reaction conditions of this study. Using values of k_2 obtained from Figure 3 and values of k' for the uncatalyzed reaction, the values for k_{-1} may be calculated from eq 6, since for the uncatalyzed reaction

$$k' = \frac{k_1 k_2}{k_{-1} + k_2}$$

The values obtained from k_1, k_{-1}, and the ratio k_1/k_{-1} at the temperatures studied are listed in Table I. The respective activation energies and activation entropies determined from the temperature dependency of k_1 and k_{-1} for reactions 1 and 1a are 16 kcal and −46 cal deg^{-1} mol^{-1} for reaction 1 and 1.0 kcal and −57 cal deg^{-1} mol^{-1} for reaction 1a. The ratio of k_1 to k_{-1}, listed in Table I, is the equilibrium constant for the reaction $Cu^{2+} + NO_3^- \rightleftarrows CuO + NO_2^+$. $\Delta H°$ for this reaction is estimated to be 15.2 kcal. Slama,[4] who assumed a rapid equilibrium between reactions 1 and 1a, obtained a value of 39 kcal for $\Delta H°$.

TABLE I

RATE CONSTANTS FOR REACTIONS 1 AND 1a AT SEVERAL DIFFERENT TEMPERATURES

Temp, °C	$10^5 k_1$, sec^{-1}	$10^2 k_{-1}$, sec^{-1}	$10^3 k_1/k_{-1}$
310	3.8 ± 0.4	1.3	2.9
328	6.5 ± 0.5	1.4	4.6
350	9.2 ± 0.4	1.4	6.6

The large negative entropy of activation for reaction 1 is suggestive of a coming together of like-charged species or a separation of oppositely charged species. In view of the thermal instability of the transition metal nitrates, it would seem plausible that reaction 1 is the decomposition of a dinitrate copper(II) molecule or a nitratocuprate anion to give nitryl ion and copper oxide.

That catalysis occurs in reaction 2 suggests that the catalytic activity is not specific to copper(II) oxide and that other metal oxides could possibly act as catalysts. Also copper(II) oxide could possibly act as a catalyst for other acid–base reactions in nitrate melts which involve the production of nitryl ion. Preliminary investigations have shown that Fe(III) oxide is also a catalyst for the reaction of copper(II) ion in nitrate melts. Since oxidation of Fe(III) to a higher oxidation state, such as Fe(IV) or Fe(VI), is known, it seems reasonable that such higher oxidation states could be responsible for the catalytic activity of Fe_2O_3. If this were the case, then one might consider the oxidation of Cu(II) to Cu(III) as providing a possible path for catalysis by CuO.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA

Cations and Oxycations of Iodine. VI. Solutions of Some Iodine Compounds in Disulfuric Acid

BY R. J. GILLESPIE AND K. C. MALHOTRA

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The blue solutions of iodine in oleum have been reinvestigated using both $H_2S_2O_7$ (45% oleum) and 65% oleum as a solvent by cryoscopy, conductivity, and absorption spectra measurements. It is concluded that iodine is oxidized to the I_2^+ cation although the oxidation is apparently not complete in $H_2S_2O_7$ at 25°. KI and ICl also produce the I_2^+ cation in oleum, the latter by disproportionation to I_2^+ and $I(SO_4H)_2^+$. ICl_3 ionizes to give the ICl_2^+ ion. Sulfur dioxide which is a product of the oxidation of iodine is shown to be a nonelectrolyte. There is no evidence that the +1 oxidation state of iodine is stable in oleum either as the cation I^+ or in any other form.

Introduction

The blue color of the solutions obtained by oxidizing iodine in solution in fluorosulfuric acid has been shown in part IV of this series[1] to be due to the I_2^+ cation rather than the I^+ cation. The previous evidence for the I^+ cation[2] was mainly based on the results of spectrophotometric, conductometric, and magnetic studies of solutions of iodine and iodine monochloride in 65% oleum. This paper presents the results of a new and more comprehensive study of the behavior of iodine, potassium iodide, iodine monochloride, and iodine trichloride both in 65% oleum and in 44.94% oleum which has the composition of disulfuric acid, $H_2S_2O_7$. The general properties of the disulfuric acid solvent system have recently been investigated and the results of studies of the mode of ionization of a large number of simple electrolytes have been published.[3,4] These results formed the basis of the present study of the somewhat complex ionizations of iodine compounds in this solvent. The solvent $H_2S_2O_7$ was preferred to 65% oleum which was used by Symons, *et al.*,[2] because of the complexity of this medium which has a composition between $H_2S_3O_{10}$ and $H_2S_4O_{13}$ and in fact contains

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[1] R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1577 (1966).

[2] J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 12 (1961).

[3] R. J. Gillespie and K. C. Malhotra, *ibid.*, *A*, 1994 (1967).

