3. *Unstable Intermediates. Part XIII.* Iodine Cations in Solution.*

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Spectrophotometric, conductometric, and magnetic studies of solutions of iodine and iodine monochloride in 65% oleum show that only one iodine-containing species is formed; that the iodine is all in the +1 valency state; that the number of positive ions is equal to the number of iodine atoms; that the iodine-containing species has an intense absorption band at 640 mμ and relatively weak bands at 500 and 410 mμ; and that the effective magnetic moment is 1·5 B.M. per g.-atom of iodine.

Similar solutions have been prepared in fluorosulphonic acid and 100% sulphuric acid, but attempts to do so in sulphur trioxide, sulphuryl chloride, boron trichloride, and boron trifluoride–trifluoroacetic acid failed.

The simplest postulate is that all the iodine is converted into iodine cations having an electronic configuration $5s^25p^4$, subject to a large crystal-field stabilization and splitting of the electronic energy levels of the free cation by the surrounding solvent.

In previous papers, magnetic and spectrophotometric studies of blue solutions formed by reaction of iodine with oleum have been interpreted in terms of the formation of " free " iodine cations.[1-3] The term " free " implied that the iodine cations were not covalently bonded specifically to any nucleophile, although, in order for them to be formed at all, there must be very strong interaction with the solvent. That this must be the case can be deduced from a consideration of the changes in free energy involved.[4]

To explain the limited results then obtained, it was necessary to postulate at least two other species, namely, I_3^+, and an unidentified species containing iodine in the +1 valency state. I_3^+ was identified by comparison of the spectra of blue solutions in 65% oleum with those of brown solutions of iodine in dilute oleums.[2]

The aim of the present work was to obtain more information about these systems, particularly about the iodine cations, and to identify any other species present. Magnetic and spectrophotometric properties of solutions of iodine monochloride in various oleums and of iodine and iodine monochloride in fluorosulphonic acid and solutions of sulphur trioxide in sulphuryl chloride have been studied and conductivity in 65% oleum measured.

Experimental

Materials.—For most experiments " AnalaR " sulphuric acid was satisfactory. For spectrophotometry it was distilled, after refluxing, from potassium persulphate. This treatment decreased the optical density in the 200 mμ region to one-fifth (the O.D. at 200 mμ in a 1 cm. cell was 0·02). Oleums were prepared by addition of sulphur trioxide to purified sulphuric acid;[5] pure dry nitrogen was passed slowly through oleum previously freed from sulphur dioxide and kept at 40°, and then through sulphuric acid at 0°. Oleum concentrations were estimated by titration with water to minimum conductivity (100% H_2SO_4), a small conductivity cell fitted with short platinum wire electrodes about 4 cm. apart being used. This method was easier and more accurate than that used previously.[1]

Iodine monochloride was purified by the method of Buckles and Mills.[6]

Analyses.—The cycle from 100% sulphuric acid to concentrated oleum and back, described previously,[1] was repeated for solutions of iodine monochloride, and it was found that, in

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* Part XII, preceding paper.

[1] Symons, *J.*, 1957, 387.
[2] Symons, *J.*, 1957, 2186.
[3] Connor and Symons, *J.*, 1959, 963.
[4] Bell and Gelles, *J.*, 1951, 2734.
[5] Arotsky and Symons, *Trans. Faraday Soc.*, 1960, **56**, 1426.
[6] Buckles and Mills, *J. Amer. Chem. Soc.*, 1953, **75**, 552.

contrast to iodine, the iodine monochloride used to prepare the blue solutions was recovered quantitatively in its molecular form.

