$	322	354
CCl <sub>4</sub> <sup>f</sup>	460	$4.0 \times 10^{-3}$	152	..	...	...	...
C <sub>6</sub> H <sub>12</sub> <sup>f</sup>	466	$4.5 \times 10^{-3}$	165	..	...	...	...
CF <sub>3</sub> COOH	450	$2.3 \times 10^{-2}$	121 <sup>g</sup>	450	$6.0 \times 10^{-3}$	124	...

<sup>a</sup> Within experimental error tetrabutylammonium dichloroiodide and tetramethylammonium dichloroiodide gave the same spectrum in each solvent. <sup>b</sup> These values were those obtained when dissociation was completely suppressed by excess chloride ion. <sup>c</sup> The solutions were allowed to stand in the dark for from four to fourteen days until maximum absorbance was observed. <sup>d</sup> Both tetrabutylammonium dichloroiodide and tetramethylammonium dichloroiodide were insoluble in *t*-butyl alcohol. The peaks observed represent those of undissociated dichloroiodide ion formed by the reaction of iodine chloride with excess hydrochloric acid. <sup>e</sup> After five minutes this value had dropped to  $5.0 \times 10^4$ . <sup>f</sup> The dichloroiodides were insoluble in this solvent. <sup>g</sup> The value reported<sup>2b</sup> before was 105. It was found that this value was somewhat low because of difficulties encountered in dissolving the halogen in trifluoroacetic acid and in analyses of the solutions. Values ranging from 120 to 123 were obtained by the most careful measurements in the present investigation.

formation of the iodine chloride-propionitrile complex also brings the spectrum of iodine chloride much nearer to that of the dichloroiodide ion (Table I) where the peak is at 338  $m\mu$  with a molar absorbancy index a little more than double that of complexed iodine chloride. In pure propionitrile the peak for iodine chloride at 356  $m\mu$  is as near to that of dichloroiodide ion as it is to that of the iodine chloride-propionitrile complex in cyclohexane. The height of this iodine chloride peak is about the same as that of the iodine chloride-propionitrile complex, however. This further shift could be the effect of solvent on the spectrum of complexed iodine chloride or it could indicate the formation of some dichloroiodide ion. Since two iodine chloride molecules would have to react to form one dichloroiodide ion and since the peak for the latter is roughly twice that of iodine chloride, no appreciable change in molar absorbancy index would be expected. A further effect of increasing the mole fraction of propionitrile was the appearance of a second peak in the iodine chloride spectrum at 229  $m\mu$ . As given in Table I this peak is characteristic of the dichloroiodide ion, and is not characteristic of the iodine chloride-propionitrile complex as is shown in Fig. 1 by the spectrum in 10 mole % propionitrile.

A comparison of the spectra of iodine chloride and dichloroiodide ion in the various solvents listed in Table I shows a similar formation of dichloroiodide ion in the dilute solutions of iodine chloride in acetonitrile, valeronitrile, ethyl alcohol and *t*-butyl alcohol. Also the peaks of iodine chloride in these solvents and in acetic acid around 350  $m\mu$ , which were measured in more concentrated solutions, are close enough to the dichloroiodide peak so that they could be interpreted as being caused either by iodine chloride alone or by mix-

tures of iodine chloride and dichloroiodide ion. In the case of ethylene chloride, a relatively non-complexing solvent, the peaks of iodine chloride and dichloroiodide ion are much farther apart and there could be little ion present in solutions of the halogen.

