1025. *The Iodine Cation,* I$^+$, *in Iodine Pentafluoride.*

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The stable blue solutions formed by dissolving iodine or iodine monochloride in iodine pentafluoride have been shown by spectroscopic, magnetic, and conductometric measurements to contain the I$^+$ cation. The similarity between these solutions and those of iodine in oleum confirm the supposition that the coloured species in oleum is also I$^+$ rather than ISO_3^+. These observations clarify the origin of the transient blue coloration which is frequently observed during the preparation of iodine pentafluoride.

Ruff and Braida [1] reported that, when iodine was fluorinated by means of a mixture of fluorine and nitrogen, a brown solution of iodine in iodine pentafluoride was formed. In decolorising this by further addition of fluorine, a temporary blue colour was sometimes observed but no explanation of this was offered. Later work [2] confirmed the appearance of blue colours which were sometimes transient,[3] and these were ascribed to the presence of a lower fluoride of iodine, possibly iodine trifluoride.[3] Iodine itself usually dissolves in the pentafluoride to give a chocolate-brown solution.[3-5] The present work defines the conditions under which either brown or blue stable solutions of iodine in iodine pentafluoride can be formed and proves that the coloured species in the blue solutions is the unco-ordinated, univalent iodine cation, I$^+$.

Pure iodine pentafluoride is a colourless liquid which absorbs intensely in the ultraviolet region. This absorption has been studied qualitatively in the gas phase [6] and was thought to be continuous below a critical frequency of 47,500 cm.$^{-1}$ at 16° and 43,200 cm.$^{-1}$ at 60°. In the present work, complete absorption in liquid iodine pentafluoride occurred below 26,700 cm.$^{-1}$ for a 10-mm path-length and below 29,200 cm.$^{-1}$ for a 2-mm. path-length. Gaseous iodine pentafluoride at ~20 mm. pressure was found to have a well-defined absorption maximum at 51,700 cm.$^{-1}$ ($\varepsilon \sim 850$; oscillator strength, $f \sim 0{\cdot}035$) as shown by the left-hand curve in the Figure.

When iodine was dissolved in iodine pentafluoride in strictly anhydrous conditions, brown solutions were always obtained and these were stable indefinitely to sunlight, ultraviolet light, and mild heat, provided no trace of moisture was present. Such solutions showed an absorption maximum at 483 mμ (20,700 cm.$^{-1}$), typical of iodine in solvents of

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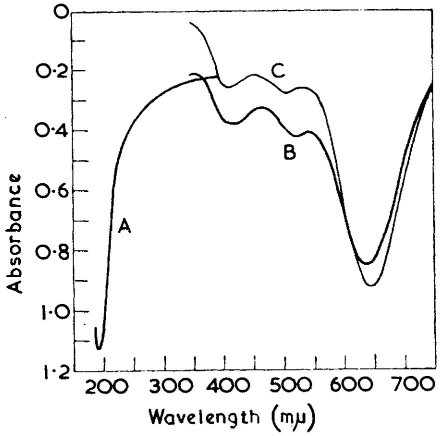
[1] Ruff and Braida, *Z. anorg. Chem.*, 1934, **220**, 43.
[2] Lord, Lynch, Schumb, and Slowinski, *J. Amer. Chem. Soc.*, 1950, **72**, 522.
[3] Aynsley, Nichols, and Robinson, *J.*, 1953, 623.
[4] Moissan, *Compt. rend.*, 1902, **135**, 563.
[5] Banks, Emeléus, and Woolf, *J.*, 1949, 2861.
[6] White and Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 1049.

moderate co-ordinating power,[7] such as xylene (485 mμ) and pyridine (480 mμ). This is consistent with the known tendency of iodine pentafluoride to act as an electron-pair donor to very strong acceptors such as antimony pentafluoride.[8] An alternative possibility is that the absorbing species is the I_3^+ ion, though this seems less likely since the absorption maximum of this species occurs at 460 mμ.[9]

When a brown solution of iodine in iodine pentafluoride was exposed momentarily to water vapour in the atmosphere and the container was then resealed, the solution slowly became blue. The reaction could be followed spectrophotometrically and, depending on the amount of moisture, the transition required weeks, days, or only hours for completion. Once formed, the blue solutions were stable to heat and light, and the colour did not change even on prolonged exposure to the atmosphere, though, of course, the solvent slowly hydrolysed and deposited a white powder of iodine oxide fluorides. It appears that oxidation of iodine by the pentafluoride is catalysed by moisture or by traces of hydrogen fluoride formed by hydrolysis of the pentafluoride, but that in the absence of such a catalyst molecular iodine is stable indefinitely in the pentafluoride.



