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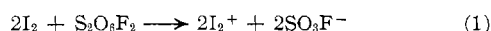
Cations and Oxyocations of Iodine. V. Formation of the I_4^{2+} Cation in Fluorosulfuric Acid

By R. J. GILLESPIE, J. B. MILNE, AND M. J. MORTON

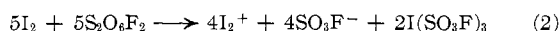
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It is shown by means of spectroscopic, cryoscopic, conductometric, and magnetic susceptibility measurements that in solution in fluorosulfuric acid the iodine cation I_2^+ dimerizes at low temperatures to the I_4^{2+} cation.

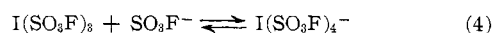
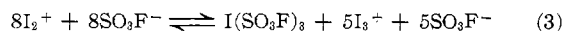
It has been shown that iodine can be oxidized to I -(SO_3F)₃, I_2^+ , I_3^+ , and I_5^+ by the appropriate amount of $S_2O_6F_2$ in solution in fluorosulfuric acid.^{1,2} In a 2:1 I_2 - $S_2O_6F_2$ solution I_2^+ is formed according to the equation



In a 1:1 I_2 - $S_2O_6F_2$ solution I_2^+ and $I(SO_3F)_3$ are formed according to the equation



No evidence was obtained for the formation of I^+ which would be expected to have a maximum concentration in a 1:1 solution. The blue color and absorption maxima at 640, 490, and 410 $m\mu$ which had previously been attributed³ to I^+ were shown to be characteristic of I_2^+ . Magnetic susceptibility measurements gave a limiting value of the magnetic moment for I_2^+ of 2.0 ± 0.1 BM at room temperature which is in good agreement with the expected value of 2.0 BM for a $^2\Pi_{3/2}$ ground state of the I_2^+ cation. The observed susceptibility however decreases with increasing concentration and the specific conductances of the 2:1 and 1:1 solutions do not increase as rapidly with increasing concentration as would be expected for the complete formation of I_2^+ . It was shown that this is because I_2^+ is not completely stable and disproportionates to an increasing extent with increasing concentration according to the equations⁴



Cryoscopic measurements were not, however, in satisfactory agreement with these conclusions. For example the 2:1 solutions gave $\nu = 1.56$ even in dilute solutions although the formation of I_2^+ according to eq 1 would require $\nu = 2.0$. Complete disproportionation would require $\nu = 1.25$ -1.4 depending on the position of equilibrium 4. It was suggested¹ that disproportionation might be much more extensive at the temperature of the freezing point measurements (-90°) than at room temperature but no firm conclusions could be reached in the absence of conductometric, spectroscopic, and magnetic measurements at low temperatures. This paper reports the results of such measurements.

Absorption Spectra.—Figure 1 shows that a dramatic change occurs in the absorption spectrum of a solution containing I_2^+ as the temperature is lowered. This change is rapid and reversible; it occurs in all solutions containing I_2^+ and is easily observed visually as the color of the solutions changes from an intense blue to a deep red-brown near the freezing point. As the temperature is lowered, the optical density of the 640- $m\mu$ peak of I_2^+ at first increases slowly, presumably because the peak becomes somewhat sharper and also because the density of the solution increases (Figure 2). Thus the molal extinction coefficient of the I_2^+ ion increases from 4500 at 25° to 5300 at -60° and, assuming that this linear increase continues to lower temperatures, to 5650 at -86° . (Extinction coefficients in this paper are quoted in molal units because the densities of the fluorosulfuric acid solutions are not known at low temperatures.) At around -50 to -60° , however, depending on the composition and concentration of the solution, the 640- $m\mu$ peak begins to decrease rapidly in intensity and new peaks appear at 470, 357, and 290 $m\mu$ (Figures 1 and 2). Since I_3^+ has peaks at 470 and 305 $m\mu$,¹ the additional peak at 357 $m\mu$ shows either that the new species is not I_3^+ or that a new species is produced in addition to I_3^+ . By studying solutions having different concentrations of iodine and different I_2 : $S_2O_6F_2$ ratios, it was possible to vary the I_2^+ concentration over a wide range. The spectra of these solutions were recorded at two temperatures at which there is a reasonable equilibrium concentration of the new species, *i.e.*, -70 and -86.5° . The results are given in Table I. A plot of the log of the optical density of the 640- $m\mu$ peak against the log of the optical density of the 357- $m\mu$ peak gave a straight line of slope 2.0 at -70° and 1.9 at -86.5° (Figure 3) showing that there is an equilibrium between 2 mol of I_2^+ and 1 mol of the species giving rise to the 357- $m\mu$ peak. The simplest interpretation of this result is that the new species is I_4^{2+}