In terms of the postulate that iodine cations are formed, the reactions involved are, presumably:

$$ICl + H_2S_2O_7 + SO_3 \longrightarrow I^+ + HS_2O_7^- + H{\cdot}SO_3Cl \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$I^+ + H{\cdot}SO_3Cl + HS_2O_7^- + 2H_2O \longrightarrow ICl + 3H_2SO_4 \quad . \; . \; . \; . \; . \; . \quad (2)$$

Iodine monochloride was estimated spectrophotometrically at **442** mμ, our data being very similar to those of others.[6] The cycle for iodine was repeated, and the previous results [1] were confirmed. In this instance the reaction sequence is:

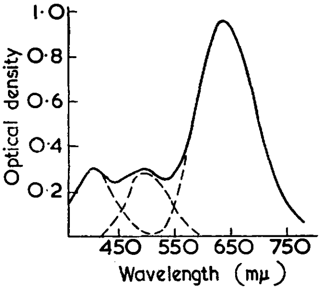
$$I_2 + H_2S_2O_7 + 3SO_3 \longrightarrow 2I^+ + SO_2 + 2HS_2O_7^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$5I^+ + 8H_2O + 5HS_3O_7^- \longrightarrow 2I_2 + HIO_3 + 10H_2SO_4 \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

and, provided the estimation is carried out promptly after dilution, the dissolved sulphur dioxide does not interfere.

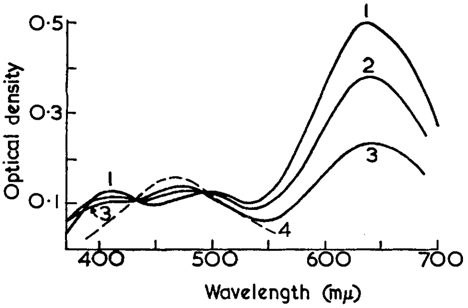
Other results which also show that all the iodine in the blue solutions is in the +1 valency state are given in the next section.

FIG. 1. *Electronic spectrum assigned to the iodine cation.*



The broken curves were derived by the method given in the Experimental section.

FIG. 2. *The effect of changing the medium on the spectrum of iodine.*



(1) 65% *oleum*; (2) 36% *oleum*; (3) 25% *oleum*; (4) *theoretical curve for* I_3^+.

Spectrophotometry.—Spectra were measured by using Unicam S.P. 500, S.P. 600, and S.P. 700 spectrophotometers. The results are summarized in Tables 1 and 2 and Figs. 1 and 2.

TABLE 1. *Spectrum assigned to the iodine cation in* 65% *oleum.*

10^{-5} $E_{max.}$ (cm.$^{-1}$)	1·57	2·00	2·44
10^{-2} $\varepsilon_{max.}$	18·5	4·6	4·9
10^{-4} $\Delta\frac{1}{2}$ (cm.$^{-1}$)	1·23	1·50	1·70

$\Delta\frac{1}{2}$ = Total width at half height.

TABLE 2. *Details of solutions of iodine and some of its compounds in various electrophilic solvents.*

Solvent	Source of iodine	Oxidant	Colour	Values for $\lambda_{max.}$ (mμ)
65% Oleum	I_2	SO_3	Blue	As Fig. 1, + band at 280 mμ (SO_2)
65% Oleum	ICl	—	Blue	As Fig. 1
H_2SO_4	I_2	HIO_3	Green	650, 460, 290
H_2SO_4	ICl	—	Brown	442, 240
$HFSO_3$	I_2	$K_2S_2O_8$	Green	642, 460
$HFSO_3$	ICl	—	Blue	—
H_2O–SO_3–SO_2Cl_2	ICl	—	Blue	645, 500, 400
HCl–BCl_3	I_2	$K_2S_2O_8$	Brown	—
BF_3–$CF_3{\cdot}CO_2H$	I_2	$K_2S_2O_8$	Brown	—
BF_3–$CF_3{\cdot}CO_2H$	ICl	—	Brown	—

