

418. *The Formation of Iodine Cations. Part II.*¹ *Spectroscopic Evidence.*

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The visible and ultraviolet absorption spectra of blue solutions of iodine in concentrated oleums are presented and compared with the spectra of solutions of iodine in dilute oleums and in sulphuric acid. The blue solutions are characterised by an intense band at 650 m μ , which is identified tentatively as a triplet-singlet transition of the iodine cation, since the results obtained from this ion in emission show that such a band should occur in this region. A small band at 1400 m μ may also be caused by the iodine cation but relatively weak bands at 470, 400, and 300 m μ are shown to be caused by two other absorbing species. Aspects of the spectroscopic, magnetic, and chemical properties of ter- and quinque-valent iodine in these solvents are reported.

It was postulated in Part I¹ that the paramagnetic species present in blue solutions obtained when iodine reacts with concentrated oleum is the free iodine cation, I⁺. Although this ion does not seem to have been studied before in solution it has been known for some time that it is present in electronically excited states when iodine vapour is decomposed by an electric arc.^{2,3} From the observed transitions between excited states, Murakawa³ has calculated the energies of the low-lying states relative to the ground state, although transitions between these levels have not been directly observed. The spectroscopic terms for the ground and low-lying excited states together with the wavelengths expected for transitions from the ground state to these levels are recorded in the Table.

Low-lying excited states for the iodine cation.

Orbital type	³ P ₂	³ P ₁	³ P ₀	¹ D ₂	¹ S ₀
Energy (cm. ⁻¹)	153,362	146,272	146,911	139,631	120,733
Transitions	³ P ₂ → ³ P ₁	³ P ₂ → ³ P ₀	³ P ₂ → ¹ D ₂	³ P ₂ → ¹ S ₀	
Wavelength (m μ)	1410	1550	728	310	

All these transitions are forbidden by atomic selection rules. The first permitted transitions lie below 200 m μ and therefore cannot be studied when sulphuric acid is the solvent. However, for elements of high atomic number, triplet-singlet transitions of moderate intensity are observed and therefore the ³P₂ → ¹D₂ transition should be readily detectable. Of the others, only the ³P₂ → ³P₁ transition is likely to be detectable, and even this should be extremely weak. Therefore solutions containing the free iodine cation should appear blue.

The spectrum of the blue solution in oleum is characterised by a strong band with a maximum at 650 m μ (Fig. 3), the intensity being about double that of the 520 m μ band of the iodine molecule. It is postulated that this band is the expected ³P₂ → ¹D₂ transition of the iodine cation shifted to shorter wavelengths by solvent interaction. A small band in the infrared region with a maximum at about 1400 m μ (not recorded in Fig. 3) may also be caused by the iodine cation but the bands at 470, 400, and 300 m μ cannot be caused by the free cation if the energy-level scheme given in the Table is correct. However, it was postulated in Part I that only part of the iodine is present as the cation, since the observed paramagnetism was somewhat smaller than that expected for I⁺. Analysis showed that most of the iodine was in the univalent state, although the possibility that zero and ter-valent iodine compounds were present in equivalent amounts was not excluded. In

¹ Part I, Symons, *J.*, 1957, 387.

² Tolansky, *Proc. Roy. Soc., A*, **149**, 269.

³ Murakawa, *Z. Physik*, 1938, **109**, 162.

particular, it was suggested that the ion ISO_3^+ might be present, and that covalent bonding might occur between the iodine cation and ions such as HSO_4^- , HS_2O_7^- , etc.

That the bands at 470, 400, and 300 $\text{m}\mu$ are not directly related to the 650 $\text{m}\mu$ band can be seen by comparing the results recorded in Figs. 1 and 3. Thus the 650 and 400 $\text{m}\mu$ bands are not observed in brown solutions of iodine in dilute oleums, but the 470 and 300

FIG. 1. Spectra of solutions of iodine in sulphuric acid and dilute oleums.

a, In sulphuric acid (98.4%); b, freshly prepared solution in oleum (2%); c, same solution immediately after prolonged heating; d, same solution after 4 hr. at room temperature.

