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Cations and Oxycations of Iodine. IV. Formation of the Cations I_2^+, I_3^+, and I_5^+ in Fluorosulfuric Acid

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Cryoscopic, conductometric, spectroscopic, and magnetic susceptibility measurements have been used to show that if iodine is oxidized with $S_2O_6F_2$ in fluorosulfuric acid, the ions I_2^+, I_3^+, and I_5^+ can be obtained. No evidence was obtained for the existence of I^+ as a stable species. The iodine cation I_2^+ has an absorption spectrum that gives rise to the blue color that has previously been attributed to I^+. I_2^+ is paramagnetic and has an effective magnetic moment of 2.0 BM.

Introduction

In part III of this series it was shown that in solution in sulfuric acid the ions I_5^+ and I_3^+ can be obtained by oxidizing iodine with iodic acid.[1] In a solution having the composition $I_2/HIO_3 = 2$ which corresponds to the +1 oxidation state for iodine, no evidence could be obtained for I^+ as a stable cation, and it was concluded that it was largely, if not completely, disproportionated into I_3^+ and IO^+. This work did not, however, solve the problem of the nature of the blue species having characteristic absorption bands at 640, 490, and 410 mμ, which is obtained by dissolving iodine or iodine monochloride in 65% oleum,[2] or iodine in IF_5 in the presence of a trace of water,[3] and which has been supposed to be I^+. In the present work, iodine was oxidized with various amounts of $S_2O_6F_2$ in solution in fluorosulfuric acid, and cryoscopic, conductometric, spectroscopic, and magnetic susceptibility measurements were made on the solutions, in order to determine the nature of the cationic iodine species formed and, in particular, to attempt to obtain further information on the supposed +1 oxidation state. The formation of iodine trifluorosulfate with excess $S_2O_6F_2$ has been discussed in a previous paper.[4]

Results and Discussion

3:1 $I_2/S_2O_6F_2$ Solutions.—The freezing points of these solutions in fluorosulfuric acid are given in Table I;[5] they decrease linearly with increasing concentration and the slope of a plot of freezing-point depression against concentration gave a value of 1.26 for ν, the number of moles of particles formed in solution by 1 mole of iodine. The conductivities of the solutions are given in Table II. By comparison with the conductivities of potassium fluorosulfate solutions at the same temperature,[6,7] values of γ, the number of moles

TABLE I

FREEZING POINTS

$10^2 m_{I_2}$	Fp, °C	$10^2 m_{I_2}$	Fp, °C
5:1 $I_2/S_2O_6F_2$		3:1 $I_2/S_2O_6F_2$	
0.00	−88.998	0.00	−89.003
0.76	−89.026	0.65	−89.029
1.89	−89.058	1.75	−89.083
2.85	−89.082	3.16	−89.148
4.04	−89.137	4.32	−89.200
5.05	−89.165	5.16	−89.245
6.24	−89.204	5.98	−89.284
1:1 $I_2/S_2O_6F_2$		2:1 $I_2/S_2O_6F_2$	
0.00	−88.997	0.00	−89.990
0.88	−89.040	0.89	−89.041
1.31	−89.058	1.92	−89.104
1.91	−89.086	2.78	−89.154
1.58	−89.122	3.74	−89.220
3.23	−89.152	4.89	−89.280
3.95	−89.183		

TABLE II

CONDUCTIVITIES

$10^2 m_{I_2}$	$10^4\kappa$, ohm^{-1} cm^{-1}	$10^2 m_{I_2}$	$10^4\kappa$, ohm^{-1} cm^{-1}
3:1 $I_2/S_2O_6F_2$ (25°)		3:1 $I_2/S_2O_6F_2$ (−78.52°)	
0.00	1.26	0.00	0.0296
0.85	15.27	1.27	2.366
1.95	33.01	1.93	3.555
2.91	47.82	2.61	4.741
3.20	52.37	3.31	5.964
4.19	67.76	3.94	7.063
4.90	78.50	4.56	8.114
5.48	87.24		
6.07	95.94		
		1:1 $I_2/S_2O_6F_2$ (25°)	
2:1 $I_2/S_2O_6F_2$ (25°)		0.00	1.44
0.00	17.34	0.32	7.27
2.22	65.36	0.56	11.76
4.53	112.5	0.97	19.06
6.47	149.0	1.27	24.10
8.53	185.5	1.65	30.03
9.95	209.3	2.27	39.15
11.75	237.6	2.93	48.19
14.15	273.8	3.54	55.99
16.24	303.0	4.17	63.62

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

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

(3) E. Aynsley, N. N. Greenwood, and D. H. W. Wharmby, *ibid.*, 5369 (1963).

(4) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1236 (1966).