Precise identification of the band maxima is rendered difficult because the bands overlap considerably. An early attempt to interpret the spectrum of iodine in 65% oleum was based upon the assumption that each band was symmetrical.[2] The spectra have now been analysed by assuming that each curve approximates to a Gaussian error curve with an equation:

$$\varepsilon = \varepsilon_0 \exp[-\alpha(\nu - \nu_0)^2]$$

where ε and ε_0 are the molar extinction coefficients at wave-numbers ν and ν_0 cm.$^{-1}$ respectively, ν_0 referring to the band maxima. Details are given in Table 1, and it will be seen that the bands previously thought to have maxima at 470 and 300 mμ are more accurately described by maxima at 500 and 280 mμ. Thus the original identification of this doublet as a property of I_3^+ was wrong. Absence of the 280 mμ band from solutions of iodine monochloride or iodine and iodate in oleum suggests strongly that this band is due to dissolved sulphur dioxide, which has an absorption band in this region and is extremely soluble in oleum.[7] Using 360 for the molar extinction coefficient of sulphur dioxide [7] at 280 mμ, we estimate from the spectrum of solutions of iodine in 65% oleum that the stoicheiometry is that required by equation (3) within ±10%.

A large number of spectra have been recorded over a wide range of conditions: after allowance for the presence of other bands such as those at 280 mμ for sulphur dioxide and at 290 and 460 mμ assigned to I_3^+,[2] the ratios of the optical densities for the three bands at 410, 500, and 640 mμ were constant. Thus, when the concentration of "free" sulphur trioxide was varied from 40% to 70%, when the temperature was changed from 12° to 40°, and when a large excess of various compounds such as sodium chloride, potassium pyrosulphate, or boric acid was added, the ratios of band heights were unaltered, within the limits of measurement. Other changes were observed under certain of these conditions, but we defer their discussion to a later paper.

By treating iodine with an equivalent of iodate we prepared blue solutions, characterized by the intense band in the 640 mμ region, in dilute oleums and even in 100% sulphuric acid. Similar blue solutions were obtained in anhydrous fluorosulphonic acid, but not in the other solvents listed in Table 2. Although no attempt has been made to elucidate the nature of the brown solutions formed, their appearance was similar to that of solutions of I_3^+ in sulphuric acid and we consider that this ion may be an important constituent in several of these solutions. Addition of dry sodium persulphate or iodine pentoxide to iodine in sulphur trioxide gave a yellow solid probably containing tervalent iodine; [2] but no blue colour was observed at any stage. If, however, a trace of water was also admitted into the system, a heavy, insoluble, dark blue oil separated, leaving a clear upper layer of sulphur trioxide. Similarly, the blue species was formed when water was added to solutions of iodine monochloride in sulphuryl chloride–sulphur trioxide mixtures.

Beer's law was accurately obeyed for solutions in oleum which were free from I_3^+, and the extinction coefficients given in Table 1 were calculated on the assumption that all the iodine introduced was present as monomeric, univalent iodine. That only one species is present in these solutions is also indicated by the two isosbestic points (Fig. 2) found when solutions obtained from iodine were diluted with moist sulphuric acid.

Conductance Measurements.—Conventional cells were used since the conductivity of oleum in the 65% region is about 100-fold smaller than that of 100% sulphuric acid. The cells, which have been described,[5] were fitted with a device for adding solutes and mixing solutions out of contact with the atmosphere. Cell constants were determined with aqueous potassium chloride, and the oleums were calibrated with sodium hydrogen sulphate or potassium chloride.[5] All measurements were at 25·00° ± 0·01°.

As with sulphuric acid,[8] plots of the concentration of added electrolyte against specific conductance are linear, after initial deviations. The results for a wide range of salts were independent of the nature of the added ions, and it was concluded that the observed conductivities were almost entirely due to $HS_2O_7^-$ ions, formed by reaction between solvent and solute.[5] Results obtained for iodine, iodine chloride, and potassium iodide are presented in Fig. 3. From the slopes of these plots, we deduce that for every molecule of solute, two, one, and two $HS_2O_7^-$ ions are formed, respectively, in accord with equations (1), (3), and (5).

$$I^- + 3SO_3 + H_2S_2O_7 \longrightarrow I^+ + SO_2 + 2HS_2O_7^- \qquad (5)$$

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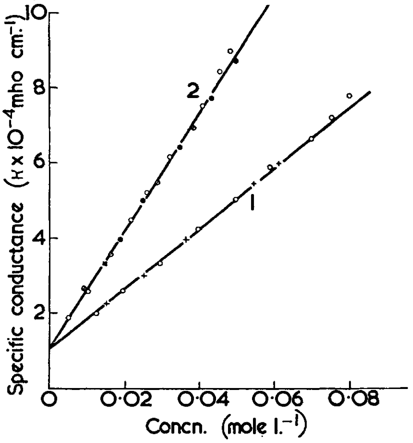
[7] Gold and Tye, *J.*, 1950, 2932.