In any event there can be no doubt of the formation of dichloroiodide ion in the dilute solutions of iodine chloride in the nitriles, ethyl alcohol and *t*-butyl alcohol. The peak absorbance at 227  $m\mu$  which is characteristic of the dichloroiodide ion in acetonitrile<sup>10</sup> was demonstrated to be a true peak and not an instrumental artifact<sup>11</sup> by variation of concentration as was the analogous peak in the spectra in other solvents where it appeared. The peak was observed in the spectra of fresh solutions of iodine chloride in all of these solvents, but in all except ethyl alcohol the amount of absorption slowly increased on standing. It was possible to show that some of the solutions in acetonitrile of the order of  $10^{-4}$  to  $10^{-5}$   $M$  reached maximum values for the absorbance at 227  $m\mu$  in about eight days. In these solutions about 78% of the dichloroiodide ion expected (one mole from two moles of iodine chloride) was observed as the maximum amount. Such solutions showed no appreciable, further change on standing in the dark. Some solutions of iodine chloride in acetonitrile formed dichloroiodide ion much more slowly than those described above. In fact, there were solutions for which the reaction was so slow that the maximum molar absorbancy index ( $2.2 \times 10^4$ ) at 227  $m\mu$  was never even approached.

With propionitrile and *t*-butyl alcohol similar results were observed, but the solutions were evi-

(10) A. I. Popov and J. N. Jessup, *THIS JOURNAL*, **74**, 6127 (1952).

(11) L. J. Sidel, A. R. Goldfarb and W. B. Kalt, *Science*, **113**, 683 (1951).

dently less stable than with acetonitrile. In *t*-butyl alcohol roughly 50% of the amount of dichloriodide possible was formed. On standing longer even in the dark the solution decomposed with loss of dichloriodide ion. In propionitrile a value of the order of 90% was reached, and on standing in the dark for long periods of time the value went even higher.

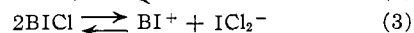
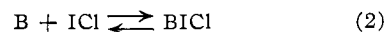
The addition of excess chloride ion in the form of either concentrated hydrochloric acid or a quaternary ammonium chloride to the solutions of iodine chloride gave approximately the amount of dichloriodide ion expected on the basis of the iodine chloride originally present (one mole of dichloriodide ion per mole of iodine chloride). This was particularly true of all of the solutions in acetonitrile including those which had already undergone extensive dichloriodide formation by reaction with the solvent. Such solutions when treated with excess chloride ion consistently gave absorption peaks at 227  $m\mu$  with molar absorptance indices (molar extinction coefficients) of approximately  $5.4 \times 10^4$  (96% of the expected value). With propionitrile or *t*-butyl alcohol as a solvent similar results were obtained only when the solutions had not undergone decomposition by standing too long. Solutions of iodine chloride in ethyl alcohol were too unstable for any such measurements to be significant.

The formation of dichloriodide ion observed in solutions of iodine chloride in the nitriles and in *t*-butyl alcohol can best be interpreted as an interaction of the halogen with the solvent or with some impurity in the solvent which eventually yielded (along with the dichloriodide ion) one or more sources of positive iodine which could be easily decomposed by chloride ion. Such a general picture is consistent with the fact that nearly all of the original iodine chloride could be accounted for when such solutions were treated with chloride ion to form dichloriodide ion. If the process which gave dichloriodide ion in acetonitrile solutions of iodine chloride was a reaction with the very small amount of water which would have been a probable impurity in the solution, it must have been a different type of interaction from that observed when a small amount of water was purposely added to the solution. This effect of added water on dilute solutions of iodine chloride in acetonitrile is illustrated by a representative experiment. A  $4.0 \times 10^{-5} M$  solution with one drop of water per 100 ml. of solution had a molar absorptance index for the dichloriodide peak at 227  $m\mu$  of  $2.2 \times 10^4$  after standing for five days. When excess chloride ion was added the molar absorptance index for the peak was  $4.2 \times 10^4$ —considerably less than the  $5.6 \times 10^4$  expected on the basis of the iodine chloride originally present. The hydrolysis which took place in this case involved the production of some of the iodine in a form (possibly iodate ion) which did not react readily with chloride ion to form dichloriodide ion.