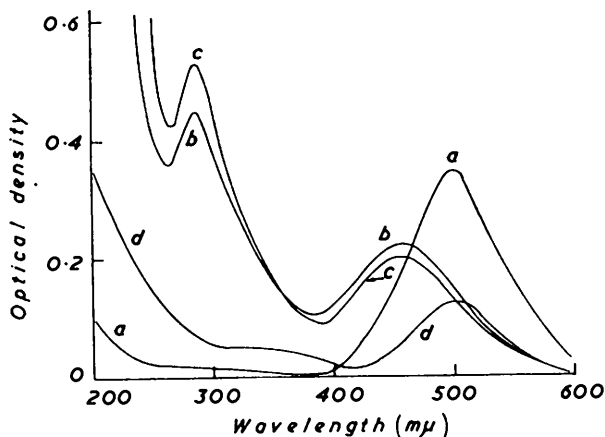
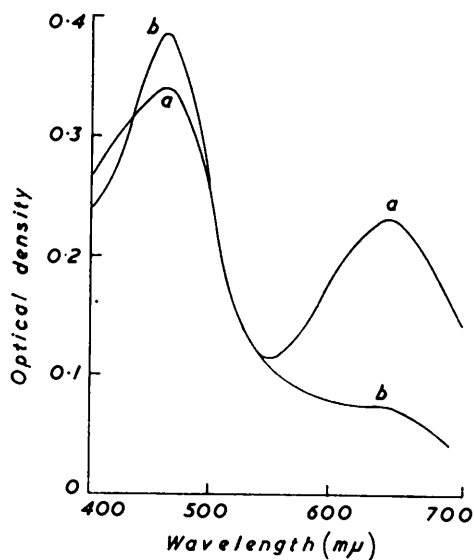
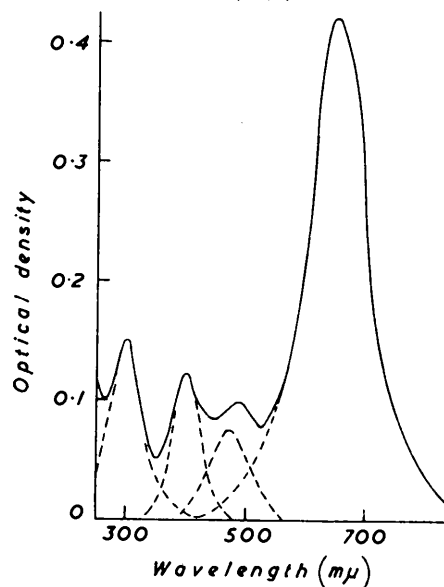


FIG. 2. Effect of heat on the spectrum of iodine in oleum (10%).



a, At room temperature, immediately after heating; b, same solution after 12 hr.

FIG. 3. Spectrum of iodine in concentrated oleum (65%).



$\text{m}\mu$ bands are still present. When sulphur trioxide is added to a solution in dilute oleum these bands decrease, and the 650 and 400 $\text{m}\mu$ bands increase in intensity (Fig. 2). The 400 $\text{m}\mu$ band is only found together with the 650 $\text{m}\mu$ band, but when a blue solution is heated the latter band gains in intensity at the expense of the former, and this effect is reversed on cooling. Such behaviour is not normally observed for two transitions of the same compound and it is accordingly concluded that the 400 $\text{m}\mu$ band is caused by a third component.

The main conclusions are that these results in no way disprove the theory that free iodine cations are present in large concentration in solutions of iodine in concentrated oleum,¹ and that the proximity of the main 650 m μ band to the expected $^3P_2 \longrightarrow ^1D_2$ transition of the cation supports the theory. Other features of these solutions, together with some properties of solutions of ter- and quinque-valent iodine (I^{III} and I^V respectively) in these solvents, are reported and discussed below.

EXPERIMENTAL

Spectrophotometric measurements were made with a Unicam SP500 quartz spectrophotometer (below 360 m μ), a Unicam SP600 glass spectrophotometer (360—900 m μ), and a Hilger Uvispek spectrophotometer (900—1600 m μ). All cells were calibrated, and controls were prepared from the same oleum used for solutions. 1 cm. cells were stoppered, but 1 mm. cells were not covered since it was found that when moisture was absorbed from the atmosphere a thin upper layer was formed which did not affect the optical density of the solution and effectively sealed off the contents of the cell. 0.1 mm. cells were obtained by the insertion of 0.9 mm. quartz spacers into 1 mm. cells.

Cells were cleaned by repeated washing with test solutions and care was taken to avoid striations in the solution since their presence seriously affected ultraviolet measurements. For readings above 900 m μ thin cells were used and a Chance OX2 infrared filter inserted in order to reduce effects of stray light. However, relatively large slit-widths were necessary and therefore little reliance can be placed on the precise optical-density values obtained in this region.

High-temperature measurements were made by pouring hot solutions into pre-heated cells, stoppering, and rapidly recording the relevant optical densities. The resulting values were compared with the spectrum of the cold solution. Iodine and solvents were purified as described in Part I.¹ Solutions of iodyl sulphate were prepared either by heating "AnalaR" potassium iodate in concentrated sulphuric acid or by heating equivalent portions of iodine and iodine pentoxide suspended in sulphuric acid.⁴ The yellow crystalline product was dissolved in sulphuric acid or oleum for spectrophotometric measurements. Aqueous solutions containing protonated hypoiodous acid, H₂OI⁺, were prepared as described by Bell and Gelles.⁵ Solutions containing I^V were prepared by shaking finely powdered potassium iodate or iodine pentoxide with sulphuric acid or oleum at room temperature.