The optical densities of the 290- and 470- $m\mu$, peaks were found to be proportional to that of the 357- $m\mu$ peak and

(1) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1577 (1966).(2) R. J. Gillespie and J. B. Milne, *ibid.*, **5**, 1236 (1966).(3) J. Arotzky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, **12** (1966).(4) An error was made in part IV¹ in the expressions giving the concentration of I_2^+ due to these equations. They should read: for 2:1 solutions

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

for 1:1 solutions

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

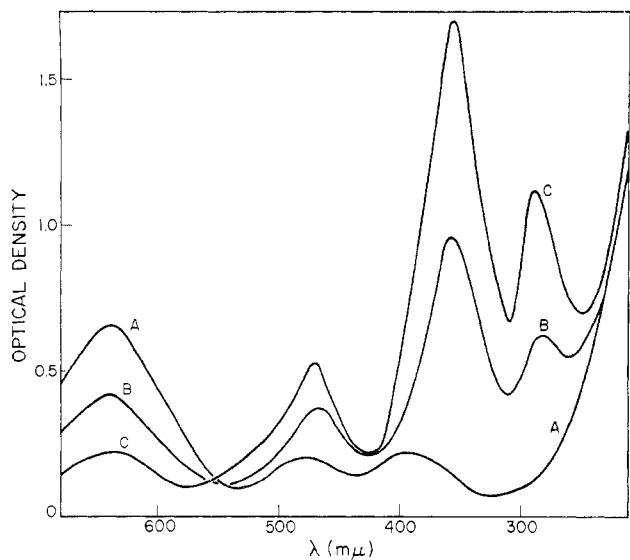


Figure 1.—Uv and visible spectrum of a 0.01435 *m* 1:1 I_2 - $S_2O_6F_2$ solution; path length, 0.01 cm: A, 23°; B, -70°; C, -86.5°.

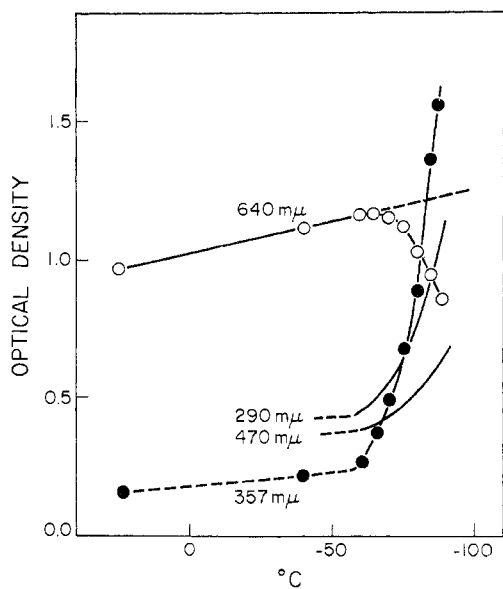
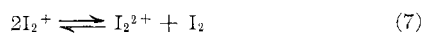
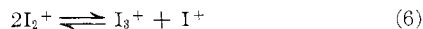


Figure 2.—Temperature dependence of the spectrum of a 1.33:1 I_2 - $S_2O_6F_2$ solution; path length, 1 mm; $m_{I_2} = 0.0027$.

it is reasonable therefore also to attribute these peaks to the I_4^{2+} ion. Reaction of I_2^+ with some other species in solution, *e.g.*, I_3^+ , $I(SO_3F)_3$, or $I(SO_3F)_4^-$, can be ruled out on the grounds that all of the points in Figure 3 lie very close to the two straight lines irrespective of the concentrations of the other species in the solutions studied. The only other reasonable possibilities are the equilibria



Although I_3^+ has characteristic peaks at 470 and 305 $m\mu$, the latter of which might possibly be shifted to 290 $m\mu$, this equilibrium is unlikely for two reasons. (1) It was found that the addition of I_3^+ to the solution did not shift the equilibrium. (2) Taking the extinc-

