would require the half-time of CrI^{2+} in 10^{-3} M I_2 to be ~90 sec.; it was observed here that less than 20% aquation had occurred after 30 min. Mechanism 2 is rejected on the basis of the conclusion that iodine does not catalyze the aquation of iodochromium(III) ion. In this regard the present system is similar to iodopentaamminecobalt(III) ion, toward which iodine does not act as an effective aquation catalyst,[10] and unlike iodopentacyanocobaltate(III) ion, toward which it does.[23]

A mechanism consistent with these several requirements consists of the rate-determining formation of CrI_3^{2+} at low concentration. This unstable species may then react with iodate ion in a relatively rapid step. This mechanism requires that intermediates formed in these subsequent steps (likely candidates are HIO_2 and HIO) react rapidly with iodochromium(III) ion and/or with CrI_3^{2+}, a reasonable hypothesis if it is accepted that iodate ion, a similar but less powerful oxidizing agent, does. That the association of CrI^{2+} and I_2 should proceed at a rate ~10^9-fold lower than the association of I^- and I_2[22] may be due to the more stringent steric requirements of the former reaction and to the altered electronic structure of the coordinated iodide ion.

Reactions with Other Oxidizing Agents.—Also examined for their oxidizing properties on iodochromium(II) ion were hydrogen peroxide and aquoiron(III) ion. Each of these was examined under the following reaction conditions: 0.01–0.05 F oxidizing agent, 0.002 M iodochromium(III), 0.948 M H^+, at 20.0° and at ionic strength 1.00 F.

In the case of hydrogen peroxide slow formation of iodine occurs. A difficulty arising in the interpretation of these experiments is that oxidation of free iodide by peroxide is not instantaneous in these circumstances, although it is rather rapid (the half-life of iodide ion under these conditions is ~3 min.).[24] The gross rate of production of I_2 estimated from the slope of absorbance *vs.* time, in four experiments with two values of $[H_2O_2]$, leads to the conclusion that the rate is approximately independent of $[H_2O_2]$, and is close to that (±30%) predicted on the basis that the reaction occurs by slow aquation of the complex followed by the more rapid reaction of free iodide with hydrogen peroxide. This does not exclude the possibility that there may exist other reaction conditions where attack of peroxide upon coordinated iodide in iodochromium(III) dominates, as it does in the case of the reaction between hydrogen peroxide and iodopentaamminecobalt(III) ion,[10] but it does appear that such conditions may be inaccessible in this case, or nearly so.

Aquoiron(III) reacts only slowly with free iodide ion under these conditions (the first half-time of 10^{-3} M iodide ion in a solution 0.02 F in Fe(III) and 1 F in $HClO_4$ at 20° is ~40 min.).[25] No oxidation of iodide ion by iron(III) was observed in this study when iron(III) was added to iodochromium(III) ion under the conditions given above, even after enough time elapsed so that substantial aquation of the complex had taken place. Conclusions cannot be drawn with regard to the effectiveness of iron(III) in oxidizing bound iodide relative to free iodide; since the complex aquates under these particular conditions of concentration and temperature at a rate comparable to that of the iron(III)–I^- reaction, the direct iron(III)–CrI^{2+} process would be undetected. No evidence was obtained here on the direct oxidation of bound iodide by iron(III); if it can occur, it does so at a rate less than about twice the aquation rate under these conditions.

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[23] R. J. Grassi and W. Wilmarth, Proceedings, International Conference on Coordination Chemistry, Uppsala, Sweden, 1962, p. 242.

[24] H. A. Liebhafsky and A. M. Mohammad, *J. Am. Chem. Soc.*, **55**, 3977 (1933).

[25] A. J. Fudge and K. W. Sykes, *J. Chem. Soc.*, 119 (1952).

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Cations and Oxy Cations of Iodine. II. Solutions of Iodosyl Sulfate, Iodine Dioxide, and Iodic Acid–Iodine Mixtures in Sulfuric Acid and Dilute Oleum

By R. J. Gillespie and J. B. Senior

Received January 27, 1964

Solutions in sulfuric acid of iodosyl sulfate, iodine dioxide, and mixtures of iodic acid and iodine having the mole ratio $HIO_3/I_2 = 3$ have been studied by means of cryoscopic and conductometric measurements. It is concluded that iodosyl hydrogen sulfate, $IO \cdot HSO_4$, which behaves as a weak electrolyte, is formed in each case. The results of similar measurements on solutions of the same solutes in dilute oleum lead to the conclusion that more sulfated species such as $(HSO_4)_2IOI(HSO_4)_2$ and $I(HSO_4)_3$ and related polymers are formed under these conditions.