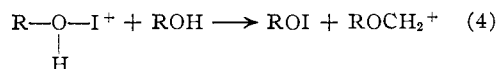
That water need not be the only impurity involved in the formation of dichloriodide ion is illustrated in a series of experiments in which iodine chloride was allowed to interact with aceto-

nitrile containing acetic anhydride (3 drops per 100 ml.). With fresh solutions the addition of excess chloride ion gave molar absorptance indices at 227  $m\mu$  in excess of  $5 \times 10^4$ . With solutions which had been standing several hours the amount of dichloriodide ion observed when chloride ion was added was much lower, and even the amount of dichloriodide ion formed by interaction with the impure solvent started to decrease.

One possible general picture of the formation of dichloriodide ion by interaction with solvent or impurity is that represented in equations 2 and 3



where B represents an electron donating solvent or impurity in the solvent or both. In the case where B was a hydroxylic substance, loss of a proton by equation 4 would lead to a hypiodite derivative. That such an ionization as equation 3 could be



slow is not unreasonable in the light of difficulties reported<sup>12</sup> with slow ionizations of such compounds as picric acid in solution. In fact, an investigation of the electrical conductance of iodine chloride solutions by Popov and Skelly<sup>13</sup> in this Laboratory has led to similar results of slow ion formation. Acetonitrile solutions of iodine chloride were prepared in a completely enclosed system in order to keep the amounts of impurities—especially water—at a minimum, but the slow rise in conductance and the formation of dichloriodide ion as measured spectrophotometrically were still observed.

Such a reaction of the solvent or of an impurity in the solvent to form a complexed positive iodine could explain the partial reversibility of triiodide formation in solutions of iodine in isopropyl alcohol which has been reported.<sup>8a</sup> In general the formation of triiodide ion in alcoholic solutions has been attributed<sup>8</sup> to reduction of the iodine by the alcohol, but such a reaction would not explain a reversible formation of triiodide ion. In the present investigation solutions of iodine chloride in ethyl alcohol were unstable and presumably reduction of the halogen did take place rapidly, but in the case of *t*-butyl alcohol either some sort of complexed positive iodine or a hypiodite must be the initial product formed along with the dichloriodide ion.

Iodine in a form similar to that resulting from the interaction of iodine chloride with solvent or impurities to give dichloriodide ion was obtained in a series of experiments summarized in Fig. 2. A solution of iodine chloride in acetonitrile was treated with one of silver nitrate in acetonitrile. After the solution was centrifuged the absorption spectra showed a small peak in the neighborhood of 460  $m\mu$  which is characteristic of complexed iodine but may also be characteristic of some other source of positive iodine in the presence of silver ion.<sup>14</sup> The addition of excess chloride ion to the

(12) See C. M. French and I. G. Roe, *Trans. Faraday Soc.*, **49**, 791 (1953), for references.

(13) A. I. Popov and N. E. Skelly, private communication.

(14) See for example R. P. Bell and E. Gettes, *J. Chem. Soc.*, 2734 (1951).

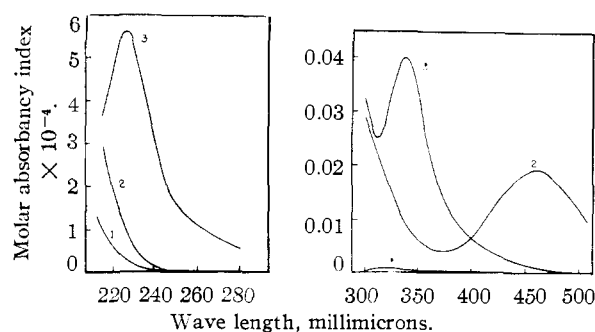
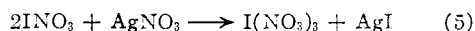


Fig. 2.—Absorption spectra of solutions of iodine chloride in acetonitrile in the presence of silver nitrate. Molar absorptivity index plotted against wave length in millimicrons: (1)  $2.0 \times 10^{-2} M$  silver nitrate for the near ultraviolet and  $2.0 \times 10^{-4} M$  in the far ultraviolet; (2)  $4.0 \times 10^{-3} M$  iodine chloride with  $1.6 \times 10^{-2} M$  silver nitrate for the near ultraviolet and  $2.0 \times 10^{-6} M$  iodine chloride with  $8.0 \times 10^{-5} M$  silver nitrate for the far ultraviolet; (3) the solutions of curve (2) after the addition of excess concentrated hydrochloric acid (one drop).