TABLE I
PHOTOMETRIC DATA

| $10^3 m_{I_2}$ | $I_2:S_2O_6F_2$ | Optical density ^a | | | | |
|----------------|-----------------|------------------------------|------|------------|------|-------------------|
| | | 640 $m\mu$ | | 357 $m\mu$ | | |
| | | 25° | -70° | -86.5° | -70° | -86.5° |
| 0.27 | 1.33:1 | 9.6 | 11.4 | 8.6 | 4.5 | 14.6 |
| 0.58 | 1.33:1 | 19.5 | 20 | 13.9 | 16 | 40 ^b |
| 1.435 | 1:1 | 52 | 43.5 | 25 | 85 | 166 |
| 0.563 | 1:1 | 29.5 | 29.7 | 18.7 | 28 | 70 |
| 0.20 | 2:1 | 5.8 | 6.75 | 5.6 | 1.2 | 7.2 |
| 9.50 | 2:1 | 260 | 94 | 50 | 300 | 540 ^b |
| 9.50 | 1.67:1 | 340 | ... | 64 | ... | 1000 ^b |
| 0.87 | 1:3 | 4 | 6.9 | 4.5 | 2.6 | 8 |
| 0.72 | 2.4:1 | 16 | 16 | 10 | 10 | 30 |

^a Optical densities per unit path length. ^b Estimated from 470- $m\mu$ peak height.

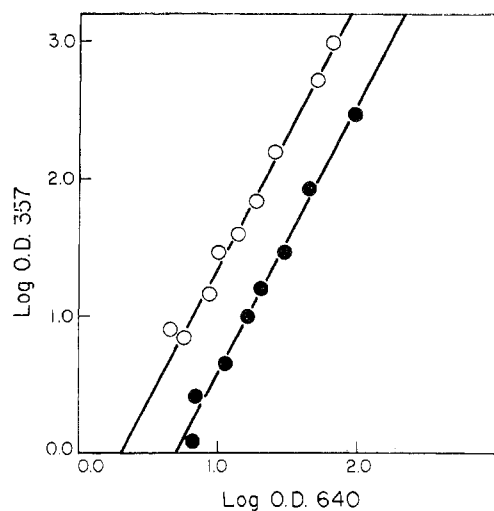


Figure 3.—Photometric plot: ●, -70°; O, -86.5°.

tion coefficient of the 290- $m\mu$ I_3^+ peak to be 11,000 at -86.5°,¹ the optical density of the 305- $m\mu$ peak at -86.5° indicated the impossible result that approximately 2 mol of I_3^+ are formed from 2 mol of I_2^+ . Equilibrium 7 giving I_2^{2+} and molecular iodine is also very unlikely for at least two reasons. (1) Iodine would react with I_3^+ in solutions containing this ion to give I_5^+ which has its own characteristic spectrum¹ and this was not observed. (2) I_2^{2+} would be expected to be paramagnetic (*cf.* O_2) and the solutions become diamagnetic at the freezing point. Assuming that I_2^+ dimerizes to I_4^{2+} with decreasing temperature, we may use the absorption spectra data to obtain the extinction coefficients of the characteristic peaks of I_4^{2+} and also to obtain values for the equilibrium constant for the dimerization equilibrium, $K_d = [I_4^{2+}]/[I_2^+]^2$. Table II gives the results of three experiments on dilute solutions having $I_2:S_2O_6F_2$ ratios of 1.33:1 or 1:1 and therefore containing sufficient $I(SO_3F)_3$ to completely repress the disproportionation of the I_2^+ (eq 3 and 4). The I_2^+ concentration can therefore be obtained from the intensity of the I_2^+ peak at 640 $m\mu$ and the decrease in the I_2^+ concentration with decreasing temperature can be attributed to its dimerization to I_4^{2+} . Hence the concentration of I_4^{2+} and the extinction coefficients for the 357-, 470-, and 290- $m\mu$ peaks may be obtained. Small approximate corrections were made for the I_2^+

