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Cations and Oxy Cations of Iodine. III. The +1 and Lower Oxidation States of Iodine in Sulfuric Acid

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The results of measurements of the conductivities and freezing points of solutions formed by adding iodine and/or iodine monochloride or iodine monobromide to solutions of iodic acid in sulfuric acid are reported. The results provide evidence for the formation of the ions I_3^+, I_5^+, I_2Cl^+, I_2Br^+, and ICl_2^+ in these solutions and show that at the concentrations studied I^+ is essentially completely disproportionated into I_3^+ and IO^+.

Introduction

Birkenbach, Goubeau, and Krall[1] obtained brown solutions by stirring iodine with a suspension of mercurous or mercuric sulfate in concentrated sulfuric acid. The solutions contained only traces of mercury salts, the mercury sulfates being converted to a white insoluble mercuric iodide–sulfate complex of uncertain composition. Similar solutions were obtained by the oxidation of iodine in sulfuric acid with iodate, periodate, permanganate, or manganese dioxide. The solutions reacted violently with benzene, forming *p*-diiodobenzene and molecular iodine. It was concluded that the solutions contained a complex of the iodine cation, I^+, and molecular iodine. The maximum amount of iodine which would go into solution corresponded to a complex $I^+\cdot{}^3/_2I_2$.

Masson[2] showed that iodine dissolves in solutions of iodosyl sulfate in concentrated sulfuric acid forming brown solutions. The solutions react smoothly with chlorobenzene, to give a mixture of chlorotriiodobenzenes and a precipitate of elementary iodine. The rapidity of the reaction, and the fact that the brown solute is stable only in strongly acid media, led to the conclusion that the iodine is present in a cationic form. From the stoichiometry of the reactions with chlorobenzene of solutions containing different ratios of iodine to iodosyl sulfate, Masson deduced the existence in the solutions of the ions I^+, I_3^+, and I_5^+. He attempted to demonstrate the cationic nature of the iodine containing species by transport number measurements using the moving boundary method but the results were inconclusive. He also suggested that it was unlikely that the I^+ cation would be stable and that therefore in solutions containing iodine in the +1 oxidation state the I^+ ion was probably largely disproportionated into IO^+, I_3^+, and I_5^+. Symons[3] obtained brown solutions with absorption bands at 290 and 460 mμ by dissolving iodine in dilute oleum and he proposed that these solutions contain I_3^+. Arotsky, Mishra, and Symons[4] claim to have obtained blue solutions with an intense absorption band at 640 mμ which is thought to be characteristic of I^+ by oxidizing iodine with iodic acid in dilute oleum and in 100% sulfuric acid.

In the present work iodic acid in solution in 100% sulfuric acid was reduced by successive additions of iodine. The freezing points and conductivities of the resulting solutions were measured. The results for the +3 oxidation state of iodine, corresponding to the mole ratio $I_2/HIO_3 = 0.33$, were discussed in part II.[5] In this paper we discuss the results for the +1 and lower oxidation states corresponding to mole ratios $I_2/HIO_3 \geqslant 2$.

Results and Discussion

Solutions of Iodic Acid and Iodine.—In each cryoscopic experiment the starting solution contained iodine and iodic acid in a different mole ratio. This solution was subjected to successive dilutions with 100% sulfuric acid, to give a range of concentrations. A curve of freezing point *vs.* the stoichiometric concentration of iodic acid was plotted from the results of each experiment, and values of the freezing point at round molal concentrations of iodic acid were obtained by interpolation. The interpolated data were plotted on a set of graphs of freezing point *vs.* the mole ratio I_2/HIO_3, each for a fixed stoichiometric molality of iodic acid. Typical curves are shown in Figure 1. From these curves were obtained values of the freezing points at the mole ratios $I_2/HIO_3 = 0.33$, 2.0, and 7.0 corresponding to the oxidation states +3, +1, and $+^1/_3$, respectively. The results for the +3 oxidation state have been discussed previously.[5] The interpolated values for the mole ratios $I_2/HIO_3 = 2.0$ and 7.0 are given in Table I.