Introduction

Chretien[1] obtained a yellow compound of trivalent iodine, to which he assigned the composition $I_2O_3 \cdot SO_3 \cdot 0.5H_2O$, by heating iodic acid in the presence of concentrated sulfuric acid. The composition of this compound was the subject of a controversy that was mainly

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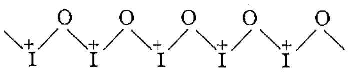
[1] P. Chretien, *Compt. rend.*, **123**, 814 (1896); *Ann. Chim. Phys.*, **15**, 367 (1898).

concerned with the number of molecules of water of hydration.[2,3] Masson and Argument[4] showed that the compound could be obtained in quantitative yield as a bright yellow crystalline precipitate by stirring together under concentrated sulfuric acid exactly equivalent amounts of iodine pentoxide and iodine. They analyzed the product by two different methods and showed conclusively that it had the composition $I_2O_3 \cdot SO_3$. The compound has frequently been formulated as iodosyl sulfate, $(IO)_2SO_4$, *i.e.*, as a salt of the iodosyl, IO^+, cation. Kikindai[5] has claimed that a somewhat poorly defined nitrate obtained from iodine and fuming nitric acid is iodosyl nitrate $IO \cdot NO_3$. The formula for iodine dioxide $(IO_2)_n$ is frequently written as I_2O_4 and for a long time it has been considered to be iodosyl iodate $IO \cdot IO_3$.

Masson and Argument[4] found that when sufficient sulfur trioxide was added to a saturated solution of iodosyl sulfate in sulfuric acid to bring the composition of the solvent above 100% H_2SO_4, the solid phase in equilibrium with the solution was no longer the yellow $(IO)_2SO_4$, but a white, crystalline, extremely moisture-sensitive substance, which they showed to have the composition $I_2O_3 \cdot 4SO_3 \cdot xH_2O$ where x could not be determined with certainty. The most probable formula was considered to be $I_2O_3 \cdot 4SO_3 \cdot H_2O$, which can be rewritten as $I(SO_4)HSO_4$, a compound intermediate between $I(SO_4H)_3$ and the normal sulfate of trivalent iodine, $I_2(SO_4)_3$, prepared by Fichter and Kappeler.[6] When aqueous sulfuric acid was added, to bring the composition of the medium below 100% H_2SO_4, the white compound decomposed, releasing iodine and iodine pentoxide, which then recombined to give iodosyl sulfate. Symons, *et al.*,[7] have formulated the white compound as $IO \cdot HS_2O_7$ on the basis of its infrared and ultraviolet spectra.

Until the recent work of Dasent and Waddington[8] there was no direct evidence that any of these compounds did indeed contain the iodosyl cation. These authors investigated the infrared spectra of iodine dioxide, the sulfate $(IO)_2SO_4$, and also the selenate $(IO)_2SeO_4$ which they prepared for the first time. They concluded that all three compounds do in fact contain the iodosyl cation but that it is present in the solid crystalline compounds as the linear polymer



The purpose of our work was to investigate the state of I(III) in sulfuric acid solution and to determine if, and under what conditions, the iodosyl cation IO^+ is formed. Since our investigation was completed Arotsky, Mishra, and Symons[7] have published the results of their similar investigations. Their conclusions, which differ from ours, are that iodosyl sulfate is a nonelectrolyte in sulfuric acid solution but forms the electrolyte $IO \cdot HS_2O_7$ in oleum.

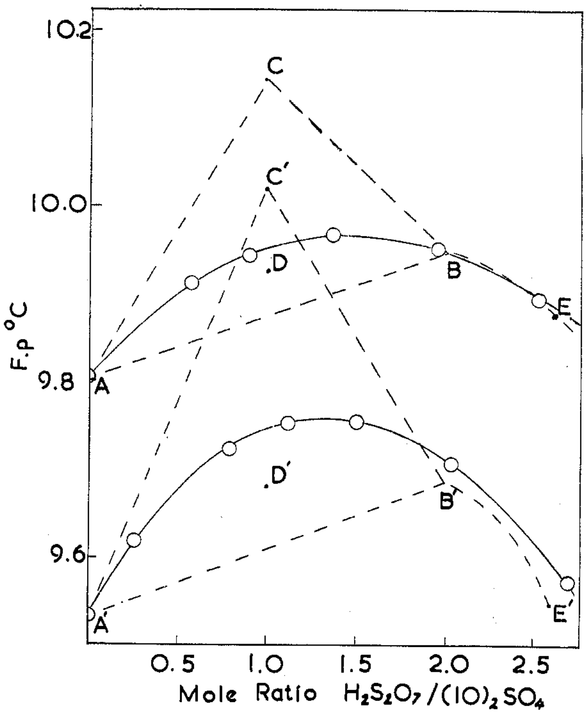


Fig. 1.—Conductometric titrations of $(IO)_2SO_4$ and "I_2O_3 + $0.6H_2O$" with $H_2S_2O_7$: ○, $(IO)_2SO_4$; ●, "I_2O_3 + $0.6H_2O$."