TABLE II
EXTINCTION COEFFICIENTS FOR THE I_4^{2+} ABSORPTIONS

| $I_2:S_2O_8F_2$ | $10^3 m_{I_2}$ | | |
|------------------------------------|----------------|--------|--------|
| | 2.7 | 5.625 | 14.35 |
| OD^a (640 $m\mu$) (25°) | 1.33:1 | 1:1 | 1:1 |
| (-86.5°) | 9.6 | 29.5 | 52.0 |
| $10^3 m_{I_2}$ (25°) | 2.13 | 6.55 | 11.6 |
| (-86.5°) | 1.52 | 3.36 | 4.42 |
| $10^3 m_{I_4^{2+}}$ (-86.5) | 0.30 | 1.59 | 3.59 |
| $OD(I_4^{2+})$ (357 $m\mu$) | 14.6 | 70 | 166 |
| (470 $m\mu$) ^b | 3.3 | 17 | 43 |
| (290 $m\mu$) ^c | 7 | 41 | 95 |
| $\epsilon(I_4^{2+})$ (357 $m\mu$) | 48,000 | 44,000 | 46,000 |
| (470 $m\mu$) | 11,000 | 11,000 | 12,000 |
| (290 $m\mu$) | 23,000 | 26,000 | 26,000 |

^a All optical densities are given per centimeter of path length.

^b Corrected for I_2^+ absorption at 470 $m\mu$. ^c Corrected for $I(SO_3F)_3$ shoulder.

absorption underlying the 470- $m\mu$ peaks and the $I(SO_3F)_3$ absorption underlying the 290- $m\mu$ peak. The results gave mean values for the extinction coefficients of 46,000 for the 357- $m\mu$ peak, 25,000 for the 290- $m\mu$ peak, and 11,000 for the 470- $m\mu$ peak. In view of the experimental difficulties in making these measurements, these values may be in error by as much as 10%. From the data in Figure 3 it was then possible to obtain mean values of the dimerization constant K_d of $23 \pm 2 \text{ mol}^{-1} \text{ kg}$ at -70° and $170 \pm 20 \text{ mol}^{-1} \text{ kg}$ at -86.5° . Finally we have $\Delta H = RT^2 \Delta \ln K / \Delta T = 10 \pm 2 \text{ kcal}$.

Magnetic Measurements.—The magnetic susceptibility of a 0.07 m solution of I_2^+ was measured from room temperature to -140° (frozen solution) and from the results, assuming that the magnetic moment of I_2^+ is 2.0 BM, the concentration of I_2^+ was calculated (Table III). The absorption spectrum of the same solution was measured between room temperature and -90° and the concentration of I_2^+ was again calculated from the extinction coefficient of the 640- $m\mu$ peak of the I_2^+ ion corrected for the temperature change according to the data in Figure 2 (Table III). Figure 4 shows that both sets of data agree reasonably well with the curve calculated from K_d and ΔH for the dimerization which confirms that the species formed at low temperature is diamagnetic and that the magnetic moment of the I_2^+ ion is indeed 2.0 BM. The ion I_4^{2+} contains an even number of electrons and would be expected to be diamagnetic.

Cryoscopy.—Freezing point depression measurements were made on both the 1:1 and 2:1 solutions. The results are given in Table IV. They agree well with those obtained previously,¹ and they show that the value of ν is 1.45–1.25 for the 1:1 solutions and 1.6–1.5 for the 2:1 solutions in the concentration ranges studied. (An allowance has been made for the interaction of the small excess SO_3 present in the solvent^{1,5} with the fluorosulfate ion: $SO_3F^- + SO_3 \rightarrow S_2O_6F^-$.) The values of ν are in reasonable agreement with values calculated from $K_d = 300$ for the dimerization at the freezing point, *i.e.*, 1.64–1.57 over the range 0.02–0.08 m in the 2:1 so-