A series of conductometric experiments was carried out, in each of which successive additions of iodine were made to an initial solution of iodic acid. Figure 2 shows typical plots of the specific conductivity *vs.* the mole ratio I_2/HIO_3. Values of the conductivity at the mole ratios 2.0 and 7.0 were obtained by interpolation (Table II).

The +1 Oxidation State of Iodine.—Values of ν, the number of moles of particles (molecules or ions), and γ, the number of moles of hydrogen sulfate ions, produced per mole of iodic acid, calculated as described

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[1] L. Birkenbach, J. Goubeau, and H. G. Krall, *Ber.*, **67B**, 197 (1934).

[2] I. Masson, *J. Chem. Soc.*, 1708 (1938).

[3] M. C. R. Symons, *ibid.*, 2186 (1957).

[4] J. Arotsky, H. C. Mishra, and M. C. R. Symons, *ibid.*, 12 (1961).

[5] R. J. Gillespie and J. B. Senior, *Inorg. Chem.*, **3**, 972 (1964).

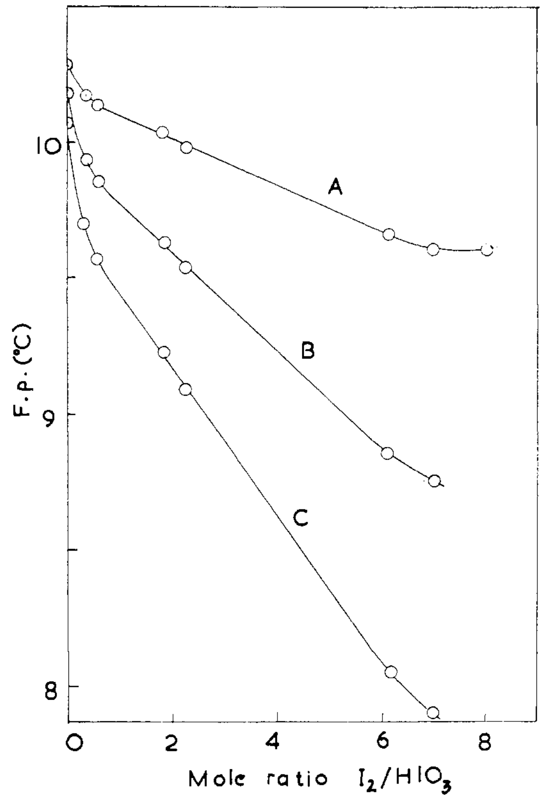

Figure 1.—Freezing points of solutions of iodic acid and iodine. Initial concentration of iodic acid: A, 0.01 *m*; B, 0.02 *m*; C, 0.03 *m*.

Table I

Interpolated Freezing Points

$10^2m_{HIO_3}$	Mole ratio I_2/HIO_3 2.0	7.0
	F.p., °C.	
1.0	10.010	9.605
1.5	9.800	9.175
2.0	9.590	8.750
2.5	9.380	8.325
3.0	9.170	7.895
3.5	8.965	7.465
	Mole ratio $ICl/(HIO_3 + 2I_2) = 5$	
0.706	9.808	
0.854	9.743	
1.077	9.532	
1.750	8.928	
2.226	8.568	

previously,[6] for solutions having the mole ratio $I_2/HIO_3 = 2.0$ are given in Table III.

Possible reactions are the formation of the iodine cation

$$HIO_3 + 2I_2 + 8H_2SO_4 = 5I^+ + 3H_3O^+ + 8HSO_4^- \quad (1)$$

$$\nu = 16, \gamma = 8, \nu - \gamma = 8$$

and the formation of un-ionized iodine(I) hydrogen sulfate

$$HIO_3 + 2I_2 + 8H_2SO_4 = 5IHSO_4 + 3H_3O^+ + 3HSO_4^- \quad (2)$$

$$\nu = 11, \gamma = 3, \nu - \gamma = 8$$

In both the above cases and for any degree of ionization of $IHSO_4$ $\nu - \gamma = 8$. The experimental values are