solution precipitated the remainder of the silver ion and gave dichloroiodide ion in the amount (molar absorptivity index of  $5.6 \times 10^4$ ) expected from the original iodine chloride used. Consequently the solution must have contained all of the iodine in the form of iodine nitrate and/or in a form similar to that which must have been present from interaction with the solvent or impurities when no silver ion was used, in order to give a quantitative yield of dichloroiodide ion. No appreciable amount of the iodine could have been used up in the reaction given in equation 5<sup>15</sup> or a lower yield of dichloroiodide would have been observed.



No considerable loss of iodine chloride by halogenation was observed when solutions of iodine chloride in acetonitrile were illuminated by diffuse sunlight. With propionitrile or valeronitrile such illumination caused chlorination as evidenced by the disappearance of dichloroiodide ion and iodine chloride and by the eventual formation of quantitative amounts of triiodide ion as measured spectrophotometrically.<sup>16</sup> Similarly dilute solutions of iodine chloride in cyclohexane were found to undergo changes in their spectra on standing even in the dark. A solution which had an absorption peak at  $466 m\mu$  of molar absorptivity index 165 when freshly prepared had a peak at  $507 m\mu$  of molar absorptivity index 194 after 24 hours. Evidently iodine was formed as the cyclohexane was chlorinated and hydrogen chloride was lost. Such a result would be expected since hydrogen halides would not be ionized in cyclohexane and no polyhalide ion would form. Such changes in cyclohexane solutions of iodine chloride as they affect the visible appearance of the solutions were commented on by Fairbrother,<sup>17</sup> but their use to explain the absorption peak at  $505 m\mu$  which he reports for iodine chloride in cyclohexane was overlooked.

(15) H. Bousset and T. Kikinda, *Compt. rend.*, **232**, 1840 (1951).

(16) R. E. Buckles, J. P. Yuk and A. I. Popov, *THIS JOURNAL*, **74**, 4379 (1952).

(17) F. Fairbrother, *J. Chem. Soc.*, 847 (1936).

The extent of dissociation of the dichloroiodide ion in various solvents was estimated at  $25^\circ$  by a spectrophotometric method.<sup>18</sup> The results are summarized in Table II. The dissociation was suppressed by a 5 to 10-fold excess of chloride ion in order to measure the molar absorptivity indices of the undissociated dichloroiodide ion in various solvents. Representative values are tabulated in the last column of Table I. From the molar absorptivity indices of the dissociated dichloroiodide ion and of the un-ionized iodine chloride (approximate) the degree of dissociation and hence the equilibrium constant of dissociation could be estimated. Neither chloride ion nor the tetraalkylammonium ions absorb appreciably at the wave lengths used. Calculations were made from data measured at several wave lengths in the region around the peak in the near ultraviolet in each case with the exception of acetonitrile and propionitrile as solvents. Only when a solution of concentration  $10^{-4}$  to  $10^{-5} M$  in either of these solvents was measured in the region of the peak, at  $227$ – $229 m\mu$ , could enough difference between the spectrum of dissociated dichloroiodide ion and that of undissociated dichloroiodide ion be found so that the order of magnitude of the equilibrium constant could be estimated.