TABLE III
MAGNETIC SUSCEPTIBILITY AND VISIBLE SPECTRUM OF A
0.108 m , 0.74:1 $I_2-S_2O_8F_2$ SOLUTION

| Magnetic data ^a | | | | Visible data ^b | | | |
|----------------------------|----------------------|---------------|---------------------|---------------------------|------------------|----------------------|---------------------|
| Temp, °C | Δw , μg | $10^3 \chi_g$ | $10^3 m_{I_2}^{+c}$ | Temp, °C | OD (640 $m\mu$) | $\epsilon_{640m\mu}$ | $10^3 m_{I_2}^{+c}$ |
| 22 | 835 | 116 | 7.6 | 22 | 1.50 | 4500 | 6.67 |
| 3 | 835 | 116 | 7.1 | 0 | 1.50 | 4750 | 6.32 |
| -25 | 830 | 124 | 6.9 | -35 | 1.19 | 5100 | 4.66 |
| -50 | 865 | 57 | 2.8 | -44 | 1.06 | 5200 | 4.08 |
| -69 | 880 | 41 | 1.9 | -48 | 0.96 | 5250 | 3.76 |
| -87 | 905 | 0 | 0.0 | -75 | 0.43 | 5550 | 1.55 |
| -100 | 905 | 0 | 0.0 | -86 | 0.24 | 5650 | 0.85 |
| -143 | 900 | 5 | 0.2 | -100 | 0.07 | 5750 | 0.24 |

^a Quartz tube constant, 1.86; diamagnetic correction, 683 μg ; solvent correction, 221 μg . ^b Path length, 0.005 cm. ^c Calculated assuming $\mu_{I_2^+} = 2.00 \text{ BM}$.

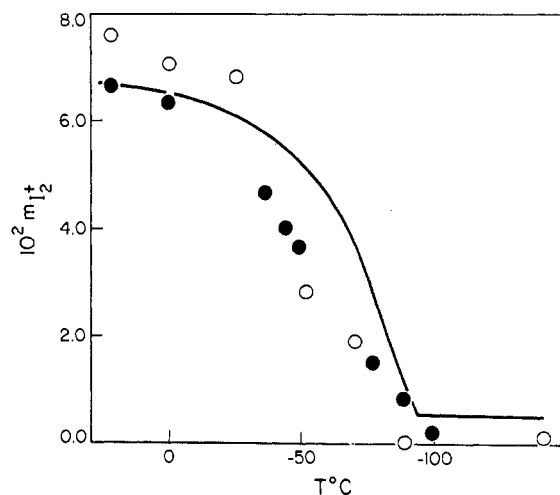
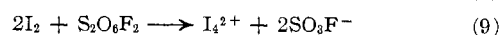
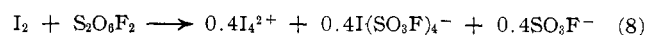


Figure 4.—Variation of I_2^+ concentration with temperature: ●, $m_{I_2^+}$ from optical density at 640 $m\mu$ and a path length of 0.005 cm; ○, $m_{I_2^+}$ from magnetic susceptibility assuming 2.0 BM; —, calculated curve.

TABLE IV
FREEZING POINT DATA

| 2:1 $I_2-S_2O_6F_2$ | | 1:1 $I_2-S_2O_6F_2$ | |
|---------------------|---------------|---------------------|---------------|
| $10^3 m_{I_2}$ | θ , °C | $10^3 m_{I_2}$ | θ , °C |
| 1.86 | 0.125 | 0.981 | 0.045 |
| 3.53 | 0.24 | 2.04 | 0.089 |
| 4.43 | 0.25 | 2.98 | 0.131 |
| 5.33 | 0.31 | 3.47 | 0.159 |
| 6.27 | 0.36 | | |
| 7.11 | 0.41 | | |
| 7.82 | 0.44 | | |

lution. At higher concentrations we expect the limiting values of $\nu = 1.2$ and 1.5 for the 1:1 and 2:1 solutions according to the equations



In eq 8 it is assumed that equilibrium 4 lies extensively to the right-hand side. It was shown previously that the equilibrium constant for this reaction is $10 \text{ mol}^{-1} \text{ kg}$ at 25° , and the conductivity results discussed in this paper show that at -86.4° it has a value of $50 \text{ mol}^{-1} \text{ kg}$. A still larger value is predicted at the freezing point of the solutions, and hence this accounts qual-

itatively for the decrease from $\nu = 1.45$ to 1.25 in dilute 1:1 solutions.