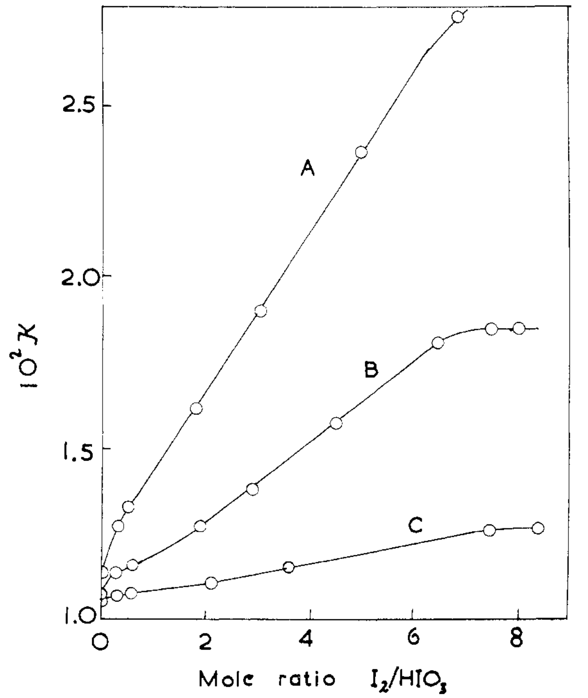

Figure 2.—Conductivities of solutions of iodic acid and iodine. Initial concentration of iodic acid: A, 0.01843*w*; B, 0.00976*w*; C, 0.00427*w*.

Table II

Interpolated Conductivities

$10^2w_{HIO_3}$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	$10^2w_{HIO_3}$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
Mole Ratio $I_2/HIO_3 = 2.0$		Mole Ratio $I_2/HIO_3 = 7.0$	
0.426	1.102	0.424	1.264
0.970	1.279	0.958	1.852
1.024	1.302	1.152	2.100
1.167	1.376	1.525	2.508
1.556	1.540	1.779	2.788
1.779	1.656	3.188	4.083
2.633	2.080		
3.325	2.321		
Mole Ratio $IBr/(HIO_3 + 2I_2) = 5.0$		Mole Ratio $ICl/(HIO_3 + 2I_2) = 5.0$	
0.557	1.381	0.530	1.358
		1.025	1.872
Mole Ratio $ICl/HIO_3 = 7.0$		1.090	2.010
1.128	2.013	1.632	2.555
2.182	3.018	2.132	3.127
		2.692	3.487

clearly inconsistent with either reaction scheme. Complete disproportionation of I^+ to the +3 and $+^1/_3$ states can be represented by the over-all equation

$$4HIO_3 + 8I_2 + 17H_2SO_4 = 5I_3^+ + 7H_3O^+ + 5IOHSO_4 + 12HSO_4^- \quad (3)$$

$$\nu = 8.5\text{–}7.25, \gamma = 4.25\text{–}3, \nu - \gamma = 4.25$$

The ranges of ν and γ shown take into account the partial ionization of iodosyl hydrogen sulfate.[5] The experimental values of ν and γ fall within these ranges, while the values of $\nu - \gamma$ are in fairly good agreement with the predicted value of 4.25. Thus eq. 3 probably represents the predominant mode of ionization in these

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[6] R. J. Gillespie and J. B. Senior, *Inorg. Chem.*, **3**, 440 (1964).