Oleum concentrations were estimated by Kunzler's "fog-clear" method,⁶ which is easy and rapid, and sufficiently accurate for most purposes.

Magnetic measurements were made as described in Part I¹ for both concentrated solutions of iodyl sulphate and the solid.

RESULTS AND DISCUSSION

Spectra of Solutions in Sulphuric Acid and Dilute Oleums (Fig. 1).—In concentrated sulphuric acid the spectrum of iodine is close to that of the vapour (curve *a*) and there appears to be no interaction with the solvent. This result agrees with those already reported^{7,8} except that the broad peak at 320 m μ reported by Bower and Scott⁸ was not observed. The solubility of iodine in dilute oleum is very much greater than in sulphuric acid and the solutions are brown. A typical spectrum is curve *b*. Curve *c* was obtained from the same solution after prolonged heating to remove sulphur trioxide so that its concentration was less than that in 100% sulphuric acid. Iodine was lost during this process and the optical-density scales have been adjusted to facilitate comparison. This spectrum underwent a marked change over a period of about 4 hr., and curve *d* represents the final result.

The appearance of a new peak at 300 m μ , and the shift of the main iodine transition

⁴ Masson and Argente, *J.*, 1938, 1702.

⁵ Bell and Gelles, *J.*, 1951, 2734.

⁶ Kunzler, *Analyt. Chem.*, 1953, **25**, 193.

⁷ Buckles and Mills, *J. Amer. Chem. Soc.*, 1953, **75**, 552.

⁸ Bower and Scott, *ibid.*, p. 3583.

towards the ultraviolet are changes which resemble the effect of "donor" solvents on the iodine spectrum. However, it is probably the iodine molecule which is now acting as donor, and it is postulated that the new complex is the ion I_3^+ , formed by partial oxidation of the element. Masson⁹ has already presented arguments which point to the presence of I_3^+ and even I_5^+ . By analogy with chlorine monoxide, the ion I_3^+ would be bent and diamagnetic, and a series of relatively low-energy transitions would be expected.

If I_3^+ is formed by the reaction $I_2 + I^+ \rightleftharpoons I_3^+$, it should be possible to influence the position of equilibrium by suitable operations. Thus when the concentration of iodine is large no free I^+ should be present and therefore the 650 $m\mu$ band should be absent, and when the concentration of I^+ is large there should be no free iodine. Qualitatively, these expectations seem to be correct, but quantitative measurements are difficult because the bands are shifted and their intensities altered by overlap with the edges of neighbouring bands. This concept is supported by the qualitative appearance of the 650 $m\mu$ band in these solutions at high temperatures. On heating, the brown colour changes to a colour corresponding to the superposition of violet and blue: a colour which corresponds very closely to that expected for a mixture of uncomplexed iodine and the iodine cation. Rapid cooling causes the immediate return of the original brown colour. It is suggested that I_3^+ dissociates into I^+ and iodine at high temperatures.

The slow change in the spectrum when the concentration of sulphur trioxide is reduced to a value corresponding to less than 100% sulphuric acid (Fig. 1, curve *c* \rightarrow curve *d*) shows that if this theory is correct, I_3^+ decomposes very slowly. The resulting violet solution has a much greater ultraviolet absorption than a pure iodine solution (compare curves *a* and *d*). This new absorption resembles that of I^{III} in sulphuric acid (see later) and it is accordingly postulated that I_3^+ decomposes to give I^{III} and iodine.

In order to check the possibility that the new peak at 300 $m\mu$ is caused by dissolved sulphur dioxide, the spectra of solutions of sulphur dioxide in sulphuric acid and oleum were measured. In each case a strong band at 280 $m\mu$ was observed, the absorption at 300 $m\mu$ being small.

Spectra of Solutions in Concentrated Oleums.—The effect of an increase in the concentration of sulphur trioxide on the absorption spectra is presented in Figs. 2 and 3. The spectra recorded in Fig. 2 show how the 650 $m\mu$ band grows at the expense of the 470 $m\mu$ band. The slight shoulder at 400 $m\mu$ in curve *a* is probably caused by the 400 $m\mu$ band which appears in concentrated oleum (Fig. 3).

When the brown solution obtained by dissolving iodine in 10% oleum was warmed to 50° the colour changed to green. It remained green when the solution was cooled (Fig. 2, curve *a*) but reverted to brown after several hours (curve *b*). If the 650 $m\mu$ band is caused by the iodine cation (and for ease of presentation this assumption will be made in the following discussion) then its formation is facilitated by an increase in temperature and, in this solvent, the process by which it is destroyed is very slow at room temperature. This decomposition is evidently a disproportionation to give I_3^+ and tervalent iodine.