(5) The freezing-point curves were all found to be linear, but on extrapolation to zero concentration they did not pass through the freezing point of the solvent. Similar behavior has previously been observed for simple metal fluorosulfates, and it has been attributed to the reaction of the fluorosulfate ion with the very small excess of sulfur trioxide which it has been shown is always present, even in the most carefully purified acid: $SO_3F^- + SO_3 \rightarrow S_2O_6F^-$. Allowance has been made for this by calculating the freezing-point depressions, not from the observed freezing point of the solvent, but from a corrected freezing point obtained by extrapolating the linear freezing-point curve to zero concentration. The difference between the observed and corrected freezing points for the solvent was generally less than 0.01°: R. J. Gillespie, J. B. Milne, and R. C. Thompson, *Inorg. Chem.*, **5**, 468 (1966).

(6) R. J. Gillespie, J. B. Milne, and J. B. Senior, *ibid.*, **5**, 1233 (1966).

TABLE III

γ VALUES AND "I^+" AND I_2^+ CONCENTRATIONS

2:1 $I_2/S_2O_6F_2$			1:1 $I_2/S_2O_6F_2$			
m_{I_2}	γ	$m_{I_2^+}$	m_{I_2}	γ	m_{I^+}	$m_{I_2^+}$
0.01	0.93	0.009	0.01	0.77	0.0077	0.0079
0.02	0.90	0.015	0.02	0.70	0.0140	0.0134
0.06	0.88	0.048	0.03	0.65	0.0195	0.0184
0.10	0.87	0.072	0.04	0.62	0.0248	0.0219
0.14	0.85	0.091	0.05	0.60	0.0300	0.0267
0.18	0.83	0.101				

3:1 $I_2/S_2O_6F_2$			
25°		−78.5°	
m_{I_2}	γ	m_{I_2}	γ
0.01	0.67	0.01	0.67
0.02	0.66	0.02	0.65
0.03	0.66	0.03	0.65
0.04	0.66	0.04	0.65
0.05	0.66		
0.06	0.66		

of fluorosulfate ion formed in solution per mole of iodine, were obtained; they are given in Table III. The mean values are $\gamma = 0.66$ at 25° and $\gamma = 0.65$ at −78.5°. These results are consistent with the reaction

$$3I_2 + S_2O_6F_2 \longrightarrow 2I_3^+ + 2SO_3F^-$$

for which we expect $\nu = 1.33$ and 0.67.[8] The spectrum of a 0.0168 *m* I_2–0.0056 *m* $S_2O_6F_2$ solution at 28° is shown in Figure 1. It is essentially the same as that given previously by Symons, *et al.*,[9] for solutions obtained by oxidizing iodine with iodic acid in sulfuric acid and attributed by them to I_3^+ and by Aubke and Cady[10] for solutions of the compound I_3SO_3F in HSO_3F and H_2SO_4. The absorptions at 305 and 470 mμ may be regarded as characteristic of I_3^+ at 28°. The third peak at 210 mμ may also be due to I_3^+, but this is less certain. The molar extinction coefficient of I_3^+ at 305 mμ was found to be 5200.[11] At −85° the spectrum is essentially unchanged, the long-wavelength peak shifting slightly to 460 mμ.

5:1 $I_2/S_2O_6F_2$ Solutions.—It was found previously that iodine can be dissolved in a solution of I_3^+ in sulfuric acid without causing any appreciable change in either the conductivity or the freezing point of the solutions.[1] Hence, it was concluded that I_5^+ is formed. A shoulder that appears at 330 mμ in the spectrum when iodine is added to a solution of I_3^+ in sulfuric acid was attributed by Symons, *et al.*,[9] to I_5^+. Freezing points of 5:1 $I_2/S_2O_6F_2$ solutions are given in Table I. They vary linearly with concentration, and from the slope of the freezing point–concentration curve a value of $\nu = 0.82$ was obtained. This is in good agreement with the value of 0.80 expected for the formation of I_5^+ according to the equation

$$5I_2 + S_2O_6F_2 \longrightarrow 2I_5 + 2SO_3F^-$$

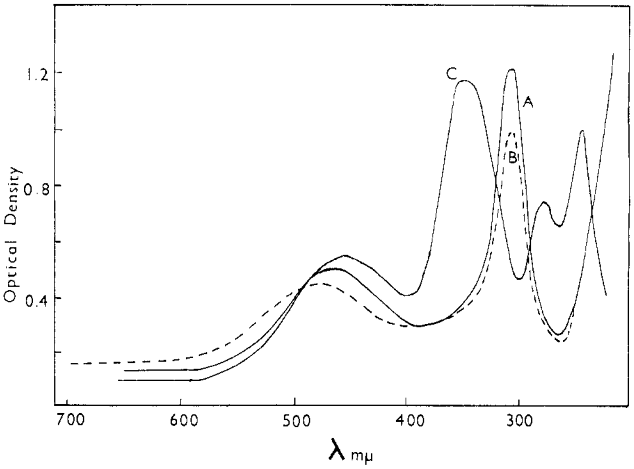

Figure 1.—Absorption spectra of 3:1 and 5:1 $I_2/S_2O_6F_2$ solutions: A, 3:1 $I_2/S_2O_6F_2$ (−85°), $m_{I_2} = 0.0168$, path length = 0.01 cm; B, 3:1 $I_2/S_2O_6F_2$ (28°), $m_{I_2} = 0.0168$, path length = 0.01 cm; C, 5:1 $I_2/S_2O_6F_2$ (−85°), $m_{I_2} = 0.0093$, path length = 0.03 cm.