TABLE III

VALUES OF ν AND γ

$10^2 m_{HIO_3}$	ν	γ	$\nu - \gamma$
Mole Ratio $I_2/HIO_3 = 2.0$			
1.0	8.5	3.52	5.0
1.5	8.3	3.51	4.8
2.0	8.1	3.43	4.7
2.5	7.9	3.39	4.5
3.0	7.8	3.35	4.4
3.5	7.7	3.33	4.4
Mole Ratio $I_2/HIO_3 = 7.0$			
1.0	16.0	7.60	8.4
1.5	15.5	8.10	7.4
2.0	15.2	8.13	7.1
2.5	15.0	8.15	6.9
3.0	14.9	8.16	6.7
3.5	14.8	8.10	6.7
Mole Ratio $ICl/(HIO_3 + 2I_2) = 5.0$			
0.5	16.0	7.8	8.2
1.0	15.9	7.7	8.2
1.5	15.7	7.8	7.9
2.0	15.4	7.9	7.5
2.5	..	7.8	..

solutions. However, the observed values of $\nu - \gamma$ are somewhat larger than 4.25, particularly at low concentrations, indicating that some I^+ or $IHSO_4$ may be present.

TABLE IV

CONDUCTIVITIES OF SOLUTIONS OF $I(py)_2NO_3$ AND $I(py)_2ClO_4$ AT 25°

$I(py)_2NO_3$		$I(py)_2ClO_4$	
$10^2 w$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	$10^2 w$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
0.188	1.060	0.158	1.047
0.711	1.239	0.474	1.070
1.667	1.805	0.948	1.136
2.376	2.245	1.518	1.254
		2.099	1.403

The disproportionation of I^+ can be written

$$4I^+ + H_2O + 2HSO_4^- = IO^+ + I_3^+ + 2H_2SO_4 \quad (4)$$

and it is clear that the equilibrium will be shifted in favor of an increasing amount of disproportionation with increasing concentration. In the much more dilute solutions studied spectrophotometrically by Arotsky, Mishra, and Symons[4] a greater proportion of I^+ could exist in equilibrium and indeed their spectra had bands at 650, 460, and 290 mμ indicating that both I^+ and I_3^+ were present in appreciable amounts. We have made similar absorption spectra measurements and we find that solutions containing the solutes in the mole ratio $I_2/HIO_3 = 2.0$ have the strong absorption band at 640 mμ characteristic of I^+ and also a strong band at about 460 mμ overlapping with the 500 and 410 mμ bands of I_3^+. Insufficient data were obtained to permit a quantitative treatment but the results indicate that only about one-third of the iodine was present as I^+, the rest having undergone disproportionation.

Solutions of Dipyridineiodine(I) Salts.—It was hoped that when $I(py)_2NO_3$ and $I(py)_2ClO_4$ were dissolved in sulfuric acid they would liberate the iodine cation I^+. The results of conductivity measurements on solutions of $I(py)_2NO_3$ and $I(py)_2ClO_4$ are given in Table IV. Solutions of $I(py)_2NO_3$ are pale yellow, showing that an iodosyl compound is formed, presumably through oxidation of I^+ by the nitronium ion, NO_2^+, with reduction of the latter to NO^+

$$I(py)_2NO_3 + 5H_2SO_4 = 2(py)H^+ + NO^+ + H_3O^+ + IOHSO_4 + 4HSO_4^-; \quad \gamma = 5\text{–}4 \quad (5)$$

Taking K_b for $IOHSO_4$[5] as 0.025 mole kg.$^{-1}$, it can be shown that γ should decrease from approximately 4.5 at 0.005w to 4.2 at 0.02w. In fact γ is almost constant, with values close to 4.4, in this concentration range, in reasonable agreement with prediction.

If I^+ were produced quantitatively, the reaction would be

$$I(py)_2NO_3 + 5H_2SO_4 = 2(py)H^+ + NO_2^+ + H_3O^+ + I^+ + 5HSO_4^-; \quad \gamma = 5 \quad (6)$$

in less satisfactory agreement with experiment.

