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

The Fluorosulfuric Acid Solvent System. V. Iodine Trifluorosulfate

BY R. J. GILLESPIE AND J. B. MILNE

Received January 31, 1966

The results of nmr, freezing point, and conductivity measurements on 1:7 and 1:3 I_2–$S_2O_6F_2$ solutions in fluorosulfuric acid are reported. They show that iodine trifluorosulfate is the highest fluorosulfate formed in solution in fluorosulfuric acid. Iodine trifluorosulfate behaves as an ampholyte in fluorosulfuric acid and reacts with water at low temperatures to give iodosyl fluorosulfate, $IOSO_3F$. Acid and base ionization constants have been determined.

Introduction

Iodine trifluorosulfate was first prepared by Roberts and Cady by allowing iodine to react with peroxydisulfuryl difluoride.[1] Salts such as $KI(SO_3F)_4$ have also been prepared showing that iodine trifluorosulfate can behave as an acid.[2] The tripositive oxidation state of iodine is extensively disproportionated in aqueous solution, except in the presence of a large excess of strong acid, but it has been shown to be stable in sulfuric acid and dilute oleum.[3,4] Solutions of 3:1 HIO_3–I_2, $(IO)_2SO_4$, and $(IO_2)_n$ in sulfuric acid contain iodosyl hydrogen sulfate which is partially ionized

$$IO \cdot SO_4H \rightleftharpoons IO^+ + SO_4H^-$$

The IO^+ ion probably exists in a solvated form such as $[I(OH)SO_4H]^+$ or $[I(OH_2)(SO_4H)_2]^+$. In oleum, dehydration occurs to give iodine tri(hydrogen sulfate) $I(SO_4H)_3$.

The purpose of the present work was to study the oxidation of iodine by $S_2O_6F_2$ in fluorosulfuric acid solution to see which positive oxidation states of iodine are stable in this solvent. This paper is concerned with only the +3 oxidation state. The formation of lower oxidation states is discussed in a following paper.[5]

Results and Discussion

The ^{19}F nmr spectrum of a solution of iodine in excess peroxydisulfuryldifluoride consists of only two peaks, one of which is due to the excess $S_2O_6F_2$. From the areas of the peaks and the known composition of the solution it was readily shown that the only product was iodine trifluorosulfate. Of course, other products might have been formed in amounts too small to have been detected in the spectrum. The ^{19}F resonance of $I(SO_3F)_3$ was found to be 6.6 ppm to low field of the peroxydisulfuryl difluoride resonance in a solution of I_2–$S_2O_6F_2$ having the mole ratio 1:43.2. Thus, in agreement with Roberts and Cady,[1] we find that at room temperature the main product of the reaction of $S_2O_6F_2$ with iodine is $I(SO_3F)_3$. Presumably the structure of $I(SO_3F)_3$ is analogous to that of ClF_3 and BrF_3 and it would therefore be expected to have an AX_2 ^{19}F nmr spectrum. However, at all temperatures down to the freezing point of $S_2O_6F_2$ (−55.4°) only a single peak was observed for $I(SO_3F)_3$. This must be a consequence of rapid inter- or intramolecular exchange of fluorosulfate groups. Alternatively $I(SO_3F)_3$ may exist as a dimer or higher polymer involving fluorosulfate bridges, but again some exchange mechanism is necessary to account for the nmr spectrum.

Table I gives the results of cryoscopic measurements on 1:7 I_2–$S_2O_6F_2$ solutions in fluorosulfuric acid; they are expressed in terms of ν, the number of moles of solute particles produced per mole of iodine. The mean value of $\nu = 6.2$ is in reasonable agreement with the value of 6.0 expected for the reaction

$$I_2 + 7S_2O_6F_2 \longrightarrow 2I(SO_3F)_3 + 4S_2O_6F_2$$

Peroxydisulfuryl difluoride has previously been shown to behave as a nonelectrolyte in fluorosulfuric acid.[6] The ^{19}F nmr spectrum of a fluorosulfuric acid solution of 1:7 I_2–$S_2O_6F_2$, $m_{I_2} = 0.1082$, consisted of only two peaks separated by 1.6 ppm. The smaller high-field peak increased in intensity on adding further $S_2O_6F_2$ and is assigned to $S_2O_6F_2$. The low-field peak must, therefore, be due to $I(SO_3F)_3$, and HSO_3F. This assignment was confirmed by measurement of the peak areas. The spectrum was the same at −90° as at 25°. We conclude that there is rapid exchange between $I(SO_3F)_3$ and HSO_3F even at low temperatures.