Ultraviolet and visible absorption spectra of (A) IF_5 (gas), (B) I^+ in IF_5, and (C) I^+ in oleum.

The visible absorption spectrum of the blue solution is shown in the Figure, where it is compared with the spectrum of iodine in 67% sulphuric acid oleum. The close similarity is further emphasised by the detailed spectroscopic data summarised in the Table. The Table also includes published values for oleum solutions which have been shown [9,10] to contain the I^+ cation. Iodine pentafluoride is thus the second known solvent which is compatible with this cation and is, in fact, the first pure compound capable of acting in this way. In common with oleum, it has the required characteristics of a high dielectric constant to promote ionic dissociation, low co-ordinating power to prevent the formation of a complex, and only mild oxidising power (insufficient to generate higher oxidation states).

Visible spectra of blue solutions of iodine.

$\lambda_{max.}$ (mμ)			$\nu_{max.}$ (cm.$^{-1}$)			$\varepsilon_{max.}$		
IF_5	oleum	ref. 9	IF_5	oleum	ref. 9	IF_5	oleum	ref. 9
418	413	417	23,900	24,200	24,000	301	355	490
508	507	500	19,700	19,700	20,000	326	369	460
641	648	637	15,600	15,400	15,700	884	1280	1850

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[7] Gmelin, " Handbuch der Anorganischen Chemie," Syst. No. 8, " Iod."
[8] Woolf, *J.*, 1950, 3678.
[9] Arotsky, Mishra, and Symons, *J.*, 1961, 12.
[10] Arotsky and Symons, *Quart. Rev.*, 1962, **16**, 252.

The spectrum of the iodine cation in iodine pentafluoride consists of three equally spaced bands, as required for a spectrum which arises from the ligand-field splitting of the three *p*-orbitals into a lower singlet and an upper doubly degenerate pair.[9] The spacing between the bands corresponds to the spin–orbit coupling energy and is 4150 cm.$^{-1}$ (11·9 kcal./g.-ion). The lowest-energy transition (15,600 cm.$^{-1}$, 44·6 kcal./g.-ion) is the most intense, as expected, and corresponds to the ligand-field splitting of the *p*-orbitals; as the I^+ cation has four *p*-electrons, it follows that the ligand-field stabilisation energy of the ground state is approximately two-thirds of this, *i.e.*, 29·8 kcal./g.-ion. It is perhaps surprising that the ligand-field splitting effected by unsymmetrical solvation with iodine pentafluoride is so close to that effected by oleum, as shown in the Table.

The half-band width, $\Delta\nu_{\frac{1}{2}}$, for the most prominent band at ~15,500 cm.$^{-1}$ is 3140 cm.$^{-1}$ for the iodine pentafluoride solution and 3060 cm.$^{-1}$ for the oleum solution. By means of the relation $f \approx 4{\cdot}6 \times 10^{-9}\varepsilon_{\text{max.}} \cdot \Delta\nu_{\frac{1}{2}}$, the oscillator strength, *f*, for the I^+ cation is calculated to be 0·013 in iodine pentafluoride and 0·018 in oleum solutions. These are moderately large values for a transition which becomes allowed only when the inversion symmetry of the electronic states is distorted.

The calculation of $\varepsilon_{\text{max.}}$ implies a knowledge of the concentration of the absorbing species. The simplest proposal is that iodine pentafluoride oxidises iodine to I^+ and is itself reduced to the same oxidation state:

$$IF_5 + 2I_2 = 5[I^+F^-] \quad \ldots\ldots \quad (1)$$

On this basis each mole of iodine, I_2, gives rise to 2·5 g.-ions of the cation I^+. The fluoride ion is known [11,12] to be a strong ligand towards the pentafluoride and is therefore considered to form a complex, as IF_6^-:

$$6IF_5 + 2I_2 = 5I^+ + 5IF_6^- \quad \ldots\ldots \quad (2)$$

This description of the blue solutions implies that the dissolved species, $I^+IF_6^-$, is, in a sense, the trifluoride of iodine, as originally suggested.[3]