The solutions of $I(py)_2ClO_4$ were deep green, indicating extensive disproportionation. For complete disproportionation we could write

$$4I(py)_2ClO_4 + 12H_2SO_4 = 8(py)H^+ + 4HClO_4 + I_3^+ + IO^+ + H_2S_2O_7 + 10HSO_4^- \quad (7)$$

However, in view of the fact that IO^+ has been shown to react with $H_2S_2O_7$ to give $I(HSO_4)_3$[5] this equation is probably better written in the form

$$4I(py)_2ClO_4 + 12H_2SO_4 = 8(py)H^+ + 4HClO_4 + I_3^+ + I(HSO_4)_3 + 9HSO_4^- \quad (8)$$

For this reaction $\gamma = 2.25$. An almost constant value of $\gamma = 2.1$ was obtained from the conductivity results. For the formation of I^+ without disproportionation we have

$$I(py)_2ClO_4 + 3H_2SO_4 = 2(py)H^+ + HClO_4 + I^+ + 3HSO_4^- \quad (9)$$

for which $\gamma = 3$, in poorer agreement with the experimental results.

The $+^1/_3$ Oxidation State.—Reaction to give I_3^+ would take place according to the equation

$$HIO_3 + 7I_2 + 8H_2SO_4 = 5I_3^+ + 3H_3O^+ + 8HSO_4^-$$

$$\nu = 16, \gamma = 8, \nu - \gamma = 8$$

The observed values given in Table III for the mole ratio $I_2/HIO_3 = 7$ are in good agreement with the predicted values. The small decrease in ν with increasing concentration can probably be accounted for in terms of the incomplete ionization of the water produced.[7] An alternative hypothesis which was considered and rejected by Masson,[2] namely, that triply charged ions are formed, may be represented by the equation

$$3HIO_3 + 11I_2 + 24H_2SO_4 = 5I_5^{3+} + 9H_3O^+ + 24HSO_4^-$$

$$\nu = 12.7, \gamma = 8$$

This ionization scheme is not consistent with the freezing point results. Symons, *et al.*,[8] have reported some similar conductivity measurements, and they

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(7) S. J. Bass, R. J. Gillespie, and J. V. Oubridge, *J. Chem. Soc.*, 837 (1960).

(8) J. Arotsky, H. C. Mishra, and M. C. R. Symons, *ibid.*, 2582 (1962).

suggested that the break in the conductivity curve at the mole ratio $I_2/HIO_3 = 7.0$ is consistent with the formation of I_3^+ although they give no detailed interpretation of their results. These authors observed as we have done that the conductivity remains essentially constant at mole ratios of greater than 7. We have also observed that the freezing point similarly becomes constant at this mole ratio. The only interpretation of these results is that iodine takes part in a reaction in which there is no increase in the number of hydrogen sulfate ions or of the total number of solute particles. This reaction can only be the formation of I_5^+

$$I_3^+ + I_2 = I_5^+$$

Mixed Polyhalogen Cations.—A number of experiments were carried out in which iodine monochloride was added to a solution containing iodine and iodic acid in the mole ratio $I_2/HIO_3 = 2.0$. Values of the freezing points and conductivities of these solutions interpolated at the composition $ICl/(2I_2 + HIO_3) = 5$ are given in Tables I and II. The experimental values of ν and γ (Table III) are in satisfactory agreement with the values predicted by the equation

$$HIO_3 + 2I_2 + 5ICl + 8H_2SO_4 = 5I_2Cl^+ + 3H_3O^+ + 8HSO_4^-$$
$$\nu = 16, \gamma = 8$$

The results are equally consistent with the existence of the equilibrium

$$2I_2Cl^+ = I_3^+ + ICl_2^+$$

More ICl dissolves in the solution after the composition $ICl/(2I_2 + HIO_3) = 5$ has been reached, but the solutions begin to exhibit a vapor pressure of ICl which up to this composition is quite negligible, and there is very little further change in the conductivity of the solution and only a small decrease in the freezing point. It appears therefore that I_2Cl^+ reacts with ICl, at least partially, to form $I_3Cl_2^+$, or perhaps with I_3^+ and/or ICl_2^+ to form I_4Cl^+ and/or $I_2Cl_3^+$. Possibly there is an equilibrium between all these pentaatomic species. No previous evidence has been given for the ion I_2Cl^+, but molten iodine monochloride has an appreciable conductivity which has been attributed[9] to the self-dissociation

$$2ICl = I^+ + ICl_2^-$$

In this solution the I^+ cation is almost certainly solvated by an ICl molecule and thus the self-dissociation is probably more correctly written

$$3ICl = I_2Cl^+ + ICl_2^-$$

A similar conductivity experiment in which IBr was added to a solution of $2I_2 + HIO_3$ gave a value of γ of 7.7 at the composition $IBr/(2I_2 + HIO_3) = 5.0$ which is consistent with the formation of I_2Br^+ according to the equation