Cryoscopic measurements on 1:3 I_2–$S_2O_6F_2$ solutions gave a mean value of $\nu = 1.94$ (Table I), which is in good agreement with the value of 2.0 expected for the reaction

$$I_2 + 3S_2O_6F_2 \longrightarrow 2I(SO_3F)_3$$

The conductivities of 1:3 I_2–$S_2O_6F_2$ solutions are given in Table II and Figure 1. Values of γ, the number of moles of fluorosulfate ions produced per mole of iodine, were obtained from the results by comparison of the observed conductivities with those of solutions of potassium fluorosulfate.[7] The values given in Table III are less than 0.1. Hence, iodine trifluorosulfate is a very weak electrolyte. In order to ascertain whether $I(SO_3F)_3$ ionizes as an acid or a base, the conductivities of solutions obtained by adding successive amounts of KSO_3F to a 1:3 I_2–$S_2O_6F_2$ solution were measured (Table IV). The conductivity increased immediately and no minimum conductivity was observed even at very low

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(1) J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 352 (1960).

(2) M. Lustig and G. H. Cady, *Inorg. Chem.*, **1**, 714 (1962).

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

(4) R. J. Gillespie and J. B. Senior, *Inorg. Chem.*, **3**, 1149 (1964).

(5) R. J. Gillespie and J. B. Milne, *ibid.*, in press.

(6) R. J. Gillespie, J. B. Milne, and R. C. Thompson, *ibid.*, **5**, 468 (1966).

(7) J. Barr, R. J. Gillespie, and R. C. Thompson, *ibid.*, **3**, 1149 (1964).

TABLE I

FREEZING POINTS

1:7 I_2–$S_2O_6F_2$			1:3 I_2–$S_2O_6F_2$		
$10^2m_{I_2}$	Fp, °C	ν	$10^2m_{I_2}$	Fp, °C	ν
0.00	−88.998	...	0.00	−89.000	...
0.21	−89.049	6.18	0.83	−89.063	1.93
0.44	−89.104	6.13	1.28	−89.097	1.93
0.67	−89.164	6.30	1.76	−89.135	1.95
0.88	−89.216	6.30	2.34	−89.182	1.98
		6.23	2.82	−89.213	1.92
					1.94

TABLE II

ELECTRICAL CONDUCTIVITIES OF 1:3 I_2–$S_2O_6F_2$ SOLUTIONS

25°		−78.5°	
$10^2m_{I_2}$	$10^4\kappa$, ohm^{-1} cm^{-1}	$10^2m_{I_2}$	$10^6\kappa$, ohm^{-1} cm^{-1}
0.00	1.404	0.00	2.656
0.18	1.714	0.23	5.099
0.41	2.120	0.33	6.035
0.57	2.342	0.40	6.652
0.73	2.617	0.50	7.110
0.93	2.878	0.61	7.672
1.21	3.189	0.72	8.496
1.74	3.765	0.88	8.841
2.18	4.213		

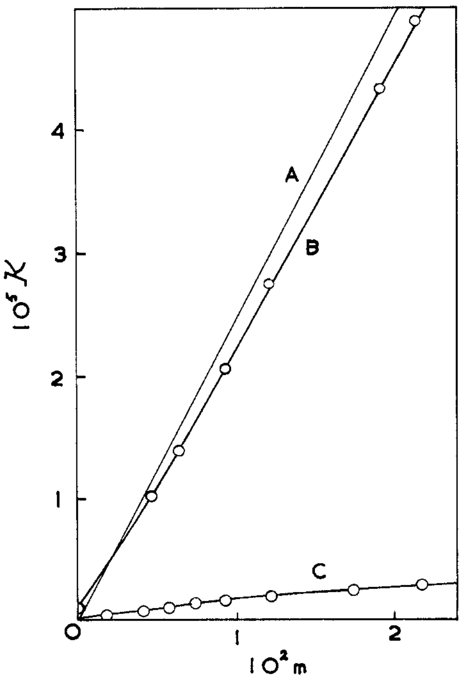

Figure 1.—Conductivities of solutions of $I(SO_3F)_3$ and $I(SO_3F)_3$–KSO_3F (Tables II and IV): A, KSO_3F; B, $I(SO_3F)_3$–KSO_3F, calculated curve (O, experimental points); C, $I(SO_3F)_3$.