Results

Cryoscopy.—A number of cryoscopic experiments were performed in which the starting solution, which contained iodine and iodic acid in a definite mole ratio, was subjected to successive dilutions with 100% sulfuric acid to give a range of concentrations. A curve of freezing point *vs.* 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. A plot of the interpolated freezing points *vs.* the mole ratio I_2/HIO_3 was made for each stoichiometric molality of iodic acid. The results are presented in detail in part III.[9] For our present purpose the freezing points of solutions containing iodine and iodic acid in the mole ratio $I_2/HIO_3 = 0.33$ are of particular interest and the interpolated values are given in Table I. The results of cryoscopic experiments on solutions of iodosyl sulfate and on solutions of iodine dioxide are also given in Table I. Two cryoscopic titrations of a solution of iodosyl sulfate with a solution of disulfuric acid were carried out and the results are given in Table II and Fig. 1.

Conductometry.—A series of experiments in each of which successive additions of iodine were made to an initial solution of iodic acid was carried out. Curves were plotted of specific conductivity *vs.* the mole ratio I_2/HIO_3, and values of the conductivity at mole ratios of particular interest were obtained by interpola-

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[2] F. Fichter and A. Dinger, *Helv. Chim. Acta*, **19**, 607 (1936).

[3] R. K. Bahl and J. R. Partington, *J. Chem. Soc.*, 1258 (1935).

[4] I. Masson and C. Argument, *ibid.*, 1702 (1938).

[5] T. Kikindai, *Compt. rend.*, **238**, 1229 (1954).

[6] F. Fichter and H. Kappeler, *Z. anorg. allgem. Chem.*, **91**, 134 (1915).

[7] J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 2582 (1962).

[8] W. E. Dasent and T. C. Waddington, *J. Chem. Soc.*, 3350 (1960).

[9] R. Garrett, R. J. Gillespie, and J. B. Senior, to be published.

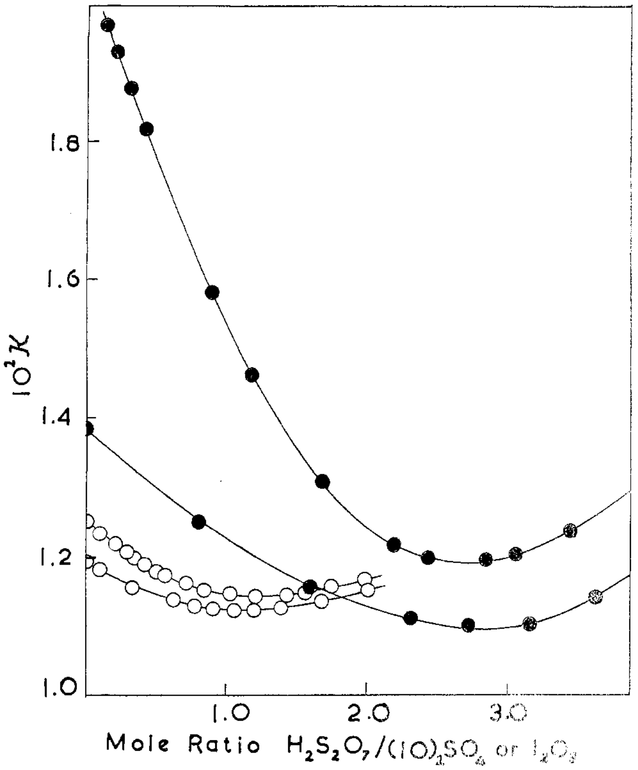

Fig. 2.—Cryoscopic titrations of $(IO)_2SO_4$ and "$I_2O_3 + 0.6H_2O$" with $H_2S_2O_7$: ○, $(IO)_2SO_4$; ●, "$I_2O_3 + 0.6H_2O$."

Table I

Freezing Points

0.33I₂–HIO₃		(IO)₂SO₄		(IO₂)ₙ	
10^2m	F.p., °C.	10^2m	F.p., °C.	10^2m	F.p., °C.
1.00	10.170	1.459	10.142	0.701	10.247
1.50	10.050	1.695	10.085	1.111	10.174
2.00	9.925	2.324	10.004	1.758	10.053
2.50	9.800	2.699	9.922	2.514	9.908
3.00	9.670	3.154	9.884	3.092	9.801
3.50	9.555	3.776	9.806		
		3.855	9.786		
		4.149	9.695		
		5.612	9.482		
		7.059	9.267		