Conductivity Measurements.—The equilibrium $2I_2^+ \rightleftharpoons I_4^{2+}$ does not directly affect the conductivities of solutions in fluorosulfuric acid which are due largely to the fluorosulfate ion. However, in any solutions containing $I(SO_3F)_3$ equilibrium 4 affects the conductivity. It has been previously shown that $K_a = [I(SO_3F)_4^-]/[I(SO_3F)_3][SO_3F^-] = 10 \text{ mol}^{-1} \text{ kg}$ at 25° and it was necessary to determine the equilibrium constant at -86.5° in order to be able to give a complete interpretation of the conductivity results at this temperature of any solutions containing $I(SO_3F)_3$. Hence the conductivities of solutions obtained by adding potassium fluorosulfate to a solution of iodine trifluorosulfate were measured (Table V). At 25° the results were in excellent agreement with those obtained previously and at -86.4° they agreed well with a curve calculated on the basis of $K_a = 50 \text{ mol}^{-1} \text{ kg}$ (Figure 5).

TABLE V
CONDUCTIVITY OF $I(SO_3F)_3$ - KSO_3F SOLUTIONS^a

| $m(KSO_3F)$ | $10^5 \kappa, \text{ ohm}^{-1} \text{ cm}^{-1}$ | | γ | |
|-------------|---|---------------|------------|---------------|
| | 25° | -86.4° | 25° | -86.4° |
| ... | 97.7 | 2.89 | ... | ... |
| 0.0089 | 202.5 | 6.61 | ... | 0.4 |
| 0.0242 | 408.8 | 14.83 | 0.66 | 0.35 |
| 0.0440 | 691.8 | 29.00 | 0.64 | 0.40 |
| 0.0899 | 1420 | 68.89 | 0.68 | 0.51 |
| 0.1317 | 2075 | 106.2 | 0.71 | 0.60 |
| 0.1681 | 2621 | 135.4 | 0.75 | 0.65 |

^a $m[I(SO_3F)_3] = 0.0687$.

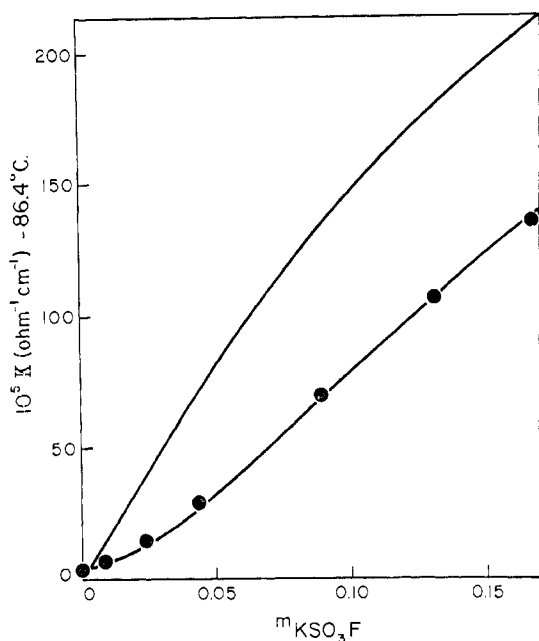
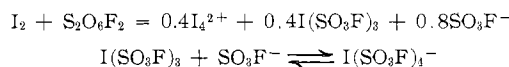


Figure 5.—Conductivities at -86.4° for addition of KSO_3F to $0.0687 \text{ m } I(SO_3F)_3$: —, calculated curve for $K_a = 50$ and $K_b = 2 \times 10^{-4}$; ●, experimental points.

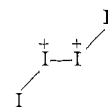
The conductivities of 1:1 I_2 - $S_2O_6F_2$ solutions are given in Figure 6 and Table VI. They are in excellent agreement with the conductivity expected from the equations



for which $\gamma = 0.8-0.4$ depending on the extent of formation of $I(SO_3F)_4^-$. The observed values of 0.75–0.72 at room temperature agree well with those obtained previously for the same concentration range and the values of 0.70–0.63 at -86.4° show the expected decrease with the increasing formation of $I(SO_3F)_4^-$ and are, in fact, in excellent agreement with conductivities calculated on the basis of $K_a = 50 \text{ mol}^{-1} \text{ kg}$ (Figure 6).

The 2:1 I_2 - $S_2O_6F_2$ solutions had conductivities which gave an essentially constant value of $\nu = 0.9$. The expected value for the formation of I_4^{2+} according to the equation $2I_2 + S_2O_6F_2 \rightarrow I_4^{2+} + 2SO_3F^-$ is 1.0. Perhaps there is still a small amount of disproportionation as observed at room temperature.