[4] R. J. Gillespie and K. C. Malhotra, *ibid.*, *A*, 1933 (1968).

an equilibrium mixture of several polysulfuric acids and free SO_3. Consequently it is much more difficult to give a simple interpretation of the results of freezing point and conductivity measurements in 65% oleum than in $H_2S_2O_7$. However we have studied the conductivities of solutions of some iodine compounds in 65% oleum as we felt that a satisfactory interpretation might be possible by comparing the results with those obtained in $H_2S_2O_7$.

Results and Discussion

Absorption Spectra.—Solutions of I_2, ICl, and ISO_3F in $H_2S_2O_7$ all give the characteristic spectrum of I_2^+ with a strong peak at 640 mμ and weaker peaks at 510 and 420 mμ.[1,2] In each case however the characteristic peak of the I_3^+ ion at 300 mμ was also present in the spectrum although rather weakly. It appears that, in the case of iodine, oxidation to I_2^+ is incomplete, the remainder of the iodine being oxidized only to I_3^+ while iodine in the +1 oxidation state disproportionates to give mainly I_2^+ and some I_3^+ as the lower oxidation states, and, as will be shown later, iodine in the +3 oxidation state, probably $I(SO_4H)_3$. The extent of oxidation of iodine in oleum of various compositions was measured by means of the intensity of the 640-mμ peak. Oxidation occurs only slowly, particularly in the more dilute oleums but equilibrium appeared to be reached in 24–36 hr after which no change in the intensity of the 640-mμ peak was observed. Figure 1 shows a plot of the apparent extinction coefficient of the I_2^+ ion at 640 mμ against the composition of the oleum. It reaches a maximum of 2750 M^{-1} cm^{-1} in oleum having a composition ≥75% SO_3. We presume that this value represents the true extinction coefficient of I_2^+ in $H_2S_2O_7$ as a value of 2600 M^{-1} cm^{-1} has been obtained[1] for the extinction coefficient of I_2^+ in fluorosulfuric acid. We concluded that the formation of I_2^+ is complete in 75% oleum, at least 95% complete in 65% oleum, but only approximately 75% complete in 45% oleum ($H_2S_2O_7$). In a solution of ICl in 85% oleum the absorption spectrum showed the formation of 0.43 mol of I_2^+ per mole of I_2.

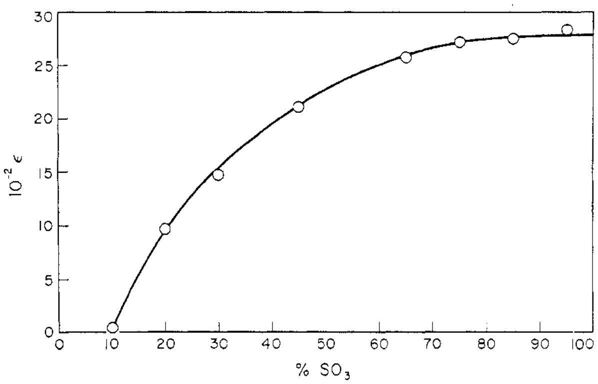

Figure 1.—Variation of the apparent extinction coefficient for the I_2^+ ion with oleum composition for solutions of iodine in oleum.

Freezing Point and Conductivity Measurements in $H_2S_2O_7$.—The results of the cryoscopic and conductometric measurements are given in Tables I and II. It has been shown previously[4] that the ionization of electrolytes in $H_2S_2O_7$ may be represented by the general equation

$$\text{solute} + sH_2S_2O_7 \longrightarrow aX^+ + aHS_3O_{10}^- + bY + cH_2SO_4$$

where all of the X^+ ions are not necessarily identical and Y represents all of the uncharged species. The freezing point depression produced by any solute is proportional to the total number of particles produced in solution by that solute. However because of the extensive self-dissociation of the solvent which produces

Table I

Conductivities of Solutions in $H_2S_2O_7$

10^2m	$10^3\kappa$, ohm^{-1} cm^{-1}	10^2m	$10^3\kappa$, ohm^{-1} cm^{-1}	10^2m	$10^3\kappa$, ohm^{-1} cm^{-1}
SO_2		KI		I_2	
6.50	3.7175	9.87	8.5892	0.90	3.962
12.61	3.7310	11.90	9.5504	1.36	4.068
18.58	3.7476	13.40	10.2269	1.94	4.254
		15.03	10.9083	2.40	4.424
ICl		16.51	11.5503	2.91	4.551
1.07	3.8580	18.01	12.0630	3.94	4.881
3.05	4.1837	19.53	12.6036	4.99	5.222
4.02	4.3886			5.87	5.533
5.52	4.6225	ICl_3		7.65	6.083
6.50	4.7885	1.04	3.9884	8.65	6.439
8.03	5.1053	3.53	4.7593	10.90	7.1821
9.51	5.3426	5.90	5.5118	11.87	7.459
11.50	5.7164	6.90	5.9046	12.25	7.552
13.00	6.0382	9.48	6.8030	13.08	8.014
15.01	6.4038	12.29	7.7545	15.05	8.454
16.12	6.5763	13.30	8.0452	16.68	8.933
		14.70	8.5300	17.94	9.352
KI		17.45	9.3799	19.93	9.892
1.35	4.3012	20.38	10.2271	21.10	10.245
3.80	5.4830	21.77	10.5581		
5.84	6.5330	23.72	11.1629		
7.94	7.6035				