KSO_3F concentrations, indicating that initially, at least, $I(SO_3F)_3$ behaves as a base. However, the slope of the conductivity curve is less than that for KSO_3F alone, and eventually the total conductivity becomes less than that of solutions containing only KSO_3F (Figure 1), indicating acidic behavior at higher concentrations. This is indeed the behavior expected for an ampholyte. Initially, the added fluorosulfate represses a basic ionization which we represent as

$$I(SO_3F)_3 \rightleftharpoons I(SO_3F)_2^+ + SO_3F^-$$

TABLE III

VALUES OF γ AND K_b FOR 1:3 I_2–$S_2O_6F_2$ SOLUTIONS

25°			78.5°		
$10^2m_{I_2}$	γ	10^5K_b, mole kg^{-1}	$10^2m_{I_2}$	γ	10^6K_b, mole kg^{-1}
0.5	0.080	1.7	0.2	0.036	1.3
1.0	0.072	2.7	0.4	0.032	2.0
1.5	0.067	3.5	0.6	0.030	2.7
2.0	0.061	3.8	0.8	0.024	2.3
		2.9	1.0	0.022	2.4
					2.1

TABLE IV

CONDUCTIVITIES OF KSO_3F–1:3 I_2–$S_2O_6F_2$ SOLUTIONS AT 25°

10^2m		$10^4\kappa$,	10^2m		$10^4\kappa$,
I_2	KSO_3F	ohm^{-1} cm^{-1}	I_2	KSO_3F	ohm^{-1} cm^{-1}
0.00	0.00	1.127	0.00	0.00	2.065
0.67	0.00	2.156	0.587	0.00	2.961
0.67	0.02	2.464	0.587	0.47	12.38
0.67	0.09	3.529	0.587	0.65	16.12
0.67	0.11	3.943	0.587	0.94	22.75
0.67	0.13	4.342	0.587	1.23	29.67
0.67	0.20	5.578	0.587	1.94	45.50
0.67	0.31	7.870	0.587	2.17	51.08

but, as the concentration of SO_3F^- increases, the acidic ionization of $I(SO_3F)_3$ gradually becomes more important

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

From the γ values for the 1:3 I_2–$S_2O_6F_2$ solutions (Table III), mean values of $K_b = [I(SO_3F)_2^+][SO_3F^-]/[I(SO_3F)_3]$ of 2.9×10^{-5} mole kg^{-1} at 25° and 2.1×10^{-6} mole kg^{-1} at −78° were obtained. From the conductivities of solutions containing excess potassium fluorosulfate a value of $K_a = [I(SO_3F)_4^-]/[I(SO_3F)_3][SO_3F^-]$ of 10 mole^{-1} kg was obtained. A theoretical conductivity curve for the KSO_3F–1:3 I_2–$S_2O_6F_2$ solutions calculated with the aid of these equilibrium constants is in excellent agreement with the experimental points (Figure 1). The basic ionization is presumably responsible for the rapid exchange of fluorosulfate between $I(SO_3F)_3$ and HSO_3F that is indicated by the nmr spectrum.

Solutions of $I(SO_3F)_3$ in fluorosulfuric acid are pale yellow. There is no absorption in the spectrum above 300 mμ but at shorter wavelengths there is a strong absorption, the maximum of which was not observed.

Addition of water to a 1:3 I_2–$S_2O_6F_2$ solution produced little change in either the freezing point or the conductivity at −78° until approximately 1 mole of water had been added for each mole of $I(SO_3F)_3$ (Table V and Figure 2). Thereafter, the conductivity increased and the freezing point decreased as expected for the solute water. We conclude that water reacts with $I(SO_3F)_3$ according to the equation

$$I(SO_3F)_3 + H_2O \longrightarrow IO(SO_3F) + 2HSO_3F$$

At room temperature solutions of $I(SO_3F)_3$ containing water rapidly acquired a deep blue-green color; it appears that disproportionation occurs. The deep blue-green color is shown in a following paper[5] to be characteristic of I_2^+ but the other products of the disproportionation are uncertain.

TABLE V

FREEZING POINTS AND CONDUCTIVITIES OF H_2O–1:3 I_2–$S_2O_6F_2$ SOLUTIONS AT −78.5°

10^2m		$10^1\kappa$,	10^2m		Fp,
I_2	H_2O	ohm^{-1} cm^{-1}	I_2	H_2O	°C
0.00	0.00	0.392	0.00	0.00	−89.000
1.00	0.00	0.909	2.82	0.00	−89.213
1.00	1.13	4.306	2.82	1.79	−89.199
1.00	2.35	8.101	2.82	3.64	−89.190
1.00	3.59	23.83	2.82	5.43	−89.248
1.00	4.77	48.54	3.82	7.20	−89.335
1.00	5.88	70.56			

Experimental Section

The techniques used for the purification of fluorosulfuric acid and for cryoscopic and conductometric measurements in this solvent have been described elsewhere.[6,7] Peroxydisulfuryl difluoride was prepared by the method of Cady and Shreeve.[8] Shawinigan reagent grade iodine was used directly. The nmr spectra were obtained with a Varian HR 60 spectrometer.