TABLE II  
DISSOCIATION OF DICHLOROIODIDE ION<sup>a</sup> IN VARIOUS SOLVENTS AT  $25^\circ$

Solvent	$-\log K$
$\text{C}_2\text{H}_4\text{Cl}_2$	$4.21 \pm 0.15^b$
$\text{CH}_3\text{COOH}$	$3.72 \pm 0.20^b$
$\text{C}_2\text{H}_5\text{OH}$	$3^c$
$\text{CH}_3\text{OH}$	$2.5^c$
$\text{H}_2\text{O}^d$	$2.22^d$
$\text{CH}_3\text{CN}$	$7^e$
$\text{CH}_3\text{CH}_2\text{CN}$	$8^e$

<sup>a</sup> Both tetramethylammonium dichloroiodide and tetrabutylammonium dichloroiodide were used. The results were the same within experimental error. <sup>b</sup> The measure of the precision sets the 95% confidence limits of the average. <sup>c</sup> An approximate value obtained by measurements in the near ultraviolet. The instability of the solutions of the dichloroiodides in the presence of excess chloride ion made more accurate measurements impossible. <sup>d</sup> G. H. Faull, *THIS JOURNAL*, **56**, 522 (1934). <sup>e</sup> An approximate value obtained by measurements on  $10^{-5}$ – $10^{-4} M$  solutions in the region  $225$ – $230 m\mu$ .

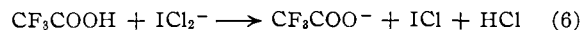
The expected trend of the dissociation constants to lower values in solvents of lower polarity and of lower tendency to complex with the molecular halogen was observed. In alcohols, for example, dissociation was more extensive than it was in ethylene chloride. The same type of trend was noted in the case of the triiodide ion<sup>16</sup> and the tribromide ion.<sup>19</sup> The extent of dissociation in the polar, complexing solvents acetonitrile and propionitrile, however, was unusually low.

Complete dissociation of dichloroiodide ion was observed in trifluoroacetic acid as shown by the fact that the spectra of the quaternary ammonium dichloroiodides and that of iodine chloride in this solvent were virtually identical (see Table I)

(18) A. I. Popov, K. C. Brinker, L. Campanaro and R. W. Rinehart, *THIS JOURNAL*, **73**, 514 (1951).

(19) R. E. Buckles and J. P. Yuk, *ibid.*, **76**, 5048 (1953).

Since trifluoroacetic acid does not tend to complex effectively with halogens<sup>2b</sup> the reaction shown in equation 6 must take place effectively because of a very low tendency for hydrogen chloride to ionize in the highly acidic medium.



**Acknowledgment.**—The authors wish to thank Dr. A. I. Popov and Mr. N. E. Skelly of this Laboratory and Dr. L. I. Katzin of the Argonne National Laboratories for interesting and provocative discussions of the results reported in this article.

### Experimental Part

**Iodine Chloride.**—Resublimed iodine chloride, m.p. 27.4–27.5°, <sup>20</sup> was prepared and purified by methods described before.<sup>2b,21</sup>

**Quaternary Ammonium Halides.**—The commercial tetramethylammonium chloride and iodide (Eastman Kodak) were recrystallized several times from ethanol and water. Tetrabutylammonium iodide was prepared from tributylamine and *n*-butyl iodide by the method described by Laitinen and Wawzonek<sup>22</sup> except that ethyl acetate was used as a solvent. The product, m.p. 145–146°, was obtained in 91% yield. Tetrabutylammonium chloride was prepared from the iodide. The addition of 35 g. (0.15 mole) of silver oxide to a solution of 100 g. (0.27 mole) of tetrabutylammonium iodide in 500 ml. of hot water produced the hydroxide and silver iodide which was allowed to coagulate before the separation by filtration. The filtrate was neutralized with hydrochloric acid and allowed to evaporate. The very hygroscopic product was dried by a stream of warm, dry air. It was then dried at reduced pressure over phosphorus pentoxide. After crystallization from a mixture of benzene and ethyl acetate 68–71 g. (90–95%) of tetrabutylammonium chloride, m.p. 93–95° (sealed tube), was obtained.