The conductivity of these solutions at 25° was found to increase slowly with time. It appears that I_5^+ or I_2 formed in the equilibrium

$$I_5^+ \rightleftharpoons I_2 + I_3^+$$

is slowly oxidized at 25°. The absorption spectrum at −85° is shown in Figure 1: there are peaks at 450, 345, 270, and 240 mμ. The peak at 450 mμ cannot be due to I_3^+ since the 305-mμ peak of I_3^+ is missing. These four bands must, therefore, be due to I_5^+ although a small amount of I_3^+ could be present, the 305-mμ peak of I_3^+ being masked by the strong band at 345 mμ.

1:1 and 2:1 $I_2/S_2O_6F_2$ Solutions.—The absorption spectra of a 1:1 $I_2/S_2O_6F_2$ solution at 28° are shown in Figure 2. The three peaks at 640, 490, and 410 mμ have been attributed by previous workers to the species I^+;[2,3] the intensities of all three peaks vary in the same manner with iodine concentration confirming that they are indeed due to the same species. If this is I^+, then we have

$$I_2 + S_2O_6F_2 \longrightarrow 2I^+ + 2SO_3F^- \qquad (1)$$

for which we expect $\nu = 4$ and $\gamma = 2$. The freezing points of the 1:1 solutions are given in Table I. The freezing point appears to vary linearly with concentrations over the small concentration range studied and the slope gives $\nu = 1.21$. The conductivities of the solutions are given in Table II and Figure 3, and γ values at interpolated concentrations are given in Table III. Both ν and γ are much smaller than expected for the formation of I^+. Equilibrium with un-ionized ISO_3F would give smaller γ values (eq 2)

$$I^+ + SO_3F^- \rightleftharpoons ISO_3F \qquad (2)$$

but could not give $\nu < 2$. Moreover the I^+ concentrations obtained from the conductivity results, assuming equilibrium 2, $m_{I^+} = \gamma m_{I_2}$ (Table III), do not agree with values determined, as described later, from the

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[7] J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, **3**, 1149 (1964).

[8] Throughout this paper ν and γ are defined as the total number of moles of solute particles and fluorosulfate ions, respectively, formed from 1 mole of iodine.

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

[10] F. Aubke and G. H. Cady, *Inorg. Chem.*, **4**, 269 (1965).

[11] Concentrations throughout this paper are in molal units as the solutions were made up by weight, but the extinction coefficients are quoted in the customary molar units. They were calculated assuming that the densities of the solutions are the same as that of the solvent, *i.e.*, $\rho_{25^\circ} = 1.726$.

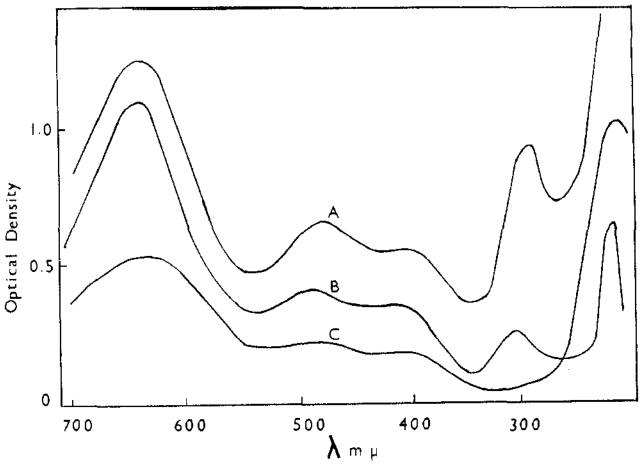

Figure 2.—Absorption spectra of 1:1 and 2:1 $I_2/S_2O_6F_2$ solutions: A, 2:1 $I_2/S_2O_6F_2$, $m_{I_2} = 0.164$, path length = 0.005 cm; B, 2:1 $I_2/S_2O_6F_2$, $m_{I_2} = 0.372$, path length = 0.01 cm; C, 1:1 $I_2/S_2O_6F_2$, $m_{I_2} = 0.0186$, path length = 0.01 cm.

