

70. *The Formation of Iodine Cations. Part I. Magnetic Evidence.*

By M. C. R. SYMONS.

Magnetic-susceptibility measurements on blue solutions of iodine in oleum show that they contain a paramagnetic material. Calculation based on the assumption that the paramagnetism is a property of the iodine gives a magnetic moment of 1.9 ± 0.1 B.M. per iodine atom for 0.1M-solutions and 2.5 ± 0.4 B.M. for 0.01M-solutions. It is postulated that the iodine is present partly as the free cation I^+ , which should have two unpaired electrons in the ground state, and partly as the ion ISO_3^+ or the molecule $IHSO_4$, both of which should be diamagnetic. Analysis shows that the iodine is entirely in the +1 valency state, and the complete non-volatility of the iodine at high temperatures and the great thermal stability of the solutions are properties which conform with the above postulate.

THIS paper describes an attempt to prepare and study the free iodine cation I^+ . Previously, the two properties of this ion which have been looked for in solutions likely to contain it are its positive charge and its high electrophilic power. Unfortunately, other species such as protonated hypiodous acid, IOH_2^+ , which may be present together with the free cation, are also positively charged and likely to be powerful electrophilic reagents, and hence considerable ambiguity may arise when these techniques are used.

There are, however, two other properties of the iodine cation which do not suffer from this ambiguity, namely, the electronic spectrum of the ion and its magnetism. Of these, the magnetism should provide the most conclusive evidence since the free ion in its ground state should contain two unpaired electrons and hence be paramagnetic, whereas it is highly probable that all possible covalently bonded compounds will be diamagnetic.

Accordingly a systematic attempt has been made to find conditions under which the free cation could exist in detectable concentration. At first it was hoped that electron-resonance techniques could be used and hence that concentrations smaller than $10^{-4}M$ could be detected; however, for reasons discussed below this approach proved unsatisfactory and therefore it was necessary to use far less sensitive magnetic-susceptibility methods. For such measurements to be conclusive concentrations greater than $10^{-2}M$ were required.

Sulphuric acid was chosen as solvent since it is electrophilic, has a very high dielectric constant, and has already proved so successful¹ in the study of the nitronium ion, NO_2^+ . Recent spectroscopic studies of solutions of iodine in sulphuric acid show that there is no interaction such as is found with donor solvents, the spectrum being close to that of iodine vapour.^{2,3} No indication of any ionisation such as $I_2 \rightleftharpoons I^+ + I^-$ or $2I_2 \rightleftharpoons I^+ + I_3^-$ was found. Thus, despite its high dielectric constant, sulphuric acid is unable to support such a dissociation. Indeed, if it could, one would expect reaction to occur, since as is well known, iodide ion is readily protonated and oxidised by concentrated sulphuric acid.

Clearly an electrophilic reagent more powerful than sulphuric acid is required to displace the iodine cation from the molecule :



Further, if the compound AI^- is unstable such an equilibrium might move to favour a high concentration of the cation.

Such an electrophilic reagent is sulphur trioxide. As it is added to a saturated solution of iodine in sulphuric acid (about $10^{-3}M$) the colour slowly changes from violet through brown and green to an intense blue, and sulphur dioxide is evolved. These blue solutions possess certain striking features, when compared with solutions in sulphuric acid. The

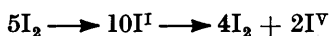
¹ Ingold, "Structure and Mechanism in Organic Chemistry," Bell & Sons, Ltd., London, 1953, p. 269.

² Bower and Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 3583.

³ Buckles and Mills, *ibid.*, p. 552.

apparent solubility of iodine is increased more than a hundred-fold: the solutions may be heated to 200° with no loss of iodine whatsoever: in the absence of any compound which can be iodinated, the solutions may be refluxed for a prolonged period without decomposition and are stable for many months at room temperature.

Quantitative measurements show that addition of water to re-form sulphuric acid liberates only 80% of the iodine initially present, the remainder having been converted at some stage into iodate. This result can most simply be explained by the postulate that all the iodine is present in the blue solutions in the +1 valency state, and that when water is added, disproportionation into iodine and iodate occurs:



The most striking property of the blue solutions is that they contain a paramagnetic species. This is taken as good evidence for the presence of the free iodine cation, since it is very difficult to formulate any other reasonable compound which should be paramagnetic. However, the calculated magnetic moment is considerably smaller than would be expected if all the iodine were present as the free cation, which probably means that it is present in equilibrium with other compounds such as IHSO_4 , IHS_2O_7 , or ISO_3^+ in which it is covalently bonded. These and other possibilities are discussed below.