Consistently with reaction (2), addition of potassium fluoride to a blue solution of iodine in iodine pentafluoride resulted in the solution's becoming brown again; potassium fluoride forms a complex with the solvent, enhancing the concentration of the IF_6^- ion,[11] and this forces the equilibrium towards the left-hand side. An alternative scheme, which is considered less likely, is reduction of the pentafluoride to the +3 state:

$$4IF_5 + 3I_2 = 5I^+ + 5IF_4^- \quad \ldots\ldots \quad (3)$$

Blue solutions of the iodine cation in oleum are stated to be paramagnetic with a magnetic moment of 1·5—1·9 B.M.,[10,13] and this has been confirmed in the present work. Magnetic measurements on the blue solutions in iodine pentafluoride also reveal the presence of a paramagnetic species and, on the assumption that all the iodine reacts according to equation (2), the derived magnetic moment, when corrected for the actual diamagnetic contribution of the solvent, is ~2 B.M. at room temperature.

Blue solutions of iodine in iodine pentafluoride had a higher electrical conductivity than that of the pentafluoride itself. The pure solvent has a conductivity [14] of $5{\cdot}4 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ at 25° and this was increased by a factor of 8 when about 2 mg. of iodine per ml. were dissolved to give a blue solution. Electrolysis in a three-compartment cell resulted in the migration of the blue colour towards the cathode as expected. With pure iodine pentafluoride in the cathode and the anode compartment, and the blue solution in the central compartment, this migration could be clearly seen with currents of the order of 0·1 milliamp. In addition, iodine was deposited at the cathode (as in the electrolysis

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[11] Emeléus and Sharpe, *J.*, 1949, 2206.

[12] Hargreaves and Peacock, *J.*, 1960, 2373.

[13] Symons, *J.*, 1957, 387.

[14] Rogers, Spiers, Panish, and Thompson, *J. Amer. Chem. Soc.*, 1956, **78**, 936.

of pure iodine pentafluoride itself[15]) and this dissolved in the catholyte to give a solution which was initially brown. Reversal of the direction of the current led to the gradual disappearance of this colour, to the migration of the deep blue cations through the central compartment, and their discharge at the new cathode to give a brown solution. Fluorine was evolved at the anode. As the solvent underwent electrolysis simultaneously, the intensity of the blue colour increased progressively, owing to the increasing concentration of iodine cations formed by the slow reaction of the deposited iodine with the solvent. These processes can be summarised as follows:

Self-dissociating solvent: $2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

Blue solute (equation 2): $6IF_5 + 2I_2 = 5I^+ + 5IF_6^-$

Cathode reactions: $5IF_4^+ + 5e = 4IF_5 + \frac{1}{2}I_2$

$I^+ + e = \frac{1}{2}I_2$

Anode reaction: $IF_6^- - e = IF_5 + \frac{1}{2}F_2$

The migration of the coloured iodine cations could not be observed in oleum solutions because of the abnormally high mobility of the $HS_2O_7^-$ ion which carried virtually all the current by a proton-switch mechanism.[16] Nevertheless, it was shown[9] that the coloured species must either be unsolvated ion I^+ or the co-ordinated species ISO_3^+, but it was difficult to decide definitely between these alternatives.[10] The present work establishes that the solute is the unco-ordinated I^+ in both oleum and iodine pentafluoride, since there is no possibility of solvation by sulphur trioxide in iodine pentafluoride, and the detailed spectroscopic and magnetochemical similarity between the blue solutions in the two solvents is a strong argument for the presence of a species common to both.

Iodine monochloride also gave blue, paramagnetic solutions in iodine pentafluoride. the absorption peaks occurring at 420, 515, and 645 mμ for this solute. There was no spectroscopic evidence for undissociated molecular iodine monochloride, the visible spectrum of which is well known.[17] Iodine pentafluoride has a dielectric constant[14] of 37·5 at 18° and this, coupled with its low-co-ordinating power, enables it to dissolve the monochloride as unco-ordinated I^+Cl^-. This behaviour is paralleled by oleum solutions of iodine monochloride.[9]

The ability of iodine pentafluoride to dissolve iodine cations may account for some reactions of the pentafluoride which are otherwise difficult to explain. For instance, when iodine pentafluoride was mixed with benzene at room temperature, the product contained no fluorine derivatives of benzene but was mainly iodobenzene, together with a small amount of di- and tri-iodobenzene;[18] it is possible that the pentafluoride is reduced by benzene to the +1 state and that the powerful nucleophile I^+ iodinates the benzene more rapidly than the benzene can be fluorinated by the pentafluoride. Again, a mixture of one mol. of iodine pentafluoride and two mol. of iodine reacts smoothly with olefins to give the corresponding fluoroiodoalkanes.[19] For example, $CF_3{\cdot}CF{:}CF_2$ gave $CF_3{\cdot}CFI{\cdot}CF_3$ in 99% yield. As nucleophilic addition to fluoro-olefins is known to occur very readily, it appears that the reagent is effectively I^+F^-, as shown in equation (1).