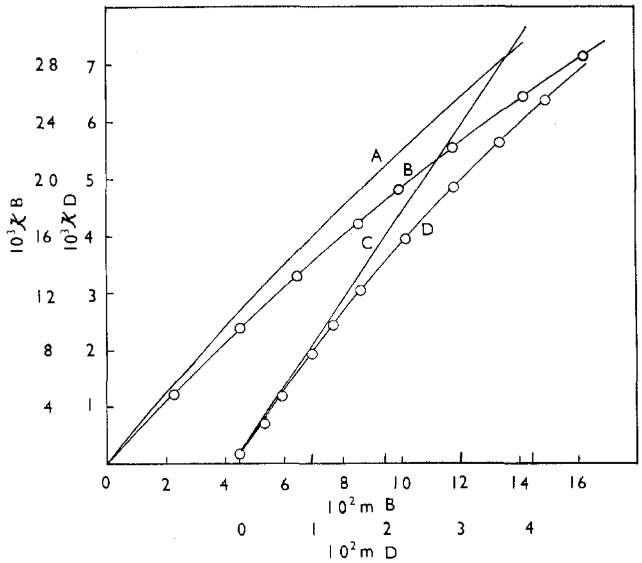

Figure 3.—Conductivities of 1:1 and 2:1 $I_2/S_2O_6F_2$ solutions at 25°: A, curve for $\gamma = 1.0$; B, experimental curve for 2:1 $I_2/S_2O_6F_2$; C, curve for $\gamma = 0.8$; D, experimental curve for 1:1 $I_2/S_2O_6F_2$.

absorption spectra and magnetic susceptibilities (Figure 4).

It was suggested in part III that if the +1 oxidation state exists in solution in sulfuric acid, it must be extensively disproportionated to the $+^1/_3$ and +3 oxidation states.[1] For the fluorosulfuric acid solvent system the corresponding equation would be

$$2I_2 + 2S_2O_6F_2 \longrightarrow 4I^+ + 4SO_3F^- \rightleftharpoons I_3^+ + SO_3F^- + I(SO_3F)_3$$

However, in order to account for the observed γ values, disproportionation would have to be very extensive and the characteristic peaks of I_3^+ should appear in the spectrum, but they are not observed. It is clear that our results are not consistent with the formation, in fluorosulfuric acid solution, of I^+ either quantitatively or even extensively disproportionated to I_3^+ and $I(SO_3F)_3$.

On addition of iodine to a solution having the composition 1:1 $I_2/S_2O_6F_2$ to give the composition 2:1 $I_2/S_2O_6F_2$ it was found that the three peaks at 640, 490, and 410 mμ in the absorption spectrum increase in intensity and at the composition of $2I_2/S_2O_6F_2$ they are approximately twice as intense (Figure 2.). In addition, a small peak appears at 300 mμ which can be assigned to I_3^+. Also, the peak at 490 mμ is increased in intensity with respect to that at 410 mμ, probably because of the underlying I_3^+ peak at 470 mμ. In another experiment in which $S_2O_6F_2$ was added to a 2:1 $I_2/S_2O_6F_2$ solution, keeping the concentration of iodine constant until the composition 1:1 $I_2/S_2O_6F_2$ was reached, the intensity of the peaks at 640, 490, and 410 mμ decreased slightly, while the small peak attributed above to I_3^+ disappeared on the first addition of $S_2O_6F_2$ (Table IV). Clearly, the species responsible for the peaks at 640, 490, and 410 mμ is already present in the 2:1 $I_2/S_2O_6F_2$ solution and its amount is not increased, but rather it appears to be slightly decreased by further addition of $S_2O_6F_2$. This suggests that the species is I_2^+ rather than I^+ and that it is formed according to the equation