EXPERIMENTAL

Materials.—When iodine resublimed *in vacuo* was used in place of "AnalaR" iodine, which was used for most experiments, identical results were obtained. Similarly, 65% oleum supplied by B.D.H. Ltd. behaved in a manner substantially the same as oleum prepared in the following way: sulphur trioxide was distilled from a mixture of "AnalaR" sulphuric acid and phosphoric oxide and dissolved in sulphuric acid (also distilled *in vacuo*). To avoid contamination with grease, all ground-glass joints were sealed with phosphoric acid. All other reagents were of "AnalaR" grade; water was purified by twice distilling it from alkaline permanganate.

Magnetic-susceptibility Measurements.—These were made with a conventional Gouy balance at room temperature. The electromagnet was operated at a field strength of 8000 gauss, with pole pieces 3 cm. apart. The air-damped balance was accurate to ± 0.01 mg. The measuring tube was calibrated by use of nickel chloride solution and water, the results agreeing within 2%. In all experiments, and in the calibration, a correction was made for the diamagnetism of the empty tube. The results were calculated by the method outlined by Dodd and Robinson.⁴ Results for two typical experiments are recorded in Table 1. Six determinations were made with freshly prepared solutions in which the concentration of iodine was close to 0.1M, and a further six after these solutions had been diluted ten-fold. The last column of Table 1 contains

TABLE 1.

Cols. 1—5 give the experimental results for two typical magnetic-susceptibility measurements, and col. 6 gives the average results and maximum deviations for six experiments with $[\text{I}_2] = 0.1\text{M}$ and six with $[\text{I}_2] = 0.01\text{M}$.

p_{I_2} is the wt. fraction of I_2 in g./per g. of solution, χ_A the g.-atom susceptibility, χ_A' the susceptibility after correction for diamagnetism, μ the magnetic moment in B.M. per iodine atom, and δw the difference (in g.) between the weight of the tube and its contents in the presence and in the absence of the magnetic field.

| p_{I_2} | δw | $10^6 \chi_A$ | $10^6 \chi_A'$ | μ | μ_{av} |
|------------------|------------|---------------|----------------|-------|------------------------|
| 0 | 0.01290 | — | — | — | — |
| 0.0147 | 0.01002 | 1297 | 1377 | 1.82 | 1.90 ± 0.1 (0.1M) |
| 0.00147 | 0.01229 | 3020 | 3100 | 2.71 | 2.50 ± 0.4 (0.01M) |

the average of these determinations and the maximum deviations observed. However, as can be seen from the Table, when the concentration of iodine was small the results are derived from very small differences between large numbers, and small but constant errors could well account for the apparent increase in μ .

⁴ Dodd and Robinson, "Experimental Inorganic Chemistry," Elsevier Publ. Co., Amsterdam, 1954, p. 384.

Oleum for blank determinations and for the preparation of solutions was carefully de-aerated before use. The iodine solutions were prepared by dissolving a known weight of iodine in oleum (65% SO₃ by wt.), care being taken to prevent loss of hydrogen iodide during the time of reaction. Finally, to ensure that the reaction was complete, and to drive off dissolved sulphur dioxide, the solutions were heated to 100° and cooled before use. The iodine concentrations in the blue solutions were checked by spectrophotometric measurements at 645 mμ after suitable dilution with 65% oleum.

In an attempt to check the possible formation of IHSO₄ or IHS₂O₇, solid potassium hydrogen sulphate was added to a solution of iodine (0.1M) and the susceptibility of the solution compared with that of a solution of potassium hydrogen sulphate in oleum of the same concentration (0.1M). The resulting moment of 1.58 B.M., whilst smaller than that found in the absence of the sulphate, may be somewhat inaccurate since considerable heating was required in order to dissolve the added salt.

Analytical Procedure.—If the blue solutions contain iodine in the +1 valency state, then the addition of sufficient water to convert the oleum into concentrated sulphuric acid should result in the disproportionation of the iodine into molecular iodine and iodic acid or iodate; and, as has been shown above, if a solution of iodine in sulphuric acid is treated in turn with oleum and water, 80% should be recovered as the element and 20% as iodate. The following experiments were devised to test this concept.