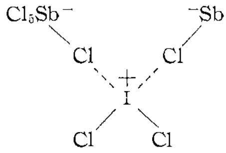
$$HIO_3 + 2I_2 + 5IBr + 8H_2SO_4 = 5I_2Br^+ + 3H_3O^+ + 8HSO_4^-$$

When ICl was added to solutions of iodic acid alone in 100% H_2SO_4 the conductivity increased until a mole ratio of approximately 7.0 was reached. Values of γ of 7.8 and 7.6 obtained in two experiments at the composition $ICl/HIO_3 = 7.0$ are consistent with ionization according to

$$HIO_3 + 7ICl + 8H_2SO_4 = 3I_2Cl^+ + 2ICl_2^+ + 3H_3O^+ + 8HSO_4^-$$

The ions I_3^+, I_2Cl^+, and I_2Br^+ presumably have structures that resemble those of ICl_2^+, which is known to have a bond angle of 90° when it is coordinated with other ions such as $SbCl_6^-$ to give a very approximately square-planar arrangement around iodine (I).[10] The $TeBr_2$ molecule has a bond angle of 98 ± 3°.[11] This is isoelectronic with IBr_2^+, which seems a very plausible ion although no evidence for it has yet been obtained.

In the case of the polyhalide cations I_2Cl^+ and I_2Br^+ it seems reasonable to suppose that the iodine will carry the majority of the positive charge (II). One can only speculate on the structure of I_5^+. One possibility is III and another possible shape is that shown in IV and V which also illustrate two plausible electronic structures.



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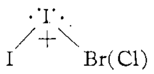

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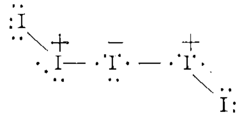
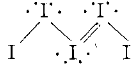
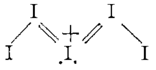


III



IV



V

Experimental

Experimental details concerning the cryoscopic and conductometric measurements were described in part I.[6] Full details of the results of the cryoscopic and conductometric measurements are available elsewhere.[12] Practical grade iodine monochloride and iodine monobromide were purified by fractional freezing. Dipyridineiodine(I) nitrate was prepared as described by Carlsohn.[13] Silver nitrate (5.1 g.) was warmed with 6 ml. of pyridine until it had all dissolved. The solution was cooled and the resulting solid product filtered and dissolved in 30 ml. of chloroform. Iodine (7.8 g.) was added and the mixture stirred until reaction was complete. Silver iodide was filtered off and the filtrate poured slowly, with stirring, into 60 ml. of ether. The product was filtered off, washed with ether containing a little pyridine, and dried in a vacuum desiccator over sulfuric acid. Dipyridineiodine(I) perchlorate[13] was prepared by dissolving 5 g. of mercurous perchlorate in a solution of 6 g. of iodine in 27 ml. of pyridine. The solution was filtered and the filtrate treated with 40 ml. of benzene. The product was filtered off, washed with ether, and dried in a vacuum desiccator over sulfuric acid.

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(9) N. N. Greenwood and H. J. Emeléus, *J. Chem. Soc.*, 987 (1950).

(10) C. G. Vonk and E. H. Wiebenga, *Acta Cryst.*, **14**, 859 (1959).

(11) M. T. Rogers and R. A. Spurr, *J. Am. Chem. Soc.*, **69**, 2102 (1947).

(12) Full details of the experimental results have been deposited as Document No. 8219 with the DAI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service. Library of Congress.

(13) H. Carlsohn, *Angew. Chem.*, **45**, 580 (1932); **46**, 747 (1933).