Table II

Cryoscopic Titrations of $(IO)_2SO_4$ with $H_2S_2O_7$

Mole ratio $H_2S_2O_7/(IO)_2SO_4$	m^s $(IO)_2SO_4$	F.p., °C.	Mole ratio $H_2S_2O_7/(IO)_2SO_4$	m^s $(IO)_2SO_4$	F.p., °C.
0.000	0.0378	9.806	0.000	0.0516	9.535
0.576	...	9.912	0.261	...	9.620
0.895	...	9.944	0.791	...	9.724
1.000	0.0357	0.951[a]	1.000	0.0558	9.746[a]
1.362	...	9.968	1.120	...	9.754
1.949	...	9.953	1.507	...	9.757
2.000	0.0341	9.950[a]	2.000	0.0553	9.712
2.512	...	9.897	2.030	...	9.709
3.086	...	9.821	2.685	...	9.575
3.846	...	9.709	3.076	...	9.459
4.694	...	9.591			

[a] Interpolated values.

tion. The results are presented in detail in part III.[9] Table III gives the interpolated conductivities for the mole ratio $I_2/HIO_3 = 0.33$. The results of conductivity experiments on solutions of iodosyl sulfate and iodine dioxide are also given in Table III. Conductometric titrations of solutions of $(IO)_2SO_4$ were made with solutions of $H_2S_2O_7$ (Table IV and Fig. 2). The final addition of oleum was carefully made so as to bring the composition of the solution as close as possible to the stoichiometry $(IO)_2SO_4 + 2H_2S_2O_7$. This solution was then "back titrated" with potassium sulfate. Similar conductometric titrations of solutions having the composition $HIO_3 + 0.33I_2$ were carried out. A solution of this composition may be regarded as containing the solute "$I_2O_3 + 0.6H_2O$." Conductivities have been plotted against the mole ratio $H_2S_2O_7$/"I_2O_3." At the mole ratio $H_2S_2O_7/I_2O_3 = 1.6$ the composition of the solution is the same as that of a solution of $I_2O_3 \cdot SO_3$ or $(IO)_2SO_4$.

Table III

Conductivities

0.33I₂–HIO₃		(IO)₂SO₄		(IO₂)ₙ	
10^2w, mole kg.$^{-1}$ of soln.	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	10^2w, mole kg.$^{-1}$ of soln.	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	10^2w, mole kg.$^{-1}$ of soln.	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
0.427	1.069	0.146	1.0484	0.137	1.047
0.975	1.138	0.318	1.0552	0.506	1.070
1.175	1.176	0.771	1.0796	1.101	1.132
1.568	1.250	1.275	1.1130	1.686	1.215
1.837	1.298	1.937	1.1626	2.371	1.324
2.253	1.386	2.376	1.1974	3.064	1.443
2.656	1.465	3.039	1.2505		
3.380	1.622	3.834	1.3138		
5.708	2.055	0.202	1.0509		
		0.760	1.0788		
		1.257	1.1124		
		1.973	1.1639		
		2.661	1.2165		
		3.677	1.2933		
		4.848	1.3785		
		7.010	1.5254		

Values of ν, the number of moles of particles produced in solution by one mole of solute, and γ, the number of moles of hydrogen sulfate ions produced in solution by one mole of solute, were calculated from the experimental results as described in part I[10] and are given in Table V.

Discussion

Solutions of Iodosyl Sulfate and of $HIO_3 + 0.33I_2$ in H_2SO_4.—The values of ν and γ for both solutes are best explained by reactions 1 and 2 with about 50% ionization of iodosyl hydrogen sulfate according to eq. 3.

$$(IO)_2SO_4 + H_2SO_4 = 2IOHSO_4 \qquad (1)$$
$$\nu = 4\text{–}2,\ \gamma = 2\text{–}0,\ \nu - \gamma = 2$$

$$3HIO_3 + I_2 + 9H_2SO_4 = 5IOHSO_4 + 4H_3O^+ + 4HSO_4^- \qquad (2)$$
$$\nu = 6\text{–}4.33,\ \gamma = 3\text{–}1.33,\ \nu - \gamma = 3$$

$$IOHSO_4 \rightleftharpoons IO^+ + HSO_4^- \qquad (3)$$

The extremes of the ranges for ν and γ given for eq. 1 and 2 correspond to 100 and 0% ionization of $IO \cdot HSO_4$.

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

TABLE IV

CONDUCTOMETRIC TITRATIONS OF $(IO)_2SO_4$ AND OF $0.33I_2$–HIO_3 WITH $H_2S_2O_7$

Mole ratio $H_2S_2O_7/(IO)_2SO_4$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
0 (w = 0.0328)	1.254
0.087	1.2
0.195	1.220
0.265	1.209
0.325	1.201
0.392	1.192
0.485	1.182
0.563	1.174
0.693	1.164
0.842	1.155
1.024	1.147
1.206	1.144
1.429	1.146
1.570	1.150
1.754	1.156
1.984	1.167

Mole ratio $K_2SO_4/(IO)_2SO_4$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
0.0611	1.160
0.1682	1.158
0.2094	1.160
0.2825	1.167
0.4751	1.206