$$2I_2 + S_2O_6F_2 \longrightarrow 2I_2^+ + 2SO_3F^- \qquad (3)$$

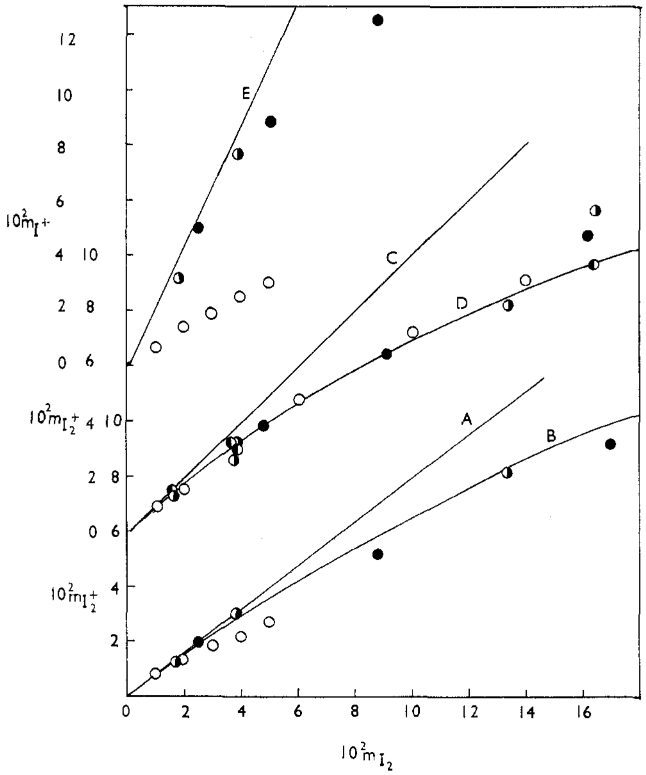

Figure 4.—I_2^+ and "I^+" concentrations from conductivity, absorption spectra, and magnetic susceptibility for 1:1 and 2:1 $I_2/S_2O_6F_2$ solutions. A: Expected curve for 1:1 solutions in absence of disproportionation. B: Calculated for $K_5 = 2.0$. Experimental results: ○, conductivity; ●, magnetic susceptibility; ◑, optical density of 640-mμ peak. C: Expected curve for 2:1 solutions in absence of disproportionation. D: Calculated for $K_5 = 2.0$. Experimental results: ○, conductivity; ●, magnetic susceptibility; ◑, optical density of 640-mμ peak; ◐, optical density of 290-mμ peak. E: Expected curve for quantitative formation of "I^+." Experimental results: ○, conductivity; ●, magnetic susceptibility; ◑, optical density of 640-mμ peak.

TABLE IV

OPTICAL DENSITY OF I_2^+ PEAKS IN I_2–$S_2O_6F_2$ SOLUTIONS OF VARYING COMPOSITION[a]

Peak, mμ	$I_2/S_2O_6F_2$ composition			
	2.0:1	1.6:1	1.3:1	1.0:1
640	1.42	1.46	1.42	1.33
490	0.50	0.46	0.46	0.41
410	0.48	0.46	0.46	0.43

[a] $m_{I_2} = 0.0388$; path length = 0.01 cm.

for which we expect $\gamma = 1$. The observed γ values (Table III) decrease somewhat with increasing concentration and Figure 3 shows that they approach the expected value of $\gamma = 1$ at very low concentrations. The conductivity results for the 1:1 $I_2/S_2O_6F_2$ solution are also in agreement with the formation of I_2^+ since in this case the over-all equation will be

$$5I_2 + 5S_2O_6F_2 \longrightarrow 4I_2^+ + 4SO_3F^- + 2I(SO_3F)_3 \qquad (4)$$

for which we expect $\gamma = 0.8$. We seen in Table III and Figure 3 that the observed values increase with decreasing concentration and approach the expected value at low concentrations. In addition to the peaks at 640, 490, and 410 mμ, which we now attribute to I_2^+, the spectrum of the 1:1 $I_2/S_2O_6F_2$ solution contains a short-wavelength absorption at 210 mμ which can be attributed to $I(SO_3F)_3$ which has a strong absorption in this region.[4] On addition of $S_2O_6F_2$ to a 2:1 solution to give a 1:1 solution, the composition changes from $I_2^+ + SO_3F^-$ to ${}^4/_5I_2^+ + {}^4/_5SO_3F^- + {}^2/_5I(SO_3F_3)$. Thus, we expect a 20% decrease in the intensity of the characteristic peaks of I_2^+ and the experimental results in Table IV are in reasonable agreement with this prediction.

We have already noted the presence of a small peak at 305 mμ due to I_3^+ in the 2:1 $I_2/S_2O_6F_2$ solution, and Figure 2 shows that its intensity, relative to the other peaks, increases with increasing concentration. The I_3^+ presumably arises from disproportionation of I_2^+ and it is reasonable to assume that the other product is $I(SO_3F)_3$, *i.e.*

$$8I_2^+ + 8SO_3F^- \rightleftharpoons I(SO_3F)_3 + 5I_3^+ + 5SO_3F^- \qquad (5)$$

This equilibrium would account for the decrease in γ with increasing concentration. We have shown in a previous paper[4] that $I(SO_3F)_3$ is amphoteric, and, at the relative concentrations of $I(SO_3F)_3$ and SO_3F^- that are present in the solutions we are considering, the acidic behavior predominates. Hence the equilibrium

$$I(SO_3F)_3 + SO_3F^- \rightleftharpoons I(SO_3F)_4^- \qquad (6)$$

must also be taken into account. The equilibrium constant, $K = [I(SO_3F)_4^-]/[SO_3F^-][I(SO_3F)_3]$, has been found to have the value 10 mole^{-1} kg.[4] From eq 5 and 6 it may be shown that

$$m_{I_2^+} = \frac{40m_{I_2}(2\gamma - 1) - 5\gamma + 8}{40 + 3m_{I_2}\gamma} \qquad (7)$$

for the 2:1 solutions and

$$m_{I_2^+} = \frac{8\gamma(10m_{I_2} + 1) - 4\gamma}{40 + 3m_{I_2}\gamma} \qquad (8)$$

for the 1:1 solutions. Concentrations of I_2^+ obtained from the conductivity results by means of the above expressions are plotted against m_{I_2} in Figure 4.