Conclusions.—The above spectroscopic, magnetic, cryoscopic, and electrical conductivity data establish clearly that the I_2^+ ion dimerizes extensively at low temperatures to give the I_4^{2+} ion. This new species is diamagnetic and has absorption bands at 470, 357, and 290 μ . The structure of the ion is not known at present but a tetrahedral structure, a square-planar structure, or an acyclic chain structure might appear reasonable. A simple qualitative molecular orbital treatment of tetratomic molecules based on s and p orbitals only leads to the conclusion that a stable tetrahedral molecule can contain a maximum of 20 valence electrons while a square-planar molecule can contain a maximum of 22 valence electrons. Since I_4^{2+} has 26 valence electrons, it would appear that it cannot have either a square-planar or a tetrahedral shape and the only possibility would be an acyclic chain, *i.e.*



However if d orbitals make an appreciable contribution to the bonding, this conclusion is no longer necessarily valid. For a tetrahedral molecule the bonding orbitals are a_1 , e, and t_2 , accommodating 12 electrons, and in addition there are 4 lone-pair orbitals a_1 and t_2 . The next lowest set of orbitals are probably the antibonding t_1 set, and, if these are stabilized by the contribution of d orbitals, then the tetrahedron could accommodate another 6 electrons, and a 26-electron system would represent a stable closed-shell configuration. Thus if d orbitals make a significant contribution to the bonding, it is possible that I_4^{2+} has a tetrahedral structure. The results of structural investigations on this ion will be of great interest.

Experimental Section

The methods used for the preparation of materials, the measurement of the conductivities and freezing points, and the calculation of ν and γ values have been given previously.^{1,5-7} I_2 - $S_2O_6F_2$ mixtures in exact stoichiometric ratios were added to

(6) J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Can. J. Chem.*, **46**, 149 (1968).