Table II

Freezing Points of Solutions in $H_2S_2O_7$

10^2m	Fp, °C	10^2m	Fp, °C	10^2m	Fp, °C
KI		SO_2		I_2	
1.87	34.93	1.09	35.06	1.33	35.02
3.67	34.69	3.48	34.91	1.79	34.99
5.41	34.38	5.22	34.82	2.86	34.86
7.13	34.05	5.68	34.77	3.24	34.81
8.78	33.77	7.84	34.64	4.83	34.61
10.42	33.44	8.86	34.58	5.32	34.56
11.92	33.11	12.44	34.41	6.91	34.33
13.42	32.79	14.71	34.24	7.49	34.25
14.94	32.45	17.64	34.09	8.34	34.13
16.50	32.08	17.94	34.05	9.52	33.92
18.06	31.71			11.58	33.62
19.65	31.35	ICl_3		12.53	33.38
		2.21	34.88	13.91	33.18
ICl		5.67	34.37	14.95	32.97
1.82	34.99	8.05	33.96	15.95	32.73
3.57	34.85	9.32	33.73	17.23	32.52
5.80	34.67	10.61	33.48	18.29	32.26
8.58	34.38	11.97	33.22	19.62	31.98
9.78	34.30	12.77	33.05	20.07	31.83
11.49	34.10	13.91	32.82	23.26	31.07
13.50	33.86	15.21	32.55		
16.47	33.53	16.26	32.32		
18.22	33.31	18.71	31.75		
		22.43	30.88		

both H_2SO_4 and $HS_3O_{10}^-$, the relation between the freezing point depression and the concentration of solute is rather complicated and the freezing point depression produced by a given solute is most readily interpreted by comparison of the observed freezing points with reference curves constructed from the observed curves for some standard electrolytes, *e.g.*, the strong base nitromethane which ionizes according to the equation

$$CH_3NO_2 + 2H_2S_2O_7 \longrightarrow CH_3NO_2H^+ + HS_3O_{10}^- + H_2SO_4$$

and sulfuric acid which is essentially a nonelectrolyte.[3,4] The experimental results are compared with such standard curves in Figure 2. The freezing point depressions are determined essentially by $\nu = 2a + b$ and by c. For nitromethane $a = 1$, $b = 0$, $c = 1$, and $\nu = 2$. The values of ν and c determined by comparison with the reference curves in Figure 2 are given in Table III.

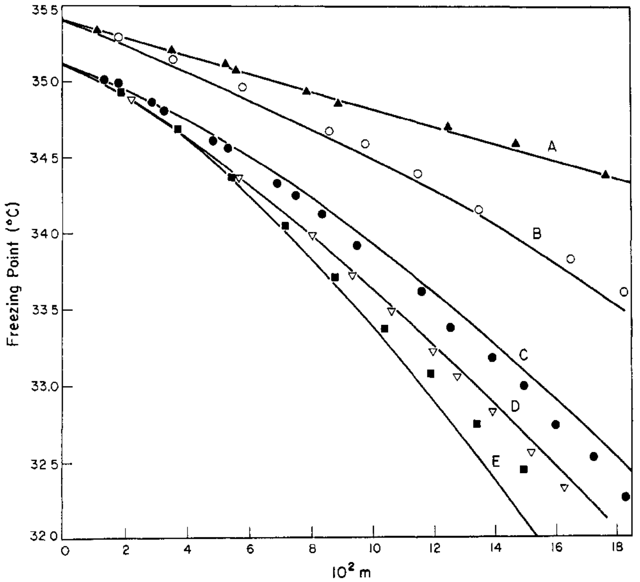

Figure 2.—Freezing points of solutions in $H_2S_2O_7$. Reference curves: (A) nonelectrolyte, $a = 0$, $b = 1$, $\nu = 1$; displaced vertically by 0.3°; (B) $0.6X^+ + 0.6HS_3O_{10}^- + Y + 1.2H_2SO_4$, $a = 0.6$, $b = 1$, $c = 1.2$, $\nu = 2.2$; displaced vertically by 0.3°; (C) $X^+ + HS_3O_{10}^- + 2.5H_2SO_4 - 0.5Y$, $a = 1$, $b = 0.5$, $c = 2.5$, $\nu = 2.5$; (D) $X^+ + HS_3O_{10}^- + Y + 2H_2SO_4$, $a = 1$, $b = 1$, $c = 2$, $\nu = 3$; (E) $1.5X^+ + 1.5HS_3O_{10}^- + 0.75Y + 3.75H_2SO_4$, $a = 1.5$, $b = 0.75$, $c = 3.75$, $\nu = 3.75$. Solutes: △, SO_2; ○, ICl; ●, I_2; ▽, ICl_3; ■, KI.