Acknowledgment.—We thank the Directorate of Chemical Sciences of the United States Air Force Office of Scientific Research and the National Research Council of Canada for generous financial aid. J. B. M. also thanks the National Research Council of Canada for the award of a studentship.

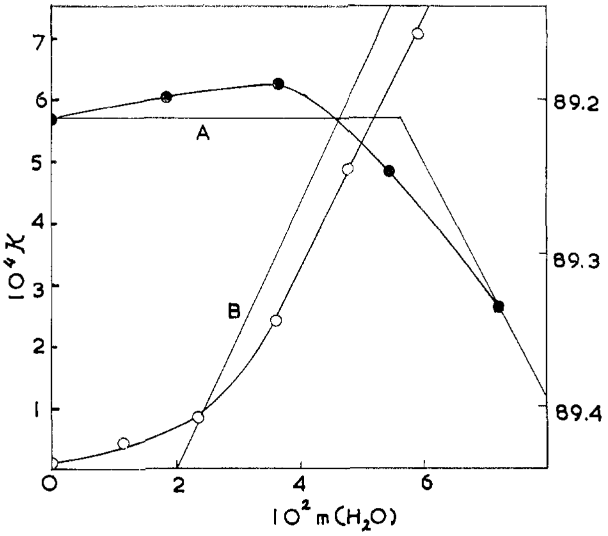

Figure 2.—Conductivities and freezing points of $I(SO_3F)_3$–H_2O solutions (Table V): ○, conductivities; ●, freezing points; A, predicted freezing point curve; B, predicted conductivity curve.

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[8] G. H. Cady, and J. M. Shreeve, *Inorg. Syn.*, **7**, 124 (1963).

CONTRIBUTION FROM AVERY LABORATORY OF CHEMISTRY
OF THE UNIVERSITY OF NEBRASKA, LINCOLN, NEBRASKA

Thiocyanogen: Its Spectra and Heat of Formation in Relation to Structure[1]

BY CECIL E. VANDERZEE AND ARVIN S. QUIST[2]

Received August 11, 1965

By means of solution calorimetry, $\Delta H_f°[(SCN)_2(l)]$ has been found to be 74.3 ± 1 kcal/mole at 25°. This is about 4 kcal/mole less than the value estimated from bond energies for the structure N≡C—S—S—C≡N. Spectroscopic data obtained in this study support those of other investigators and are fully in accord with the above structure.

Introduction

The only thermodynamic datum pertaining to thiocyanogen is the standard electrode potential, *viz.*

$$2SCN^- \rightleftharpoons (SCN)_2 + 2e^- \qquad E° = -0.77 \text{ v} \tag{1}$$

reported by Bjerrum and Kirschner,[3] who postulated the presence of $(SCN)_2$ in the decomposition of aqueous auric thiocyanate. The first successful isolation of $(SCN)_2$ was reported by Söderbäck[4] in an extensive study of the properties of thiocyanogen. These two extensive studies[3,4] showed that the compound was stable only in the absence of water and in the pure state only at temperatures well below room temperature. Since Söderbäck's initial isolation of solid $(SCN)_2$, the only other report of its isolation is that of Seel and coworkers.[5,6] Söderbäck's preparation, isolated from ether, melted between −2 and −3°. Seel and Wesemann[5] obtained a product melting at 15 to 16° from the decomposition of nitrosyl thiocyanate in liquid SO_2 as solvent. Later Seel and Müller[6] reported that the preparation of $(SCN)_2$ from AgSCN and Br_2 in liquid SO_2 was much easier, but they did not report the melting point of their product obtained by this method.

In this study, several preparations of solid $(SCN)_2$ by the method of Seel and Müller[6] failed to yield a product melting above 0°. In every case, the liquid form was unstable, as reported by other workers.[4–6] Since there appeared to be no practical route to the heat of formation by way of a condensed phase, attention was turned to solution calorimetry.

The most clean-cut and quantitative reaction of thiocyanogen in solution appears to be the oxidation of iodide in acid solution, which is given by eq 2.

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[1] From the Ph.D. Thesis of Arvin S. Quist, July 1959.

[2] Minnesota Mining and Manufacturing Company Fellow, 1956–1957; DuPont Teaching Fellow, 1957–1958; National Science Foundation Fellow, 1958–1959.

[3] N. Bjerrum and A. Kirschner, *Kgl. Danske Videnskab. Selskabs, Skrifter, Naturvidenskab Math. Afdel.*, [8] **5**, 1 (1918).

[4] E. Söderbäck, *Ann. Chem., Liebigs*, **419**, 217 (1919).

[5] F. Seel and D. Wesemann, *Chem. Ber.*, **86**, 1107 (1953).

[6] F. Seel and E. Müller, *ibid.*, **88**, 1747 (1955).