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

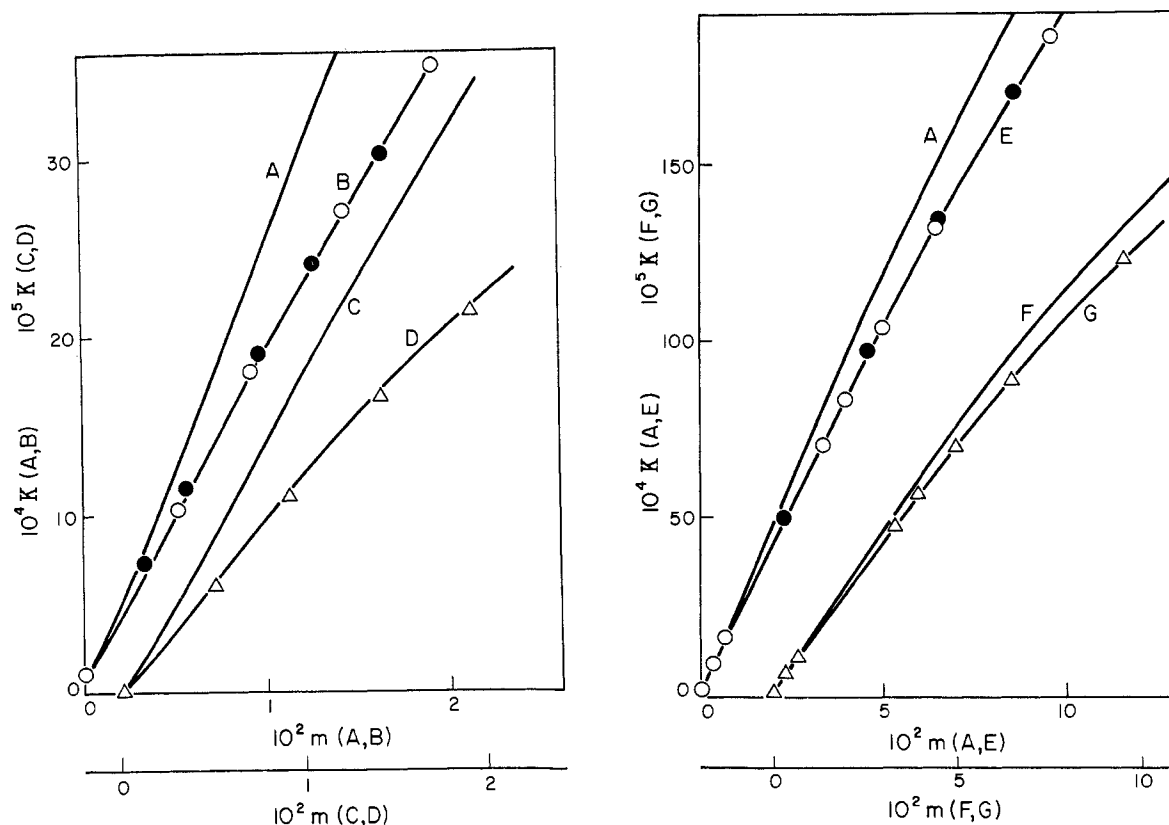


Figure 6.—Conductivities of I₂-S₂O₈F₂ solutions. Left side: A, KSO₃F (25°); B, 1:1 solutions (25°); ●, previous results; ○, this work; C, KSO₃F (-86.4°); D, 1:1 solutions (-86.4°). Right side: A, KSO₃F (25°); E, 2:1 solutions (25°); ●, previous results; ○, this work; F, *o*-phenylenediamine/2 (-86.4°); G, 2:1 solutions (-86.4°).

TABLE VI
CONDUCTIVITIES OF I₂-S₂O₈F₂ SOLUTIONS

| 10 ² m I ₂ | 10 ⁴ ohm ⁻¹ cm ⁻¹ | | γ | |
|----------------------------------|--|--------|------|--------|
| | 25° | -86.4° | 25° | -86.4° |
| 2:1 Solutions | | | | |
| ... | 1.11 | 0.007 | ... | ... |
| 0.031 | 8.96 | 0.588 | 0.85 | 1.0 |
| 0.063 | 15.95 | 1.078 | 0.85 | 1.0 |
| 3.31 | 70.68 | 4.75 | 0.87 | 0.92 |
| 3.95 | 83.42 | 5.67 | 0.87 | 0.92 |
| 4.96 | 103.3 | 6.99 | 0.87 | 0.90 |
| 6.46 | 131.6 | 8.82 | 0.87 | 0.90 |
| 9.52 | 185.7 | 12.23 | 0.87 | 0.91 |
| 1:1 Solutions | | | | |
| 0.0 | 1.14 | 0.007 | ... | ... |
| 0.518 | 10.28 | 0.599 | 0.75 | 0.70 |
| 0.926 | 18.11 | 1.100 | 0.74 | 0.66 |
| 1.435 | 27.10 | 1.649 | 0.73 | 0.65 |
| 1.930 | 35.20 | 2.135 | 0.72 | 0.63 |

the cryoscope or conductivity cell in the form of concentrated solutions in fluorosulfuric acid which were prepared in a drybox. Magnetic susceptibility measurements were made by the Gouy method using an Alpha Scientific Laboratory Model AL 7500 electromagnet, a Sartorius Vacuum Electrono microbalance, and a variable-temperature experimental arrangement built after a design from Earnshaw.⁸

The absorption spectra were taken on a Bausch and Lomb

Spectronic 505 or 600 spectrophotometer and quartz inserts were used to give path lengths down to 0.005 cm. The cells were clamped inside a quartz dewar with planar windows and cooled with a stream of nitrogen boiled off from a dewar. The temperature was measured with a thermocouple and could be controlled to 0.5° by adjusting the nitrogen flow. The spectra were very sensitive to traces of moisture, and the cells had to be vigorously dried and filled under very dry conditions in a drybox. The problem of adsorbed water was particularly serious when an insert was used to give very short path lengths because of the very large surface-to-volume ratio in the cell.

Theoretical conductivity curves for solutions obtained by adding KSO₃F to I(SO₃F)₃ were plotted from the expression

$$m_{KSO_3F} = \frac{\alpha[K_a\beta - (K_b/\beta)] + K_a\beta^2 + \beta + K_b}{1 + K_a\beta + (K_b/\beta)}$$

where α is the initial molality of I(SO₃F)₃, β is the molality of SO₃F⁻ in solution, and K_a and K_b are the acid and base equilibrium constants for I(SO₃F)₃. For I₂:S₂O₈F₂ = 1:1 and $K_a = 50$ mol⁻¹ kg

$$m_{I_2} = \frac{\beta(50\beta + 1)}{0.8 + 20\beta}$$

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(8) A. Earnshaw, private communication, Department of Chemistry, Leeds University.