TABLE III

SUMMARY OF ν, γ, AND c VALUES

	a	b	ν $(2a + b)$	γ	c Conductivity	Cryoscopy	Titration
I_2	1.0	0.5	2.5	0.9	2.5	2.5	2.6
KI	1.5	0.75	3.75	1.5	3.75	3.75	...
ICl	0.6	1	2.2	0.6	1.2	1.2	...
ICl_3	1	1	3	1	2	2	2.1
SO_2	1	0	1	0	0	0	...

The conductivities of solutions of electrolytes in $H_2S_2O_7$ are determined primarily by the concentration of the $HS_3O_{10}^-$ ion and hence γ, the number of moles of $HS_3O_{10}^-$ ion produced by 1 mol of solute, can be obtained by comparison with the conductivity curve of a standard electrolyte, *e.g.*, nitromethane for which $\gamma = a = 1$ and $c = 1$. The experimental results are compared with such standard curves in Figure 3. Values of a and c determined in this way are listed in Table III.

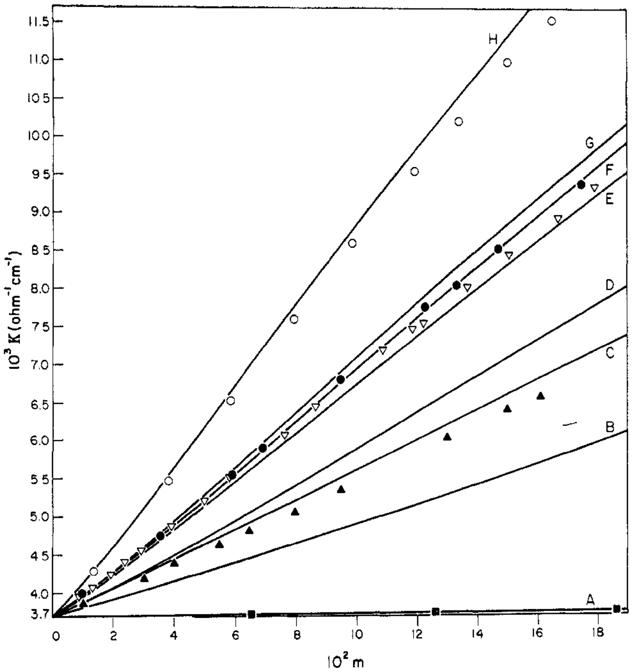

Figure 3.—Conductivities of solutions in $H_2S_2O_7$. Reference curves: (A) SO_2; (B) $0.4HS_3O_{10}^- + 0.8H_2SO_4$; (C) $0.6HS_3O_{10}^- + 1.2H_2SO_4$; (D) $0.66HS_3O_{10}^- + 1.66H_2SO_4$; (E) $0.9HS_3O_{10}^- + 2.25H_2SO_4$; (F) $HS_3O_{10}^- + 2.0H_2SO_4$; (G) $HS_3O_{10}^- + 2.5H_2SO_4$; (H) $1.5HS_3O_{10}^- + 3.75H_2SO_4$. Solutes: ■, SO_2; ▲, ICl; ▽, I_2; ●, ICl_3; ○, KI.

Sulfur Dioxide.—Iodine and potassium iodide are oxidized in oleum and sulfur dioxide is the reduction product. It is accordingly necessary to know its behavior as a solute in $H_2S_2O_7$. Whereas sulfur dioxide has an extremely small solubility in sulfuric acid[5] and, when produced as a reaction product, contributes almost nothing to the freezing point depression and conductivity, it is quite soluble in disulfuric acid.[5] The freezing point and conductivity measurements show that sulfur dioxide behaves as a nonelectrolyte in solution in disulfuric acid, *i.e.*, $\nu = 1$ and $\gamma = 0$. The absorption spectrum is essentially identical with that of a dilute solution in sulfuric acid and very similar to the spectrum of sulfur dioxide in the liquid and gaseous states.[6] Thus sulfur dioxide affects the freezing point but not the conductivity of disulfuric acid and this must be allowed for in interpreting measurements on solutes that are oxidized and thus produce sulfur dioxide.

