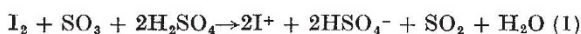


Colour of Solutions of Iodine in Oleum

THE blue colour which appears when iodine reacts with oleum has been discussed in terms of the formation of the iodine cation, I^+ (refs. 1, 2). Recently³, evidence purporting to show that iodine cations are not formed by oxidation in this medium and that the blue colour is due to an 'inclusion' compound of molecular iodine and 'polysulphuric' acid has been put forward. We wish to reconsider this conclusion.

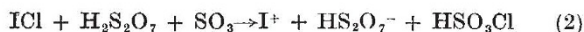
Mokhnach *et al.*³ point out that if iodine is oxidized according to the equation (theirs):



then (i) sulphur dioxide should be 'evolved'; (ii) the concentration of 'free' sulphur trioxide should decrease; (iii) the visible absorption spectrum should be unaltered when the concentration of sulphur trioxide is changed. They find that: (i) sulphur dioxide is not evolved; (ii) the concentration of sulphur trioxide does not decrease; (iii) the visible spectrum changes markedly on going from 7 to 50 per cent oleum. They conclude that iodine is not oxidized.

When reconsidering these aspects the following points should be noted:

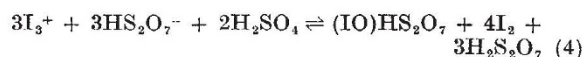
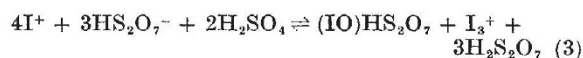
(i) Sulphur dioxide is very soluble in oleum and is not evolved on prolonged refluxing⁴. It has, however, been detected by means of its characteristic absorption band at 280 μ , and its concentration estimated thereby is quantitatively in accord with an equation of the form of (1) (ref. 2). Also, ICl reacts with oleum to give a solution with an identical spectrum in the visible region, but with no band in the 280- μ region⁵:



Dilution of these solutions to give aqueous sulphuric acid results in the complete reformation of ICl, but only 80 per cent of the original iodine is recovered, the remainder appearing as iodate. This is in accord with oxidation to I^+ .

(ii) Experimental details for the estimation of sulphur trioxide are not given. We think that the detection of the very small change in the concentration of sulphur trioxide required by equation (1), for the dilute solutions used³, would be most difficult.

(iii) The spectral changes given³ are identical with those found by us^{1,2}, and have been quantitatively interpreted in terms of the successive formation of I_3^+ (λ_{max} . 460) and I^+ (λ_{max} . 640, 500, 410) according to the equilibria:



As soon as sufficient sulphur trioxide has been added (50 per cent or more) the spectrum no longer changes.

No positive evidence in favour of the concept that the blue species is an inclusion compound between iodine and polysulphuric acid, similar to that formed in aqueous solutions of starch and comparable polymers, has been given³. We stress that recent

evidence suggests that the highest polymer in 50 per cent oleum is $H_2S_2O_7$ (ref. 5), and that the spectrum attributed by us to the iodine cation has been found in 100 per cent H_2SO_4 and HSO_3F . Furthermore, we would not subscribe to the view that, if the 'iodine cation' theory is correct, then the blue colour observed in aqueous solutions of iodine and starch might be due to these cations.

It is suggested³ that, nevertheless, iodine inclusion compounds should act as ' I^+ donors'. Indeed, the blue solutions in oleum are extremely powerful iodinating agents¹; but, so far as we are aware, inclusion compounds with starch and related polymers are not more powerful than unincorporated iodine.

Finally, despite their arguments against the postulate that iodine is oxidized³, Mokhnach *et al.* claim to have established by an electrolysis experiment that a cationic iodine species is present. We do not think that this deduction is justified from the results quoted. In their new experiment, the electrodes were immersed in the blue solution and it was found that the colour decreased in the anode but increased in the cathode compartment. We have carried out a similar experiment, but confined the blue solution to the central compartment of a Hittorf cell, the electrode compartments containing pure oleum. No migration of the blue colour was observed after the passage of 1 F. over a period of a week.

These apparently contradictory results can be reconciled, since only in the former experiment can direct oxidation or reduction of the iodine-containing species occur. We postulate that I^+ is oxidized at the anode to give trivalent iodine, probably IO^+ , which is transparent at 640 μ . An increase in absorption in the cathode compartment is not predicted, however, unless the medium is reduced to the blue species which is formed when sulphur reacts with oleum (λ_{max} . 590 μ , ref. 6) and which does not react with iodine cations.

Our inability to detect migration cannot be taken as evidence against the concept that iodine cations are present, since conductance measurements⁷ have shown that the current is carried almost exclusively by $HS_2O_7^-$ ions.

To verify this assertion we also examined the migration of coloured carbonium ions such as Ph_3C^+ under these conditions and were unable to detect any movement.

Finally, we stress that our magnetic and conductance measurements^{1,2} are quantitatively in agreement with the concept that the only iodine-containing species in these blue solutions is I^+ . We cannot see how the theory of an 'inclusion compound' can accommodate these results.

J. AROTSKY

The Harris College,
Preston.

M. C. R. SYMONS

Department of Chemistry,
The University,
Leicester.

¹ Symons, *J. Chem. Soc.*, 387, 2186 (1957).

² Arotzky, Mishra and Symons, *J. Chem. Soc.*, 12 (1961).

³ Mokhnach, Andreev, Stroganov, Komarov and Zhdanov, *Dok. Akad. Nauk, SSSR*, 130, 768 (1960); see also abstract in *Angew. Chem.* (sample English ed.), 87 (May 1961).

⁴ Brand, *J. Chem. Soc.*, 585 (1946).

⁵ Walrafen and Young, *Trans. Farad. Soc.*, 56, 1419 (1960).

⁶ Symons, *J. Chem. Soc.*, 2440 (1967).

⁷ Arotzky and Symons, *Trans. Farad. Soc.*, 56, 1426 (1960).