The Iodine Cation I_2^+

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THE intensely blue coloured solutions obtained by dissolving iodine or iodine monochloride in 65% oleum[1] or in iodine pentafluoride[2] have a characteristic absorption spectrum consisting of three peaks at 640, 490, and 410 mμ. This spectrum has been attributed to the iodine cation I^+.[1,2] A blue solution having the same spectrum is also obtained by dissolving iodine monofluorosulphate in fluorosulphuric acid[3] or by treating iodine with $S_2O_6F_2$ in fluorosulphuric acid (Figure).

The results of cryoscopic and conductimetric measurements[4,5] on solutions of mixtures of iodine and $S_2O_6F_2$ in fluorosulphuric acid are summarised in the Table. They show that $I(SO_3F)_3$, I_3^+ and I_5^+ are formed in the 1 : 3, 3 : 1, and 5 : 1 mixtures respectively. In the 1 : 1 solution the formation of I^+ would give $\gamma = 2$.

$$I_2 + S_2O_6F_2 = 2I^+ + 2SO_3F^-$$

The observed value is much smaller than this although the solution had the spectrum shown in the Figure. Addition of iodine to this solution increases the intensity of each of the three peaks until at the composition of $2I_2/S_2O_6F_2$ their intensity is approximately doubled. This result and the γ-value of 1·0 for this solution leads us to the conclusion that I_2^+ is formed essentially quantitatively and that it is this ion that has the absorption spectrum in the Figure. Formation of I_2^+ together with $I(SO_3F)_3$ also accounts for $\gamma = 0{\cdot}8$

for the 1 : 1 solution. In both the 1 : 1 and the 2 : 1 solutions the value of γ decreases somewhat with increasing concentration and the spectrum of the 2 : 1 solution has a small peak at 300 mμ which may be attributed to I_3^+.[3,6] We conclude that I_2^+ disproportionates to an increasing extent with increasing concentration

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

TABLE

Mole ratio $I_2/S_2O_6F_2$	Observed ν	γ	Corresponding reaction
1 : 3	1·93	0·07	$I_2 + 3S_2O_6F_2 = 2I(SO_3F)_3$
3 : 1	1·26	0·66	$3I_2 + S_2O_6F_2 = 2I_3^+ + 2SO_3F^-$
5 : 1	0·84	—	$5I_2 + S_2O_6F_2 = 2I_5^+ + 2SO_3F^-$
1 : 1	—	0·8*	$5I_2 + 5S_2O_6F_2 = 4I_2^+ + 4SO_3F^- + 2I(SO_3F)_3$
2 : 1	—	1·0*	$2I_2 + S_2O_6F_2 = 2I_2^+ + 2SO_3F^-$

* Limiting values at low concentration.

The molar magnetic susceptibility of the 1 : 1 and 2 : 1 solutions was found to decrease with increasing concentration of iodine. This is ascribed to the above disproportionation reaction. Extrapolation of the data to infinite dilution gave $\chi_M(I_2^+) = 1650 \pm 130 \times 10^{-6}$. This gives a value for the magnetic moment of I_2^+ of 2·0 ± 0·1 B.M. I_2^+ would be expected to have a $^2\Pi_{3/2}$ ground state and a magnetic moment of 2·0 B.M.

We have also shown by similar methods that I_2^+ is formed when iodine is oxidised with iodic acid or with $K_2S_2O_8$ in solution in fluorosulphuric acid and when iodine is oxidised with sulphur trioxide in solution in disulphuric acid, or in 65% oleum. Previous evidence[6,7] that the blue species present in 65% oleum is I^+ was obtained from conductivity measurements in solutions of iodine in 65% oleum and from the observation that on dilution of the solvent to the composition ~96% H_2SO_4 approximately 80% of the iodine is recovered in the molecular form. It was assumed that the recovered iodine resulted from the disproportionation

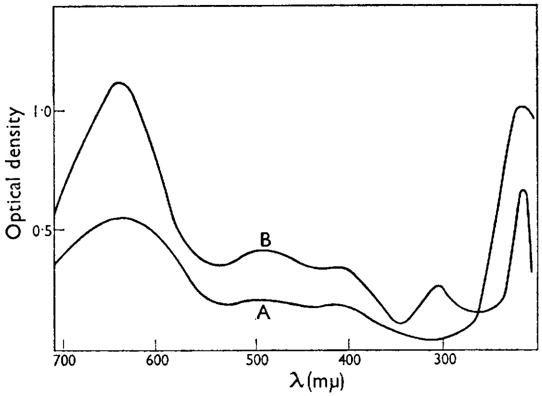
$$10\,I^+ \rightarrow 4I_2 + 2I^V$$

We have been unable to repeat the conductivity measurements and our own conductivity measurements in 65% oleum and in disulphuric acid lead us to the conclusion that I_2^+ is formed.[8] As iodine is stable in the +3 oxidation state in 96—100% H_2SO_4[7,9] the disproportionation that occurs on dilution of the solvent may be written as

$$6I_2^+ \rightarrow 5I_2 + 2I^{III}$$

which is also consistent with the recovery of approximately 80% of the iodine.

FIGURE



A 1 : 1 $I_2/S_2O_6F_2$ *solution*: *m* (I_2) = 0·0186: *path length* = 0·01 *cm.*

B 2 : 1 $I_2/S_2O_6F_2$ *solution*: *m* (I_2) = 0·0372: *path length* = 0·01 *cm.*

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[1] J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 1961, 12.
[2] E. Aynsley, N. N. Greenwood, and D. H. W. Wharmby, *J. Chem. Soc.*, 1963, 5369.
[3] F. Aubke and G. H. Cady, *Inorg. Chem.*, 1965, **4**, 269.
[4] J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, 1964, **3**, 1149.
[5] R. J. Gillespie, J. B. Milne, and R. C. Thompson, *Inorg. Chem.*, in the press.
[6] M. C. R. Symons, *J. Chem. Soc.*, 1957, 387.
[7] J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 1962, 2582.
[8] R. J. Gillespie and K. C. Malhotra, unpublished work.
[9] R. J. Gillespie and J. B. Senior, *Inorg. Chem.*, 1964, **3**, 972.