[8] Gillespie and Robinson, "Advances in Inorganic and Radiochemistry," Vol. I, p. 385, Academic Press Inc., New York, 1959.

In these reactions sulphur trioxide is consumed, and a correction has been made to accommodate this, based on experiments made on a range of oleums of different strengths.[5] This correction is negligible for any but the highest concentrations reported in this work, provided the initial strength of the solvent was greater than 50%. Thus in this range of oleums, one cannot, by measurements of conductivity, detect with any accuracy a change in the composition of the medium. This is not the case for dilute oleums $<15\%$), and we show in a subsequent paper that use can be made of this fact to give information about solutions in dilute oleums.

In these, as in the spectrophotometric studies, it was necessary to ensure that I_3^+ was absent before concordant results were obtained. Thus, plots of the type shown in Fig. 3, constructed from data obtained from freshly prepared solutions, had slopes which were some 10—20% lower than required by theory. Spectral measurements showed that the trough between the 410 and the 500 mμ band was shallower than usual for such solutions and, with the assumption that this was due to small amounts of I_3^+ which has a band at 460 mμ, the anomalous conductivities were quantitatively accommodated.

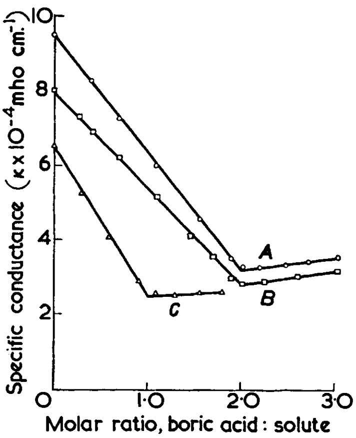
FIG. 3. *Equivalent conductance as a function of concentration of various electrolytes in* 65% *oleum.*



$KHSO_4$ *reacts to give one* $HS_2O_7^-$ *ion per mole;* K_2SO_4 *reacts to give two ions per mole.*

(1){○ $KHSO_4$ / × ICl (2){○ K_2SO_4. ◑ I_2 / ● KI

FIG. 4. *Conductometric titration plots.*



(*A*) 0·0525M-KI *solution in* 65% *oleum* + *boric acid.*
(*B*) 0·043M-I_2 *solution in* 65% *oleum* + *boric acid.*
(*C*) 0·0675M-ICl *solution in* 65% *oleum* + *boric acid.*

It has been shown that boron trichloride or boric acid has a negligible effect on the conductivity of 65% oleum.[5] The resulting solutions are thought to contain $B(HS_2O_7)_3$, by analogy with reactions in sulphuric acid.[8] These solutions reacted as weak "acids" towards $HS_2O_7^-$ ions:

$$B(HS_2O_7)_3 + HS_2O_7^- \rightleftharpoons B(HS_2O_7)_4^- \qquad (6)$$

Thus, addition of solutions of boric acid to solutions of iodine in oleum decreased the conductivity and enabled the $HS_2O_7^-$ ions to be estimated by an independent method. Again, the results were in accord with the requirements of equations (1), (3), and (5) (cf. Fig. 4).

Magnetic Susceptibility.—A conventional Gouy susceptibility balance was used, incorporating a type A electro-magnet supplied by Newport Instruments Ltd., giving a field of 15 kgauss with a current of 10 amp. and a 2 cm. pole gap. The magnet current was stabilized to 1 part in 10^4 parts with a type B.5 power supply. A 1·0 ohm resistance was wired in series with the magnet, measurements of the potential across this resistance being used to estimate the current to 1 part in 10^4. Currents of greater than 10 amp. were used so that the magnet was saturated and small variations in current resulted in only very small fluctuations in the magnetic field. An Oertling-type 146 semimicro-balance was used to measure the force, and the sample was suspended from this with a light gold chain. The balance was calibrated with air-free water.