Mole ratio $H_2S_2O_7/HIO_3$ + $0.33I_2$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
0 (w = 0.0225)	1.386
0.801	1.249
1.600	1.155
2.310	1.112
2.724	1.103
3.156	1.103
3.622	1.112
4.470	1.143
5.382	1.187

Mole ratio $H_2S_2O_7/(IO)_2SO_4$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
0 (w = 0.0249)	1.195
0.103	1.182
0.331	1.159
0.613	1.139
0.771	1.131
0.898	1.127
1.063	1.125
1.205	1.125
1.385	1.127
1.675	1.137
1.996	1.153

Mole ratio $K_2SO_4/(IO)_2SO_4$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
0.0404	1.148
0.0927	1.143
0.1670	1.141
0.2321	1.142
0.3228	1.148
0.3988	1.157

Mole ratio $H_2S_2O_7/HIO_3$ + $0.33I_2$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
0 (w = 0.0571)	2.055
0.052	2.022
0.137	1.971
0.199	1.932
0.296	1.878
0.410	1.817
0.886	1.580
1.182	1.463
1.682	1.308
2.195	1.219
2.431	1.201
2.850	1.196
3.067	1.206
3.446	1.240
3.995	1.311

TABLE V

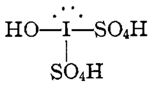
VALUES OF ν, γ, AND K_b

m	ν	γ	$\nu - \gamma$	10^2K_b(IO·HSO$_4$)
		$HIO_3 + 0.33I_2$		
0.01	5.48	2.12	3.36	2.8
0.02	4.97	1.94	3.03	2.6
0.03	4.89	1.82	3.07	2.5
0.04	4.71	1.73	2.98	2.2
		$(IO)_2SO_4$		
0.02	3.22	1.14	2.08	4.4
0.03	3.06	1.00	2.06	3.9
0.04	2.94	0.91	2.03	3.7
0.05	2.86	0.85	2.01	3.6
0.06	2.80	0.79	2.01	3.5
0.07	2.76	0.75	2.01	3.5
		$(IO_2)_n$		
0.010	4.83	2.05	2.78	
0.015	4.52	1.82	2.70	
0.020	4.30	1.70	2.60	
0.025	4.15	1.63	2.52	
0.030	4.03	1.58	2.45	

Values of $K_b = [IO^+][HSO_4^-]/[IOHSO_4]$ were calculated from the results for both $HIO_3 + 0.33I_2$ and for $(IO)_2SO_4$. For the former we have $K_b = \gamma[HSO_4^-]/(2 - \gamma)$ and for the latter $K_b = (\gamma - 1.33)[HSO_4^-]/(3 - \gamma)$. The two sets of values of K_b are each reasonably constant, but those obtained from the data on $(IO)_2SO_4$ are slightly higher than those obtained from the "$HIO_3 + 0.33I_2$" results. A possible reason for the discrepancy may be the occurrence in solutions of $(IO)_2SO_4$ of a small amount of reaction according to eq. 4 with a corresponding increase in the concentration of HSO_4^-. This reaction leads to the production of H_3O^+, and so the corresponding reaction for the solute "$HIO_3 + 0.33I_2$," for which H_3O^+ ions are already produced in reaction 2, should be of less importance.

$$(IO)_2SO_4 + 7H_2SO_4 = 2I(HSO_4)_3 + 2H_3O^+ + 2HSO_4^- \quad (4)$$
$$\nu = 6,\ \gamma = 2,\ \nu - \gamma = 4$$

It may be noted that iodosyl hydrogen sulfate probably exists predominantly in the more solvated form I



$$HO{-}\ddot{I}(SO_4H){-}SO_4H$$

I

and its ionization may be represented by the equation

$$HO{\cdot}I(HSO_4)_2 + H_2SO_4 \rightleftharpoons [H_2O{\cdot}I(SO_4H)_2]^+ + HSO_4^- \quad (5)$$

Arotsky, Mishra, and Symons[7] state that solutions of iodosyl sulfate are "nonionic," although no conductance data are given in support of this statement, and they quote only a single value of $\nu = 2.1$. They conclude that iodosyl sulfate reacts to form un-ionized iodosyl hydrogen sulfate according to eq. 1. This conclusion is inconsistent with both our cryoscopic and our conductometric results. Other possible modes of ionization such as eq. 4, 6, 7, and 8 are also inconsistent with our experimental results.