Iodine.—The absorption spectra measurements (Figure 1) showed that the formation of I_2^+ from iodine is about 75% complete in 45% oleum, *i.e.*, $H_2S_2O_7$, at room temperature. Since the I_3^+ peak at 305 mμ is

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(5) F. D. Miles and T. Carson, *J. Chem. Soc.*, 786 (1946).

(6) V. Gold and F. L. Tye, *ibid.*, 2932 (1950).

also present in the spectrum, the remaining iodine is present as I_3^+. Iodine is presumably oxidized to I_2^+ according to the equation

$$2I_2 + 6H_2S_2O_7 \longrightarrow 2I_2^+ + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

while I_3^+ would be formed according to the equation

$$3I_2 + 6H_2S_2O_7 \longrightarrow 2I_3^+ + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

The conductivity curve for iodine is close to that expected for the formation of I_2^+ (*i.e.*, $\gamma = 1$, $c = 2.5$) and is not in agreement with the calculated curve D for the quantitative formation of I_3^+ ($\gamma = 0.66$, $c = 1.66$). In fact the conductivities are slightly lower than expected for the quantitative formation of I_2^+ (curve G) and lie closer to the calculated curve E for $\gamma = 0.9$. This difference is probably significant and thus we conclude that oxidation of iodine to I_2^+ is probably incomplete. If, as suggested by the absorption spectra measurements, 75% of the iodine is converted to I_2^+ and 25% to I_3^+, the expected γ value is $0.75 + 0.17 = 0.92$ which is equal to the observed value within the experimental error. The freezing point results fit the calculated curve C for the quantitative formation of I_2^+ (*i.e.*, $a = 1$, $b = 0.5$, and $c = 2.5$) quite well although the observed freezing points are a little lower than the predicted curve. The reason for this is not clear although it should be pointed out that different metal sulfates give significantly different freezing point depressions.[3] Large cations such as Cs^+ give the largest depressions and these agree well with those obtained for various nitro compounds, *e.g.*, nitromethane which we have chosen as a convenient standard.[4] However all of these solutes give slightly smaller freezing point depressions than calculated theoretically from the cryoscopic constant and the self-dissociation constants for the solvent.[3] It seems not unreasonable that the large I_2^+ cation might be closer to ideal in its behavior than either Cs^+ or $CH_3NO_2H^+$ which would account for the freezing point depressions being slightly greater than calculated on the basis of nitromethane as a standard solute. We note also that there is no evidence from the cryoscopic results of incomplete oxidation which would give a smaller freezing point depression than for the formation of I_2^+. However this may have been obscured by a difference between the cryoscopic behavior of I_2^+ and that of the standard $CH_3NO_2H^+$. It is also possible that the oxidation was somewhat more complete in the freezing point experiments since these were made at 35–40° (the higher temperature being used to keep the solution liquid when further solute was added between measurements) while the conductivity measurements were made on the supercooled solutions at 25°.

The amount of sulfuric acid produced in the ionization of a solute can be determined by cryoscopic titration with sulfur trioxide.[4] In the titration of a 0.19 *m* solution of I_2 a value of $c = 2.6$ was obtained which is in good agreement with the expected value of 2.5.

Potassium Iodide.—As disulfuric acid oxidizes iodine to I_2^+, we expect potassium iodide also to be oxidized according to the equation

$$4KI + 18H_2S_2O_7 \longrightarrow 2I_2^+ + 4K^+ + 6HS_3O_{10}^- + 15H_2SO_4 + 3SO_2$$

i.e., $a = 1.5$, $b = 0.75$, and $c = 3.75$. We see that the experimental conductivities lie close to, but slightly below, the reference curve H for $a = 1.5$ and $c = 3.75$. Again this may be attributed to incomplete oxidation giving some I_3^+ rather than I_2^+. The freezing point results agree quite well with the reference curve E calculated for an ionization according to the above equation at concentrations up to 0.1 *m* but deviate from this curve at higher concentrations. The reason for this unexpected behavior is not clear.

Iodine Monochloride.—Absorption spectra measurements showed that 1 mol of ICl gives 0.43 mol of I_2^+ in 85% oleum. It appears that the unipositive oxidation state is not stable in oleum and that it disproportionates to I_2^+ and a higher oxidation state. In fluorosulfuric acid and sulfuric acid it has been shown that the +3 oxidation state is stable in the form of $I(SO_3F)_3$ and $I(SO_4H)_3$.[1,7] Presumably in 45% oleum iodine(III) exists as $I(SO_4H)_3$ or $I(S_2O_7H)_3$ or some intermediate form. For simplicity we will assume the formation of $I(SO_4H)_3$ and we can then write the following equation for the ionization of ICl

$$5ICl + 9H_2S_2O_7 \longrightarrow 2I_2^+ + I(SO_4H)_3 + 2HS_3O_{10}^- + 5HSO_3Cl + 4H_2SO_4$$