The results of several measurements are given in Table 3: they are in good agreement with an estimate made from the shift in the proton resonance absorption of solutions of iodine in oleum relative to that for the pure solvent,[3] and it seems that the original estimate of 1·9 B.M. was somewhat high.[1] High precision is not possible for solutions in the concentration range used previously,[1] since the estimates rest upon small differences between large weights, and diamagnetic corrections are somewhat uncertain. Therefore the data summarized in Table 3 were obtained with more concentrated solutions (0·1—1·0M).

TABLE 3. *Summary of the magnetic moments assigned to the solvated iodine cation.*

Source	I_2 in 65% oleum	ICl in 65% oleum	I_2 in 65% oleum
Method	Gouy	Gouy	N.M.R.
μ (B.M.)	1·44	1·54	1·50

DISCUSSION

Evidence for the Formation of the Iodine Cation.—Summarizing the results, we can assign the following properties to the blue solutions under consideration: (i) spectrophotometric results strongly suggest that there is a single constituent containing iodine, responsible for the bands at 640, 500, and 410 mμ. (ii) Analyses show conclusively that all the iodine is in the +1 valency state. (iii) Conductometric studies show that there is a single positive charge per iodine atom. (iv) Nuclear magnetic resonance studies show that this species is not protonated,[3] and also, combined with measurements of magnetic susceptibility, (v) that the species involved is paramagnetic.

These five results are all consistent with the concept that the blue species is the iodine cation, I^+, provided that interaction with solvent is such that three low-energy electronic transitions, one of considerable intensity, and an effective magnetic moment of about 1·5 B.M., can be explained. Before this is attempted, some alternatives will be discussed.

Alternative Interpretations.—Although attractive for various reasons, the species HI^+, I_2^+, I_2^{2+}, $HISO_4$, and HIS_2O_7 cannot be important constituents of the blue solutions since their properties are incompatible with one or other of results (i)—(v) above. However, the suggestion made earlier,[2] that ISO_3^+ is formed, requires detailed consideration. As will be shown below, the spectrophotometric and magnetic properties are interpretable, and each of the results (i)—(v) is accommodated, in terms of this formulation.

However, this alternative is no better than the simpler concept that solvated iodine cations are formed and the following properties of these solutions do not seem to be in accord with it. (i) Since iodine cations and sulphur trioxide are extremely powerful electrophiles, it is unlikely that they will bond strongly together, and hence (ii) it is hard to understand how ISO_3^+ can be formed in 100% sulphuric acid or fluorosulphonic acid since competing reactions between sulphur trioxide and water or hydrogen fluoride are strongly exothermic. Also, in dilute oleum, superimposed upon the normal reactions required to give iodine in the +1 valency state, reactions to give ISO_3^+ would give a readily detectable change in conductivity owing to reactions such as

$$H_2S_2O_7 + I^+ \longrightarrow H_2SO_4 + ISO_3^+ \quad . . . . (7)$$

$$H_2S_2O_7 + H_2SO_4 \longrightarrow HS_2O_7^- + H_3SO_4^+ \quad . . . . (8)$$

Detailed conductometric studies on solutions in dilute oleums, to be reported shortly, show that reactions (7) and (8) are insignificant. (iii) We have been unable to prepare the blue species in sulphur trioxide. This result is readily explained if this species is the iodine cation, which is unstable in the absence of a shell of polar solvent molecules, but is hard to understand if the species is ISO_3^+.