$$3HIO_3 + I_2 + 24H_2SO_4 = 5I(HSO_4)_3 + 9H_3O^+ + 9HSO_4^- \quad (6)$$
$$\nu = 7.67,\ \gamma = 3,\ \nu - \gamma = 4.67$$

$$(IO)_2SO_4 + 7H_2SO_4 = 2H_3O^+ + 2I(HSO_4)_4^- \quad (7)$$
$$\nu = 4,\ \gamma = 0,\ \nu - \gamma = 4$$

$$3HIO_3 + I_2 + 24H_2SO_4 = 9H_3O^+ + 5I(HSO_4)_4^- + 4HSO_4^- \quad (8)$$
$$\nu = 6,\ \gamma = 1.33,\ \nu - \gamma = 4.67$$

Solutions of Iodine Dioxide in H_2SO_4.—In view of its formulation as iodosyl iodate and our experimental results for iodic acid and iodosyl sulfate described in part I[10] and above, the most probable ionization scheme may be written

$$I_2O_4 + 3H_2SO_4 = 1/n(IO_2HSO_4)_n + IOHSO_4 + H_3O^+ + HSO_4^- \quad (9)$$
$$n = 1,\ \nu = 5\text{–}4,\ \gamma = 2\text{–}1,\ \nu - \gamma = 3$$
$$n = 2,\ \nu = 4.5\text{–}3.5,\ \gamma = 2\text{–}1,\ \nu - \gamma = 2.5$$
$$n = 3,\ \nu = 4.3\text{–}3.3,\ \gamma = 2\text{–}1,\ \nu - \gamma = 2.3$$

The ranges of ν and γ quoted take into account the partial ionization of IO·HSO$_4$. The observed values of ν and γ given in Table V are consistent with this reaction scheme with n increasing from 1 to 2 with increasing concentration.

Symons, *et al.*,[7] quote a single value of $\nu = 3.3$ for iodine dioxide which is not in agreement with our results, and their conclusion that iodine dioxide ionizes according to the equation

$$I_2O_4 + 2H_2SO_4 = IO\cdot HSO_4 + H_2IO_3^+ + HSO_4^- \quad (10)$$

which would require $\nu = 3$, $\gamma = 1$, and $\nu - \gamma = 2$ is not consistent with either our cryoscopic or our conductometric results. Our results are also not consistent with other possible ionization schemes such as

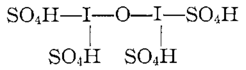
$$I_2O_4 + H_2SO_4 = HI_2O_4^+ + HSO_4^- \quad (11)$$
$$\nu = 2,\ \gamma = 1,\ \nu - \gamma = 1$$

$$I_2O_4 + 2H_2SO_4 = 2HIO_2^+ + 2HSO_4^- \quad (12)$$
$$\nu = 4,\ \gamma = 2,\ \nu - \gamma = 2$$

$$I_2O_4 + 2H_2SO_4 = I_2O_3^+ + H_3O^+ + 2HSO_4^- \quad (13)$$
$$\nu = 4,\ \gamma = 2,\ \nu - \gamma = 2$$

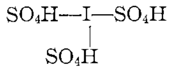
If I_2O_4 contained quadrivalent iodine, or existed as discrete molecules, some such scheme as eq. 11, 12, or 13 might possibly be followed. Thus the present results lend some additional support to the formulation of I_2O_4 as iodosyl iodate.

Solutions of Iodosyl Sulfate in H_2SO_4–SO_3.—Our results are best explained by assuming that in oleum IO^+ is converted to more sulfated forms of I(III), *e.g.*, II and III, by analogy with the behavior of arsenic trioxide in sulfuric acid and oleum.[11] The relation of these species to $IO\cdot HSO_4$ is more easily seen if the latter is written in the solvated form I.



$$\mathrm{SO_4H{-}\underset{\underset{SO_4H}{|}}{I}{-}O{-}\underset{\underset{SO_4H}{|}}{I}{-}SO_4H}$$

II



$$\mathrm{SO_4H{-}\underset{\underset{SO_4H}{|}}{I}{-}SO_4H}$$

III

In Fig. 1 the points B and B′ represent the expected freezing points of solutions containing two moles of a nonelectrolyte for each initial mole of $(IO)_2SO_4$, *i.e.*, they correspond to the complete formation of two moles of $I(HSO_4)_3$ according to the equation

$$(IO)_2SO_4 + 2H_2S_2O_7 + H_2SO_4 \longrightarrow 2I(HSO_4)_3 \quad (14)$$

The agreement between the observed freezing points and the calculated points B and B′ is therefore consistent with the formation of $I(HSO_4)_3$ at the mole ratio $H_2S_2O_7/(IO)_2SO_4 = 2$, but the fact that the freezing point curve rises above the line AB indicates the formation of some polymeric species at lower mole ratios. The simplest assumption is that the dimer II is formed. The complete formation of II at the mole ratio $H_2S_2O_7/(IO)_2SO_4 = 1.0$ would give the freezing points indicated by C and C′.

$$(IO)_2SO_4 + H_2SO_4 + H_2S_2O_7 = I_2O(HSO_4)_4 \quad (15)$$

It is clear that this dimer is by no means completely formed although the initial slopes of the freezing point curves indicate that the first additions of $H_2S_2O_7$ react largely in this manner.