Thus 0.4 mol of I_2^+ is produced per mole of ICl in agreement with the absorption spectra results. This equation gives $\gamma = 0.4$ (curve B) but the conductivity results give a value closer to 0.6 (curve C). However, $I(SO_3F)_3$ has been shown to have amphoteric properties and to ionize as a base in solution in fluorosulfuric acid according to $I(SO_3F)_3 \rightarrow I(SO_3F)_2^+ + SO_3F^-$. It is therefore not unreasonable to suppose that $I(SO_4H)_3$ ionizes as a base in the highly acidic medium $H_2S_2O_7$. If its ionization is complete, the over-all ionization of ICl in $H_2S_2O_7$ then becomes

$$5ICl + 11H_2S_2O_7 = 2I_2^+ + I(SO_4H)_2^+ + 3HS_3O_{10}^- + 5HSO_3Cl + 6H_2SO_4$$

This equation is confirmed by the fact that the freezing point results are in good agreement with the reference curve B calculated for $a = 0.6$, $b = 1$, and $c = 1.2$. It has previously been shown that HSO_3Cl behaves as a nonelectrolyte in $H_2S_2O_7$.[3]

Iodine Trichloride.—This solute gives conductivity and freezing point curves essentially identical with those of KCl which has been shown to ionize according to

$$KCl + 3H_2S_2O_7 = K^+ + HS_3O_{10}^- + HSO_3Cl + 2H_2SO_4$$

i.e., $a = 1$, $b = 1$, and $c = 2$. Accordingly, we conclude that iodine trichloride ionizes to give the ICl_2^+ ion as in

$$ICl_3 + 3H_2S_2O_7 = ICl_2^+ + HS_3O_{10}^- + HSO_3Cl + 2H_2SO_4$$

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(7) R. A. Garrett, R. J. Gillespie, and J. B. Senior, *Inorg. Chem.*, **4**, 563 (1965).

The value of $c = 2$ was confirmed by a cryoscopic titration of a 0.22 m solution of ICl_3 with SO_3 which gave a value of $c = 2.1$. It has been shown previously that the adducts $ICl_3 \cdot SbCl_5$ and $ICl_3 \cdot AlCl_3$ have the structures $ICl_2^+,SbCl_6^-$ and $ICl_2^+,AlCl_4^-$, respectively, with the cation and anion rather strongly linked together by chlorine bridges.[8] The existence of this stable cation of trivalent iodine provides some further support for the $I(SO_4H)_2^+$ ion proposed above.

Table IV

Conductivities of Solutions in 65% Oleum

10^2m	$10^4\kappa$, ohm^{-1} cm^{-1}	10^2m	$10^4\kappa$, ohm^{-1} cm^{-1}	10^2m	$10^4\kappa$, ohm^{-1} cm^{-1}
KCl		Na_2SO_4		I_2	
1.48	5.6055	2.96	15.7226	1.65	6.2468
3.26	10.6348	4.60	24.0424	2.28	8.1044
4.25	13.7246	6.02	29.8944	3.35	11.6180
6.27	19.0135	7.65	35.5648	4.18	13.7216
7.76	23.0868	9.03	39.1186	5.52	18.0674
9.94	28.8644	10.31	42.2407	6.58	21.0218
12.44	34.6220	11.60	46.4023	8.08	25.0396
14.84	38.9509	13.01	47.5908	9.32	28.7624
17.25	43.0265	14.57	49.8827	11.39	33.9986
		15.98	52.0515	12.99	37.9212
K_2SO_4				14.75	42.1836
0.21	2.6630	ICl		16.55	45.0782
1.32	8.0228	0.84	3.0521	18.31	49.6480
2.60	14.0670	1.81	4.6267		
3.62	19.0628	3.38	7.0362	KI	
5.03	27.2381	5.68	10.6285	0.99	6.0086
6.52	33.2615	8.59	15.5291	2.69	13.1830
7.22	35.74065	11.02	19.6277	4.49	20.5840
10.86	46.1455	13.65	23.8909	6.34	27.5019
13.92	52.2256	15.69	26.9526	8.16	33.5908
15.30	54.7506	18.53	31.3030	9.97	39.0368
				11.67	44.0289
		I_2		13.44	48.6259
Na_2SO_4		0.37	2.5962	15.24	51.7038
0.86	6.4282	0.82	3.8914	17.01	57.1770
2.03	11.2885	1.06	4.5283	18.80	60.7964