Electronic Transitions of Solvated Iodine Cations.—Since all the states of configuration

$5s^2,5p^4$ have the same parity, only quadrupole or magnetic dipole transitions are allowed. In a weak field these selection rules still hold, and the p-levels are not split by a symmetric cubic field. However, since two of the three $5p$-levels are only half filled, one would not expect to find the negative dipoles of the solvent surrounding the iodine cation exerting a symmetrical field. Rather, the filled level (p_z, say) will be avoided relative to the half-filled levels (p_x and p_y). This will tend to lower the energy of this level below that of the level in which the filled orbital is either p_x or p_y. The effect is similar to that of a linear Stark field on the $(p)^2$-configuration, and for convenience we will describe these levels as $^3\Sigma^-$ and $^3\Pi_i$ respectively.

Since the model still has inversion symmetry, $^3\Pi_i \longleftarrow {}^3\Sigma^-$ transitions are forbidden. The intensity can be greatly increased by further distortion such as to destroy the inversion symmetry, or by mixing the p-states with orbitals of opposite parity, such as the $5d$-level. Yet another way of increasing the intensity would be by charge-transfer from oriented solvent molecules.

The $^3\Pi$ level will be split into $^3\Pi_2$, $^3\Pi_1$, and $^3\Pi_0$, of which $^3\Pi_2$ should lie nearest to the ground state. According to Jevons,[9] the splitting between the $^3\Pi_2 \longrightarrow {}^3\Sigma^-$, $^3\Pi_1 \longrightarrow {}^3\Sigma^-$, and $^3\Pi_0 \longrightarrow {}^3\Sigma^-$ transitions should be equal, and approximately half the $^3P_2 - {}^3P_1$ separation for the ion in zero field.

Turning to the iodine cation, we tentatively suggest that the bands at 640, 500, and 410 mμ are in fact the three $^3\Pi_i \longrightarrow {}^3\Sigma^-$ transitions. The lowest-energy transition is far more intense than the others, as is required by theory, and the separation between the bands is 4400 cm.$^{-1}$ in each case. This is close to the value of 3600 cm.$^{-1}$ predicted from the known separation between the $^3P_2$ and $^3P_1$ levels of the free cation.[10] It therefore seems that all the spectral features assigned to the iodine cation are well accommodated by a simple model of a solvation shell in which there is close approach of, say, four molecules lying in a plane.

So far as we are aware, this is a novel application of crystal-field theory to a p-electron problem.

Magnetic Susceptibility of Iodine Cations.—The value of about 1·5 B.M. found for the iodine cation is very small for a system with two unpaired electrons. However, unexpectedly low values are also found for d-electron systems of the second- and third-row transition metals, and this has prompted us to see if the effect of a solvent field, such as that invoked to explain the spectrum of the iodine cation, might not also explain the small value found for its magnetic moment.

If we use a value of ζ, the spin-orbit coupling constant, of 3600 cm.$^{-1}$ estimated from the spectrum, then the magnetic moment μ should be, by adaptation of Kotani's theory,[11] about 1·4 B.M. at room temperature. Thus the $(p)^4$-configuration is equivalent to the $(t_{2g})^2$-configuration of transition-metal complexes. This comparison is very crude, and should be modified to accommodate the expected deviations from Russell–Saunders coupling and from cubic symmetry. However, the result strongly suggests that the low value obtained is, in fact, only to be expected for iodine cations in a strongly dipolar medium.

We conclude that all the results accumulated so far can readily be accommodated by the postulate that iodine cations are formed. However, as suggested above, the spectral results can also be explained if the ion ISO_3^+ is formed. If we neglect the possibility of π-bonding in this ion, then the effect of sulphur trioxide on the electrons of the iodine cation will be exactly the same as that outlined for the solvent field, and hence, with respect to the iodine–sulphur bond, there will be a $^3\Sigma$ and three $^3\Pi$ states as before. Thus the ion ISO_3^+ could possibly be paramagnetic and have three transitions of the type found

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[9] Jevons, "Report on Band Spectra of Diatomic Molecules," Physical Society, London, 1932, p. 100.

[10] Murakawa, *Z. Physik*, 1938, **109**, 162.

[11] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

experimentally. However, in view of the chemical arguments made earlier, this postulate is not favoured.

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