On the addition of $(IO)_2SO_4$ to oleum the conductivity decreases and passes through a minimum at the mole ratio $H_2S_2O_7/(IO)_2SO_4 = 1.1$ to 1.2. The reaction

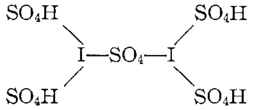
$$2IO\cdot HSO_4 + H_2S_2O_7 = I_2O(HSO_4)_2 \quad (16)$$

would give a conductivity minimum at $H_2S_2O_7/(IO)_2SO_4 = 1.0$. Further addition of $H_2S_2O_7$ would give no increase in conductivity if the reaction

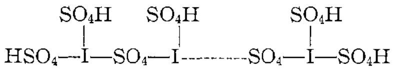
$$I_2O(HSO_4)_4 + H_2S_2O_7 = 2I(HSO_4)_3 \quad (17)$$

occurs until the mole ratio $H_2S_2O_7/(IO)SO_4 = 2.0$. Although the observed minimum occurs at a mole ratio of 1.1–1.2 over the range of mole ratios from 0.9 to 1.5, the conductivity scarcely changes. The slight increase from the minimum to the mole ratio 2.0 may be attributed to reaction 17 not proceeding quite to completion. This implies that some unreacted $H_2S_2O_7$ is present at the mole ratio 2.0 and this is consistent with the fact that this solution can be titrated to a conductivity minimum with $KHSO_4$ (Table IV).

Polymerization of iodine tris(hydrogen sulfate) (III) could give the dimer IV and the polymers V and VI. The polymer V has the composition of Masson and Argument's[4] white solid and VI of the compound $I_2(SO_4)_3$ prepared by Fichter and Kappeler.[6]

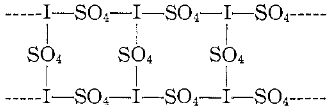


IV



$$\mathrm{HSO_4{-}\overset{\overset{SO_4H}{|}}{I}{-}SO_4{-}\overset{\overset{SO_4H}{|}}{I}{\cdots\cdots}SO_4{-}\overset{\overset{SO_4H}{|}}{I}{-}SO_4H}$$

V



VI

Arotsky, Mishra, and Symons[7] have suggested that iodosyl sulfate is converted to ionized iodosyl hydrogen disulfate $IO\cdot HS_2O_7$ in oleum. If this were the case the reaction could be written as a simple neutralization of the base $IO\cdot HSO_4$ by the acid $H_2S_2O_7$.

$$\left.\begin{matrix} IO\cdot HSO_4 \\ \upharpoonleft\downharpoonright \\ IO^+ + HSO_4^- \end{matrix}\right\} + H_2S_2O_7 = H_2SO_4 + \left\{\begin{matrix} IO\cdot HS_2O_7 \\ \upharpoonleft\downharpoonright \\ IO^+ + HS_2O_7^- \end{matrix}\right. \quad (18)$$

Since the hydrogen disulfate ion is a weaker nucleophile than HSO_4^- it would be expected that $IO\cdot HS_2O_7$ would be more extensively ionized than $IO\cdot HSO_4$. If $IO\cdot HS_2O_7$ were in fact ionized to an equal or greater extent than $IO\cdot HSO_4$, then on addition of $H_2S_2O_7$ to a solution of $IO\cdot HSO_4$ there would be either no change or a decrease in the freezing point of the solution. The observed initial rise in the freezing point (Fig. 1) is thus inconsistent with this supposition, and one must conclude either that $IO\cdot HS_2O_7$ is very little ionized or that eq. 18 does not describe the reaction that occurs on the addition of $H_2S_2O_7$ to a solution of $IO\cdot HSO_4$ in H_2SO_4.

It may be shown by means of the equations given by Flowers, Gillespie, and Robinson[12] that in the titration of the weak base $IO\cdot HSO_4$ ($K_b = 0.03$) with $H_2S_2O_7$, if the $IO\cdot HSO_7$ that is formed is fully ionized, a minimum conductivity would be obtained at the mole ratio

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[11] R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 450 (1963).

[12] R. H. Flowers, R. J. Gillespie, and E. A. Robinson, *ibid.*, **38**, 1363 (1960).

$H_2S_2O_7/(IO)_2SO_4$ = 1.8. The formation of un-ionized $IO \cdot HS_2O_7$ would lead to a decrease in the conductivity to a minimum value at the mole ratio $H_2S_2O_7/(IO)_2SO_4$ = 2.0. The observed conductivity minimum occurs, however, at a mole ratio of 1.1 to 1.2, and the conductivity then increases again indicating that conducting species are present at the mole ratio 2.0. We conclude therefore that our results are not in agreement with the formation of either ionized or un-ionized $IO \cdot HS_2O_7$ according to eq. 18.