From the optical density of the 640-mμ peak in the spectrum of a 1.9×10^{-4} *m* 1:1 $I_2/S_2O_6F_2$ solution in which disproportionation is expected to be negligible the molar extinction coefficient for I_2^+, $\epsilon[I_2^+(640)]$, was calculated to be 2560.[11] Using this value, concentrations of I_2^+ in other solutions were calculated from their spectra. These values are given in Table V and are plotted in Figure 4: it may be seen that they agree quite well with the I_2^+ concentrations determined from the conductometric data, considering the several experimental difficulties.

TABLE V

I_2^+ AND "I^+" CONCENTRATIONS FROM SPECTRA AND MAGNETIC SUSCEPTIBILITIES

Optical Density of 640-mμ Peak

2:1 $I_2/S_2O_6F_2$			1:1 $I_2/S_2O_6F_2$			
m_{I_2}	$m_{I_2^+}$	OD	m_{I_2}	$m_{I_2^+}$	m_{I^+}	OD
0.0157	0.0153	66	0.0186	0.0125	0.032	55
0.0372	0.0258	111	0.0388	0.0302	0.077	133
0.0388	0.0329	142	0.134	0.0803	0.206	354
0.134	0.0818	352				
0.164	0.1160	502				

Optical Density of 305-mμ Peak (2:1)

m_{I_2}	$m_{I_3^+}$	$m_{I_2^+}$	OD
0.0157	0.0021	0.0124	18.5
0.0372	0.0031	0.0321	27.0
0.0388	0.0058	0.0295	51.0
0.164	0.0425	0.096	37.6

Magnetic Susceptibilities

m_I	$10^6\chi_g$	$10^6\chi_m$	$m_{I_2^+}$	m_{I^+}
		HSO_3F		
0.00	−0.311	...	...	...
		2:1 $I_2/S_2O_6F_2$		
0.0479	−0.250	1320	0.038	...
0.0913	−0.210	1162	0.064	...
0.162	−0.148	1084	0.107	...
		1:1 $I_2/S_2O_6F_2$		
0.0253	−0.280	1293	0.0198	0.0498
0.0508	−0.254	1181	0.0376	0.0888
0.0879	−0.232	967	0.0516	0.125
0.170	−0.176	889	0.0915	0.222
0.235	−0.166	714	0.1015	0.246
0.328	−0.099	774	0.1540	0.373
0.879	+0.019	559	0.298	0.722
4.67	+0.015	251	0.710	1.73

It was also possible to use the extinction coefficient of I_3^+ at 305 mμ to obtain its concentration from the spectra and then we have

$$m_{I_2^+} = m_{I_2} - 8m_{I_3^+}/5$$

These results are also given in Figure 4.

If I^+ were formed according to eq 1, then from the optical density of the 1.9×10^{-4} *m* 1:1 solution, we find $\epsilon[I^+(640)] = 1020$.[11] The amount of I^+ in the more concentrated solutions in which it may be supposed to be in equilibrium with ISO_3F was then determined from the intensity of the 640-mμ peak. The results are given in Figure 4, where it may be seen that agreement with the I^+ concentrations determined from the conductivity results is poor.

The I_2^+ cation is expected to have a $^2\Pi_{3/2}$ ground state and for a species with such a high molecular weight, the energy separation between the ground state and the $^2\Pi_{1/2}$ first excited state is expected to be considerably greater than kT. Hence, the expected effective magnetic moment for I_2^+ is 2.0 BM.[12] The observed susceptibility $\chi_m(I_2)$ was found to decrease with increasing concentration in both the 1:1 and 2:1 solutions. This may be attributed to the disproportionation to give I_3^+ and $I(SO_3F)_3$. The results of magnetic susceptibility measurements on 1:1 and 2:1 solutions of various concentrations are given in Table V. Extrapolation of the values obtained at low concentration to infinite dilution gave a mean value of $\chi_m(I_2) = (1650 \pm 100) \times 10^{-6}$. This gives a value for the effective magnetic moment for I_2^+ of 2.0 ± 0.1 BM, in excellent agreement with the expected value. Using the extrapolated value for χ_m, concentrations of I_2^+ were calculated from the observed susceptibilities. These are given in Table V and have been plotted in Figure 4: they agree quite well with the I_2^+ concentrations determined by other methods.

Assuming that I^+ is formed according to eq 1 in the 1:1 solution, it is found that extrapolation of the magnetic data gives $\chi_m(I^+) = 680 \times 10^{-6}$ ($\mu = 1.3$ BM). Again, calculation of the amount of I^+ at various I_2 concentrations gives results in poor agreement with the values obtained from the conductivity data (Figure 4).