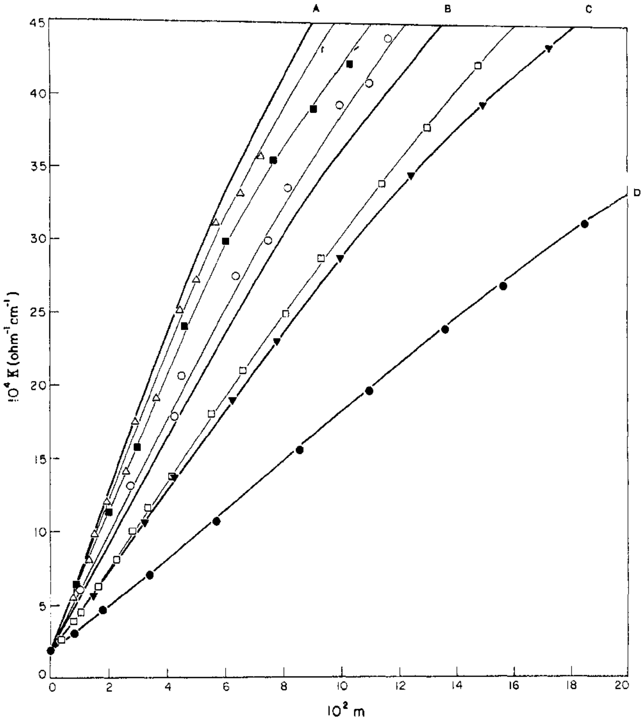

Figure 4.—Conductivities of solutions in 65% oleum. Reference curves: (A) $\gamma = 2$; (B) $\gamma = 1.5$; (C) $\gamma = 1.0$; (D) $\gamma = 0.6$. Solutes: △, K_2SO_4; ■, Na_2SO_4; ○, KI; □, I_2; ▼, KCl; ●, ICl.

Solutions in 65% Oleum.—The results of the conductivity measurements in 65% oleum are given in Table IV and Figure 4. The exact constitution of 65% oleum is uncertain. Its composition is between that of $H_2S_3O_{10}$ and $H_2S_4O_{13}$ and it appears to be an equilibrium mixture containing free SO_3 and other polysulfuric acids.[9] Accordingly the nature of the anion that is formed on the addition of a base to this solvent is also uncertain. It certainly cannot be $HS_2O_7^-$ as proposed previously by Arotsky and Symons[10] as even in 45% oleum the anion appears to be mainly $HS_3O_{10}^-$.[3] It seems probable that in 65% oleum the predominating anion is $HS_4O_{13}^-$, but there are probably relatively large amounts of other polysulfate anions, such as $HS_3O_{10}^-$ and $HS_5O_{16}^-$, in equilibrium. Fortunately a knowledge of the exact nature of the anion is not necessary in order to be able to obtain information from the conductometric results since the equilibrium mixture of the anions and their average conductivity is determined essentially by the composition of the solvent and will be hardly affected by the low concentrations of added solutes. For the purposes of writing equations we will assume that the anion is $HS_4O_{13}^-$. We found the conductivity of 65.0% oleum to be 1.88×10^{-4} ohm^{-1} cm^{-1} and all the conductivity measurements were made in a solvent having this initial conductivity. This conductivity arises from some ionization or ionizations in the solvent, *e.g.*

$$H_2S_4O_{13} + H_2S_2O_7 \rightleftarrows H_3S_2O_7^+ + HS_4O_{13}^-$$

These ionizations would be repressed by the $HS_4O_{13}^-$ ion produced by solutes. Fortunately our lack of knowledge of the nature and extent of these ionizations need not be a serious problem as useful information can be obtained by comparing the conductivity curves with those of a standard reference electrolyte. For the purposes of interpreting the present results we have chosen KCl as the reference electrolyte. As it has been established that it ionizes in $H_2S_2O_7$ according to

$$KCl + 3H_2S_2O_7 \longrightarrow K^+ + HS_3O_{10}^- + HSO_3Cl + 2H_2SO_4$$

It seems reasonable to suppose that it ionizes to give 1 mol of the conducting anion in 65% oleum. Assuming that this anion is $HS_4O_{13}^-$, we may write the equation

$$KCl + 2H_2S_4O_{13} \longrightarrow K^+ + HS_4O_{13}^- + HSO_3Cl + H_2S_3O_{10}$$

i.e., $\gamma = 1$. Reference curves for other values of γ, *e.g.*, $\gamma = 2$ and $\gamma = 1.5$, are easily constructed from the KCl curve and are shown in Figure 4. We see that K_2SO_4 and Na_2SO_4 give conductivity curves B and C close to that expected for $\gamma = 2$ (curve A). Sodium

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[8] C. G. Vonk and E. H. Wiebenga, *Rec. Trav. Chim.*, **78**, 913 (1959).

[9] R. J. Gillespie and E. A. Robinson in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press, New York, N. Y., 1965, p 162.