[*Added, June* 12th, 1963.] Since this paper was submitted it has been suggested[20] that the blue colour of iodine solutions in oleum cannot be interpreted in terms of the ligand-field splitting of *p*-orbitals. It was pointed out that the ligand field due to a single co-ordinated negative group would stabilise the $p_{\pm 1}$-orbitals and destabilise the p_0-orbital,

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[15] Banks, Emeléus, and Woolf, *J.*, 1949, 2861.

[16] Arotsky and Symons, *Nature*, 1962, **193**, 678.

[17] Greenwood, *Rev. Pure Appl. Chem.*, 1951, **1**, 84.

[18] Ruff and Keim, *Z. anorg. Chem.*, 1931, **201**, 245.

[19] Chambers, Musgrave, and Savory, *J.*, 1961, 3779.

[20] Pasternak and Piper, *Inorg. Chem.*, 1963, **2**, 429.

thus leading to a $^3\Pi$ ground state. This orbital diagram, though correct, is irrelevant to the problem since the ligand field considered here is that due to preferential solvation in the *xy*-plane; this stabilises p_0, destabilises $p_{\pm 1}$ and leads to a $^3\Sigma$ ground state. The first-mentioned orbital energy-level diagram is obtained by inverting the second.

EXPERIMENTAL

Iodine pentafluoride was prepared on the 400-g. scale (120 ml.) by passing fluorine, diluted with dry oxygen-free nitrogen, over a bed of iodine (resublimed from potassium iodide) in an all-glass apparatus previously flamed and purged with nitrogen. The fluorine was prepared by electrolysis, by means of a 10-amp. cell which had been kindly made available by Imperial Chemical Industries Limited, General Chemicals Division, Widnes, and was freed from hydrogen fluoride and other impurities by sodium fluoride and a liquid-oxygen trap. The iodine was gently warmed to initiate the self-sustaining reaction, after which it burned in fluorine with a pale yellow flame. The distillate was dark brown and was decolorised by agitating it gently in a stream of fluorine; it became successively brown, green, pale yellow, and colourless. The apparatus was then cooled in liquid oxygen, evacuated, and sealed and the iodine pentafluoride was redistilled under a static vacuum into a series of traps each with its own break-seal. It is important to avoid the presence of both mercury and tap grease during the final purification.

Solutions of iodine in iodine pentafluoride were prepared in a vacuum system by subliming a known weight of iodine into a tube and then condensing this iodine and an appropriate volume of the pentafluoride from a break-seal vessel into a trap cooled in liquid nitrogen, the final transfers being made in a grease-free system. When required, the weight of iodine pentafluoride was obtained at the end of an experiment by weighing the trap before and after emptying it.

Iodine monochloride was prepared and purified by repeated fractional freezing, as previously described.[21]

Solutions for spectroscopic examination were transferred to a 2-mm. path-length fused-silica cell in a dry, nitrogen-filled glove-box and were examined by means of a Perkin-Elmer 137 double-beam recording ultraviolet and visible spectrophotometer. When the solvent itself was examined (without compensation), complete absorption occurred at 342 mμ in the 2-mm. cell; in a 10-mm. cell, cut-out occurred at 374 mμ. The maximum of this intense ultraviolet absorption band of iodine pentafluoride itself was determined by placing one drop of the solvent on the non-window side of a 10-mm cell and recording the absorption of the vapour.

Magnetic measurements were made on sealed sample-tubes by means of a conventional Gouy balance with a variable field up to 3580 oersted. In a typical experiment, the solution was 0·0716M, it being assumed that 2·5 g.-ions of I^+ were formed per mole of iodine (see equation 2). Corrections for the diamagnetism of the solvent were made empirically by determining, in a separate experiment, the weight changes effected by the field on the same weight of pure solvent.

Electrolysis was carried out in a three-compartment cell with bright platinum electrodes. The compartments were separated from each other by means of sintered-glass discs fused to the walls of the cell. Each compartment could be filled independently and carried a B10 ground-glass cone and cap. Voltage was supplied by means of a 120-v Milne cell, and the current was measured by a milliameter.

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[21] Greenwood and Emeléus, *J.*, 1950, 987.