Finally it was found that the value of 2.0 for the equilibrium constant of the reaction described by eq 5 and 6

$$K_5 = \frac{[I(SO_3F)_3]^{1/8}[I_3^+]^{5/8}}{[I_2^+][SO_3F^-]]^{3/8}}\ \text{kg}^{3/4}\ \text{mole}^{-3/4}$$

gives a curve for the concentration of I_2^+ which is in good agreement with all of the experimental values for both the 2:1 and the 1:1 solutions (Figure 4).

Cryoscopic measurements on 2:1 $I_2/S_2O_6F_2$ solutions gave $\nu = 1.56$ (Table I). Unfortunately, this result and also $\nu = 1.21$ for the 1:1 solutions cannot be directly compared with the results of conductometric, spectroscopic, and magnetic susceptibility measurements discussed above, because of the temperature difference of ~120°. For the formation of I_2^+ in the 2:1 solution, according to eq 3, we expect $\nu = 2$, while for complete disproportionation we have

$$8I_2 + 4S_2O_6F_2 \longrightarrow I(SO_3F)_3 + 5I_3^+ + 5SO_3F^-$$

or

$$8I_2 + 4S_2O_6F_2 \longrightarrow I(SO_3F)_4^- + 5I_3^+ + 4SO_3F^-$$

i.e., $\nu = 1.25$–1.4, depending on the position of equilibrium 6. The observed value of $\nu = 1.56$ suggests that disproportionation is much more extensive at −89° than at 25°. For the formation of I_2^+ in the 1:1 solution, according to eq 4, we expect $\nu = 1.6$–2.0, depending on the position of equilibrium 6, while for complete disproportionation we have

$$2I_2 + 2S_2O_6F_2 \longrightarrow I(SO_3F)_3 + I_3^+ + SO_3F^-$$

or

$$2I_2 + 2S_2O_6F_2 \longrightarrow I(SO_3F)_4^- + I_3^+$$

i.e., $\nu = 1.0$–1.5, depending on the position of equilibrium 6. Again the observed ν value of 1.21 suggests extensive disproportionation. It will not be possible to reach any more quantitative conclusions concerning the extent of the disproportionation at low temperatures until conductometric, spectroscopic, and magnetic susceptibility measurements have been carried out at these temperatures.

The Absorption Spectrum of I_2^+.—The spectrum of I_2^+ in Figure 2 cannot be interpreted with complete certainty, but it is not inconsistent with our conclusion that the species giving rise to this spectrum is I_2^+. The electronic configurations of the ground state, the most probable lower excited states, and the corresponding spectroscopic terms follow.

$(\sigma_g5p)^2(\pi_u5p)^4(\pi_g5p)^3$	$^2\Pi_{3/2g}$, $^2\Pi_{1/2g}$	ground state
$(\sigma_g5p)^2(\pi_u5p)^3(\pi_g5p)^4$	$^2\Pi_{3/2u}$, $^2\Pi_{1/2u}$	excited states
$(\sigma_g5p)^2(\pi_u5p)^4(\pi_g5p)^2(\sigma_u5p)$	$^2\Delta_u$, $^2\Sigma^\pm$, $^4\Sigma_u^\pm$	
$(\sigma_g5p)^2(\pi_u5p)^3(\pi_g5p)^3(\sigma_u5p)$	$^4\Delta_g$, $^4\Sigma_g^\pm$, $^2\Delta_g$, $^2\Sigma_g^\pm$	

The strongest and lowest energy transition is expected to be $^2\Pi_{3/2g} \rightarrow {}^2\Pi_{3/2u}$ and this is, therefore, assigned to the 640-mμ (15,625-cm^{-1}) band. The intensity of this transition (oscillator strength, $f = 0.04$) supports its assignment as a charge-transfer band. The bands at 490 mμ (20,400 cm^{-1}) and 410 mμ (24,400 cm^{-1}) must be due to transitions to higher levels, perhaps $^2\Pi_{3/2g} \rightarrow {}^2\Pi_{1/2u}$ and $^2\Pi_{3/2g} \rightarrow {}^2\Delta_u$. We also observed a weak infrared band at 5190 cm^{-1}. This may be the transition $^2\Pi_{3/2g} \rightarrow {}^2\Pi_{1/2g}$ which would be forbidden by the g $\not\leftrightarrow$ g rule for homopolar molecules. We may note that the $^2P_{1/2}$–$^2P_{3/2}$ splitting in the iodine atom is 7600 cm^{-1}.[13]

Previous Evidence for "I^+".—Of all of the results obtained by previous workers, only two would appear to provide strong evidence that I^+, rather than I_2^+, is the species responsible for the blue color and paramagnetism of suitably oxidized solutions of iodine in strong acids.