[10] J. Arotsky and M. C. R. Symons, *Trans. Faraday Soc.*, **56**, 1426 (1960).

sulfate shows a somewhat bigger deviation from the expected curve than potassium sulfate and the difference between the two curves is apparent even at quite low concentrations. This is in contrast to the behavior of different metal sulfates in disulfuric acid which have identical conductivities up to at least 0.08 *m*. This is consistent with the fact that the molal conductivities of metal sulfates in $H_2S_2O_7$, $\lambda_m = 10^3\kappa/m$, are of the order of 60 whereas Na_2SO_4 and K_2SO_4 in 65% oleum have $\lambda_m \simeq 3$. A considerable proportion of the conductivity of a metal sulfate in $H_2S_2O_7$ is proton-transfer conduction by the anions $HS_3O_{10}^-$ and $HS_2O_7^-$ but the much lower molal conductivity in 65% oleum strongly suggests that proton-transfer conduction is less effective in this medium and that cations therefore make a much larger contribution to the total conductance than they do in $H_2S_2O_7$. Consequently, differences between different cations are not surprising and the interpretation of conductivity results in terms of the number of conducting anions produced by a given solute must be correspondingly less certain. By comparison with the conductivity of KCl we see that the iodine compounds studied have the following γ values: I_2, 1; KI, 1.5, ICl, 0.6. These are the same values as were obtained for these solutes in $H_2S_2O_7$ and strongly suggest that they ionize according to exactly analogous equations in which $H_2S_2O_7$ is replaced by $H_2S_4O_{13}$, etc. The conductivities of I_2 and KI solutions are in fact slightly greater than the reference curves and do not give any indication of the incomplete oxidation found in $H_2S_2O_7$ where the conductivities were slightly less than the reference curves. This is consistent with the absorption spectra measurements which showed essentially complete oxidation in 65% oleum. The fact that the conductivities in 65% oleum are slightly higher than the reference curves can perhaps be attributed to the fact that the I_2^+ cation is much larger than the K^+ ion. Conductivities of solutions were found to increase in $H_2S_2O_7$ with increasing cation size and from the single comparison of Na^+ and K^+ in 65% oleum this also appears to be the case in this solvent. Thus the conductivity measurements in 65% oleum provide further confirmation of the results obtained by cryoscopy and conductivity in $H_2S_2O_7$.

Experimental Section

The methods used for preparing the solvent and for the cryoscopic and conductometric measurements have been described previously.[3] All solutes were carefully dried and stored in vacuum desiccators over phosphoric oxide. The absorption spectra measurements were made as described in part IV.[1]

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Contribution from the Department of Chemistry,
Northern Illinois University, DeKalb, Illinois 60115

Bromide Ion Replacement in the *trans*-Dibromotetracyanoplatinate(IV) and *trans*-Dibromotetranitroplatinate(IV) Ions by Chloride Ion

By W. Roy Mason

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The first bromide replacement in the *trans*-$PtL_4Br_2^{2-}$ ($L^- = CN^-$ or NO_2^-) ions by chloride is catalyzed by PtL_4^{2-}. The kinetics of these reactions are described by a third-order rate law with rate dependence on chloride, platinum(IV) reactant, and PtL_4^{2-}. The third-order rate constants at 25.0° and $\mu = 1.01$ *M* are 72 and 0.76 M^{-2} sec^{-1} for $L^- = CN^-$ and NO_2^-, respectively. Activation parameters are reported for both reactions. The results are interpreted in terms of a bridged inner-sphere redox mechanism. The rate law for the reaction of *trans*-$Pt(CN)_4Br_2^{2-}$ with chloride ion also contained a second-order term independent of chloride ion concentration. This result is interpreted in terms of solvent participation.

Introduction

A variety of ligand replacement reactions of platinum(IV) complexes of the type in eq 1 (L = ammonia or

$$trans\text{-}PtL_4XZ^{2+} + Y^- \longrightarrow trans\text{-}PtL_4YZ^{2+} + X^- \quad (1)$$

L_2 = ethylenediamine; X, Y = halide or pseudohalide ligands; and Z = halide or thiocyanate ligands) have been found[1-6] to be catalyzed by square-planar platinum(II) complexes of the type PtL_4^{2+}. A mechanism for these catalyzed reactions was first postulated by Basolo, Pearson, and coworkers[1] and now seems well established. This mechanism is given in general terms for eq 1 in the eq 2–5. The ligands Y, Z, and X are

$$PtL_4^{2+} + Y^- \xrightleftharpoons{\text{fast}} PtL_4Y^+ \quad (2)$$

$$XPtL_4Z^{2+} + PtL_4Y^+ \rightleftharpoons XPtL_4ZPtL_4Y^{3+} \quad (3)$$

$$XPtL_4ZPtL_4Y^{3+} \rightleftharpoons XPtL_4^+ + ZPtL_4Y^{2+} \quad (4)$$

$$XPtL_4^+ \rightleftharpoons X^- + PtL_4^{2+} \quad (5)$$

designated as the entering, bridging, and leaving ligands, respectively, while L is an inert ligand lying in a plane about the middle of each platinum complex.

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