Fig. 3 represents an attempt to break down the overall spectrum of the blue solutions into its component bands (broken lines). Further increase in the concentration of oleum has only a minor effect on this spectrum, and an equilibrium appears to have been reached. It is reasonably certain that the 470 and 300 $m\mu$ bands are the same as are found in dilute oleum and it is accordingly postulated that there is still some residual I_3^+ in these solutions. An approximate estimate based on relative band-heights shows that I_3^+ comprises about 10% of the total iodine in the solution.

Identification of the compound responsible for the 400 $m\mu$ band is impossible at present.

Spectra of Protonated Hypoiodous Acid and of Ter- and Quinque-valent Iodine.—Quantitative measurements of these spectra are as yet incomplete, but the following qualitative features are relevant. In no instance has any well-defined peak been observed. Aqueous solutions of protonated hypoiodous acid were straw-yellow, and the slowly rising

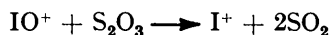
⁹ Masson, *J.*, 1938, 1708.

ultraviolet absorption showed a slight point of inflection in the 310 $m\mu$ region. Tervalent iodine solutions obtained from crystalline yellow iodyl sulphate had identical spectra in sulphuric acid and oleum. Absorption begins at about 450 $m\mu$, levels out to a plateau in the 330 $m\mu$ region, and rises steeply below 300 $m\mu$, thus closely resembling the low-wavelength portion of curve *d*, Fig. 1. Much evidence in favour of the formulation IO^+ for this yellow I^{III} species has been advanced.⁴ Unfortunately the spectrum described is so ill defined that it sheds no light on this matter. By analogy with oxygen it was thought that the ground state of this ion might be $^3\Sigma$ and therefore that it would be paramagnetic. Magnetic-susceptibility measurements on solid iodyl sulphate and on concentrated solutions in sulphuric acid and oleum show that no paramagnetic material is present. It must accordingly be concluded either that IO^+ is not paramagnetic or that IO^+ is not present in these compounds. Significant to this discussion is the observation that solid iodine dioxide is diamagnetic.¹⁰ It has been suggested that this oxide is ionic, having the structure $\text{IO}^+, \text{IO}_3^-$: if this is correct then it must be concluded that the iodyl ion IO^+ is not paramagnetic.

Quinquevalent iodine compounds dissolve in sulphuric acid and oleum to give colourless solutions having ultraviolet spectra similar to that of the iodate ion, although the long-wavelength edge is nearer the visible region. Since both sulphur dioxide and nitrite ions have a pronounced absorption peak in the 300 $m\mu$ region it was hoped that if the IV compound in these solutions were IO_2^+ then a similar band would be detected. In the absence of such a band no identification of the absorbing species can be made.

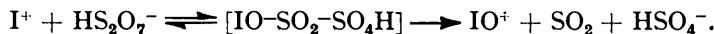
Reactivity.—Quinquevalent iodine in sulphuric acid and oleum readily decomposes to tervalent iodine and oxygen when heated. In concentrated oleum the I^{III} compound decomposes further and a green solution containing a mixture of I^{III} and I^+ results. Iodine and IV in sulphuric acid react immediately to form I^{III} at room temperature. In contrast, IV and I^+ in oleum do not react at room temperature, but I^{III} is formed slowly when the solution is heated.

When solutions of I^{III} and sulphur sesquioxide in oleum are mixed, sulphur dioxide is evolved and the 590 $m\mu$ band of sulphur sesquioxide is replaced by the 650 $m\mu$ band attributed to the iodine cation:



This reaction is rapid at room temperature, and should be compared with the conclusions drawn by Masson^{4,9} that iodine reduces oleum to sulphur sesquioxide and is itself oxidised to the tervalent state.

Addition of potassium hydrogen sulphate to a blue solution does not alter the relative heights of the visible bands but there is a marked increase in absorption in the ultraviolet. Potassium hydrogen sulphate acts as a base in this solvent, and reacts with sulphur trioxide to form KHS_2O_7 and possibly trimeric or polymeric sulphate. Co-ordination of the iodine cation with the resulting negative ions may result in the formation of a compound which has a rising ultraviolet absorption, or the formation of such a compound may facilitate the production of tervalent iodine:



Clearly, either of these interpretations would explain the decrease in paramagnetism which results when potassium hydrogen sulphate is added.¹

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¹⁰ Willmarth and Dharmatti, *J. Amer. Chem. Soc.*, 1950, **72**, 5789.