(1) On changing the composition of the solvent in a solution of iodine from 65% oleum to 96% H_2SO_4 by the addition of aqueous sulfuric acid, it was found that approximately 80% of the original iodine was recovered in the molecular form.[14] It was assumed that the iodine arose from the following disproportionation reaction which it was supposed occurred on dilution of the solvent

$$5I_2 \longrightarrow 10I^+ + 10e^-$$
$$10I^+ \longrightarrow 4I_2 + 2I^V$$

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[12] G. Herzberg, "Molecular Spectra and Molecular Structure," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p 300.

[13] "Atomic Energy Levels," Vol. III, National Bureau of Standards Circular 467, Washington, D. C., 1958.

[14] M. C. R. Symons, *J. Chem. Soc.*, 387 (1957).

Hence, it was concluded that the iodine in the blue solution in 65% oleum was in the +1 oxidation state. However, in view of the fact that the +3 oxidation state has been shown to be stable in 100% acid,[9,15] it seems probable that the disproportionation of "I+" should be written as

$$3I_2 \longrightarrow 6I^+ + 6e^-$$
$$6I^+ \longrightarrow 2I_2 + 2I^{III}$$

in which case only 66% of the iodine would be recovered. On the other hand, the disproportionation of I_2^+ may be written as

$$6I_2 \longrightarrow 6I_2^+ + 6e^-$$
$$6I_2^+ \longrightarrow 5I_2 + 2I^{III}$$

and, therefore, a recovery of 83% of the iodine would be expected. Thus, the results of these experiments, in fact, provide evidence for I_2^+ rather than I^+.

(2) The results of conductivity measurements in 65% oleum were interpreted as showing that two HSO_7^- ions (or corresponding higher polyanions) are formed for each molecule of iodine,[2] *i.e.*

$$I_2 + 4H_2S_2O_7 \longrightarrow 2I^+ + 2HS_2O_7^- + SO_2 + 3H_2SO_4$$

However, we have been unable to repeat these results and our own conductivity measurements on solutions of iodine in disulfuric acid and in oleum indicate that only one $HS_2O_7^-$ ion is formed for each molecule of iodine, *i.e.*

$$2I_2 + 4H_2S_2O_7 \longrightarrow 2I_2^+ + 2HS_2O_7^- + SO_2 + 3H_2SO_4$$

These results will be fully discussed in a later paper on the formation of I_2^+ in oleum.[16]

Experimental Section

The methods used for the measurement of the conductivities and freezing points of solutions in fluorosulfuric acid and for the calculation of ν and γ values have been given previously.[6,7,17] $I_2/S_2O_6F_2$ mixtures, in exact stoichiometric ratios, were added to the cryoscopic or the conductivity cell in the form of a concentrated solution in fluorosulfuric acid, which was prepared in a drybox. Magnetic susceptibility measurements were made by the Gouy method. A permanent magnet with a field strength of 6000 gauss and a pole gap of 1.4 cm was used in conjunction with a Mettler Gramatic balance. The Gouy tube, which filled the pole gap, was standardized with a nickel chloride solution (β = 0.204). The susceptibilities were corrected for solvent and iodine fluorosulfate diamagnetism. The absorption spectra were taken on a Bausch and Lomb Spectronic 505 or a Cary Model B recording spectrophotometer. Quartz inserts to give path lengths down to 0.005 cm and reference beam filters were used to obtain spectra of iodine solutions at concentrations comparable to those used for the conductivity and magnetic susceptibility measurements. The spectra were found to be very sensitive to traces of moisture, and the solutions had to be prepared and the cells filled under very dry conditions in a drybox. The problem of adsorbed water was particularly serious when an insert was used to give a very short path length, because of the very large surface-to-volume ratio in the cell.

Commercial fluorosulfuric acid (Allied Chemical Co.) was purified as described previously.[7] Peroxydisulfuryl difluoride was prepared by the method of Cady and Shreeve.[18]

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The Reactivity of Metal–Metal Bonds. III. The Germanium–Manganese Bond

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The reaction of pentacarbonyl(trimethylgermyl)manganese with tetrafluoroethylene gives the insertion product $(CH_3)_3GeCF_2CF_2Mn(CO)_5$ in good yield. With trifluoroethylene, the reaction products are trimethylfluorogermane and *cis*- and *trans*-$CHF{=}CFMn(CO)_5$. The reactions of the germanium–manganese compound with trifluorochloroethylene, perfluoropropene, and ethylene are also described. A comparison of these reactions with those of the analogous tin–manganese compound shows a number of unexpected differences, and these are discussed in terms of the polarity of the metal–metal bond.

Introduction

The reactivities of the Sn–Sn and Sn–Mn bonds toward several fluoroolefins were examined in previous papers.[2,3] While the Sn–Sn bond of hexamethylditin is readily cleaved under free-radical conditions to give products whose formation can best be interpreted in terms of attack by the nucleophilic $(CH_3)_3Sn\cdot$ radical on the olefins, the behavior of the Sn–Mn bond under the same conditions is obviously different. Insertion products, such as $(CH_3)_3SnCF_2CF_2Mn(CO)_5$,

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