**Quaternary Ammonium Dichloroiodides.**—The compounds were prepared in nearly quantitative yields by the addition of iodine chloride to the quaternary ammonium chlorides as described<sup>23</sup> for tetramethylammonium dichloroiodide except that the products were recrystallized from glacial acetic acid instead of isopropyl alcohol. The tetramethylammonium dichloroiodide after the recrystallization from acetic acid was washed with carbon tetrachloride to give a yellow crystalline product, m.p. 237–238°. The compound obtained after recrystallization from isopropyl alcohol containing a small amount of iodine chloride melted at 226–230°. <sup>24</sup> Tetrabutylammonium dichloroiodide separated at first as an oil, but crystallization from acetic acid followed by a wash with anhydrous ethyl ether gave a yellow crystalline product, m.p. 70–71°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>36</sub>NI<sub>2</sub>Cl<sub>2</sub>: C, 43.6; H, 8.24; ICl, 36.9. Found: C, 43.8; H, 8.34; ICl, 36.6 (iodometric).

**Purification of Solvents.**—Commercial nitriles were purified by treatment with phosphorus pentoxide.<sup>25</sup> Acetoni-

trile (Eastman Spectrograde), b.p. 81.6° (745 mm.), propionitrile (Eastman Practical), b.p. 97.0–97.1° (745 mm.), and valeronitrile (Eastman White Label), b.p. 141° (745 mm.), were obtained by this method.

Absolute ethyl alcohol was dried by the method using sodium<sup>26</sup> and a high-boiling ester. The product obtained on distillation had a b.p. 78.1° (745 mm.). Commercial methanol on distillation through a 30-inch helices-packed column yielded a product of b.p. 65.0° (745 mm.). Commercial *t*-butyl alcohol was boiled with barium oxide under reflux for several hours and then distilled from fresh barium oxide to give a product of b.p. 82.5° (745 mm.).

Cyclohexane (Eastman Practical) was vigorously shaken with several portions of fuming sulfuric acid which were about 10% of its volume. After a wash with dilute sulfuric acid the solvent was thoroughly washed with water and dried over anhydrous calcium chloride. Distillation from a small amount of phosphorus pentoxide gave a product, b.p. 81.0° (745 mm.).

The methods used for the purification of acetic acid, trifluoroacetic acid, carbon tetrachloride and ethylene chloride have been described in an earlier article.<sup>2b</sup>

**Methods of Analysis.**—Iodine chloride solutions and solutions of tetramethylammonium dichloroiodide in acetonitrile, ethanol and methanol were analyzed iodometrically using starch as the indicator. At least a 5 to 1 dilution with water was necessary for these solvents so that the starch would be effective.

Similar solutions of propionitrile and valeronitrile were analyzed iodometrically using a sufficient amount of methanol to produce single-phase solutions. The color of the liberated triiodide ion in the alcoholic solutions was of sufficient intensity for accurate use as an indicator. The end point of the titration, a colorless solution, checked within the limits of experimental error the end point observed using starch indicator. This method was also found to be especially useful for analyzing solutions of the tetrabutylammonium polyhalides in non-aqueous solvents such as ethylene chloride. In this case the formation of tetrabutylammonium triiodide prevents the application of the usual two-phase titration method.<sup>19</sup>

**Absorption Spectra.**—With the exception of the cases where specific solutions were allowed to stand the procedure involved preparation and standardization of fresh stock solutions for each series of measurements. Often measurements were repeated after a short period of time in order to determine the stability of the solutions. Solutions of iodine chloride which were allowed to stand were kept in the dark and measured periodically until there was no longer any appreciable change in their absorption spectra (4 to 14 days). After each measurement the portion of the solution measured was discarded.

Measurements were carried out at 25° in calibrated silica cells of path length 1.00 ± 0.01 cm. Complete absorption spectra curves and absorbance measurements for equilibrium data were measured with the Cary Model 11 recording spectrophotometer and in a few cases the Beckman DU and Beckman Model B spectrophotometers were used. The uniform nomenclature and symbology suggested by the National Bureau of Standards<sup>27</sup> has been used throughout this article. For each of the spectra given in the figures molar absorptancy index (molar extinction coefficient) has been plotted against wave length.

### IOWA CITY, IOWA

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(20) All m.p.'s corrected.

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