Experimental

Experimental details concerning the cryoscopic and conductometric measurements were described in part I.[10] Iodosyl sulfate was prepared by the method of Masson and Argument.[4] Ten grams of finely powdered iodine pentoxide and 5.1 g. of iodine were stirred magnetically under 97% H_2SO_4 for 2–3 days. The yellow product was filtered off in a drybox and was washed three times with small portions of 97% H_2SO_4 and three times with anhydrous nitromethane. The product was freed from nitromethane by warming gently under vacuum for several hours. It was analyzed by refluxing with water and then extracting the resulting iodine with carbon tetrachloride.

$$5(IO)_2SO_4 + 8H_2O = 6HIO_3 + 2I_2 + 5H_2SO_4$$

The iodine in the CCl_4 layer was determined with thiosulfate. Excess KI was added to the acidified aqueous layer and the resulting iodine was titrated with thiosulfate. The results of a typical analysis follow. *Anal.* Calcd.: I, 66.4; oxidation no. of I, 3.00. Found: I, 66.9, 66.8; oxidation no. of I, 2.99, 3.04.

Iodine dioxide was prepared by the method of Bahl and Partington.[3] About 20 g. of finely powdered iodic acid was heated with 70 g. of 97% H_2SO_4 for about 40 min. until it had all dissolved. After the solution had been kept in a desiccator for 1 week the yellow solid crust which formed was removed and transferred to a porous plate. This was stored in a desiccator for another week, during which time it was periodically removed and ground to a fine powder. The resulting product was washed with water until the washings were free from sulfate, with acetone until the washings were colorless, and finally with dry ether. The method of analysis was the same as for iodosyl sulfate. *Anal.* Calcd.: I, 79.9; oxidation no. of I, 4.00. Found: I, 78.3, 78.5; oxidation no. of I, 3.99, 4.01.

Acknowledgment.—We thank the Directorate of Chemical Sciences of the United States Air Force Office of Scientific Research and the National Research Council, Canada, for financial assistance. We also thank the National Research Council, Canada, for the award of a studentship (to J. B. S.).

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The Kinetics of the Electron Exchange between the 12-Tungstocobaltate(II) and the 12-Tungstocobaltate(III) Anions in Aqueous Solution[1]

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Received November 19, 1963

The kinetics of the electron exchange between the 12-tungstocobaltate(II) and 12-tungstocobaltate(III) anions has been studied at 0° in aqueous solution. Precipitation of the $[Co^{III}O_4W_{12}O_{36}]^{-5}$ with $(C_4H_9)_4NI$ was used for separation. The reaction is first order in each ion, and the effects on the rate of changes in the hydrogen ion concentration, ionic strength, temperature, cations, and dielectric constant are described. At 0° and ionic strength of 0.6 M (adjusted with LiCl) the rate constant is 0.63 ± 0.016 M^{-1} sec.$^{-1}$. An "outer-sphere" mechanism is postulated for the system and the results are compared with the theoretical predictions of Marcus.

The preparation and properties of several heteropolytungstate compounds of cobalt have been reported,[3,4] and these compounds have been shown to participate in an unusual sequence of oxidation–reduction reactions.

The oxidation–reduction pair of the 12-tungstocobaltate(II), $[Co^{II}O_4W_{12}O_{36}]^{-6}$, and the 12-tungstocobaltate(III), $[Co^{III}O_4W_{12}O_{36}]^{-5}$, ions, hereafter designated as anions I and II, respectively, particularly interested us, and a quantitative study of the exchange reaction between them was undertaken. There are no previous reports in the literature of electron exchange between heteropoly complexes and it seemed desirable to determine how readily an electron from the central atom could penetrate the extensive tungsten–oxygen "cage." Moreover, this system seems to conform to the assumptions of Marcus' theory[5–7] for predicting the rates of electron exchange. Because they are generally very fast, very few anionic electron-exchange systems have been investigated thoroughly.[8]

Experimental

Chemicals.—Reagent grade chemicals were used without further purification for the preparation of the potassium salt of anion I.[3] Anion II was prepared electrolytically as follows. A 0.02 M solution of anion I was placed in the anode compartment of an "H" cell, which was used to prevent hydrogen, formed at the anode, from reducing anion II. The electrolysis was

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[1] Supported by the U. S. Atomic Energy Commission under grant No. AT(11-1)-1001.

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[3] L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, **78**, 4503 (1956).

[4] L. C. W. Baker and V. E. Simmons, *ibid.*, **81**, 4744 (1959).

[5] R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).

[6] R. A. Marcus, *ibid.*, **26**, 872 (1957).

[7] R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

[8] D. R. Stranks, Chapter 2 in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 163.