Nearly saturated solutions of iodine in sulphuric acid (96 ± 0.1%) were prepared by cooling warm solutions, and their optical densities in the 400–600 mμ region recorded. Since these values depend somewhat on the precise water content, a further check was made by quantitatively extracting 25 ml. portions with chloroform or carbon tetrachloride and recording the spectra of the iodine in the extracts.

Oleum was added, dropwise, to the solutions of iodine in sulphuric acid until, on standing, a clear blue colour was obtained. The spectra of the blue solutions were recorded, and the aqueous sulphuric acid was added to the cooled solutions until the blue colour was entirely lost and the spectra once more showed a maximum at 500 mμ, characteristic of molecular iodine. The spectra of these solutions and of the chloroform or carbon tetrachloride extracts were again recorded. The differences between these values and those obtained initially gave, directly, the percentage of molecular iodine lost during the cycle of operations described above. The results of a typical experiment are recorded in Table 2. The average of four experiments gave a reduction of 20 ± 2% in the concentration of iodine. Optical densities were measured with a Unicam SP 600 glass spectrophotometer, the solutions being kept in calibrated cells fitted with ground-glass stoppers.

TABLE 2. *Details of spectra of various solutions prepared from iodine. Optical-density values have been adjusted where necessary so as to be directly comparable.*

| Solvent | Before addition of SO ₃ | | After addition of SO ₃ and re-dilution | | |
|------------------------------|------------------------------------|------------------|---------------------------------------------------|------------------|-------|
| | H ₂ SO ₄ | CCl ₄ | H ₂ SO ₄ | CCl ₄ | Oleum |
| λ _{max.} (mμ) | 500 | 515 | 500 | 515 | 645 |
| Optical-density..... | 0.390 | 0.420 | 0.310 | 0.335 | 0.568 |

Bower and Scott² give ε_{max.} 844 at 500 mμ for iodine in sulphuric acid, whilst Buckles and Mills³ give ε_{max.} 770 at 502 mμ. The same authors record ε_{max.} as 930 and 918 respectively at 517 mμ for iodine in carbon tetrachloride. In the present work, the value for ε_{max.} in carbon tetrachloride is taken as 923 and the value for sulphuric acid at 500 mμ as 850.

According to the theory outlined, the solutions remaining after the final extractions of iodine should contain a quantity of iodate equivalent to 20% of the iodine used initially. In order to check this, the residual solutions were diluted with water and analysed for iodate by addition of excess of potassium iodide and spectrophotometric estimation of the concentration of the resulting iodine. In every case, iodate equivalent to 20 ± 5% of the initial iodine was detected.

DISCUSSION

Interpretation of Magnetic Results.—Although the measured magnetic moment lies close to the spin-only value (1.73 B.M.) for one unpaired electron per iodine atom it is

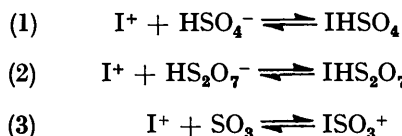
difficult to see how such a system could be formed. Conceivably, protonation might stabilize an iodine atom sufficiently to prevent recombination, but since the iodide ion itself is only a very weak base this seems unlikely. However, the analytical evidence clearly shows that the iodine is present in the +1 valency state, thereby excluding any formulation involving iodine atoms.

The low value for the measured magnetic moment of 1.9 ± 0.1 B.M. should be compared with the spin-only value of 2.83 B.M. calculated from the equation $\mu = 2\sqrt{[S(S + 1)]}$, and the value of 3.68 B.M. calculated for the 3P_2 state of the iodine cation from the equation $\mu = g\sqrt{[J(J + 1)]}$ when

$$g = 1 + [J(J + 1) + S(S + 1) - L(L + 1)]/2J(J + 1).$$

The latter equation should be applicable if the spin and orbital moments are free. However, these formulæ only apply when Russell-Saunders coupling is operative, which may well not be the case for the iodine cation, and their direct application is based on the assumption that the simple Curie law is valid. This assumption may not be legitimate and it is hoped that a study of the temperature-dependence of the paramagnetism will help to resolve the problem.

As suggested above, however, the measured moment is probably low because the concentration of iodine cation is lowered by equilibria (1), (2), or (3) :



Equilibrium (1) which seems highly probable in dilute oleum would be altered by the competing equilibrium (4),



and equilibrium (2) by further reaction of the negative ion with sulphur trioxide. Since disulphuric acid is a stronger acid than sulphuric acid, it seems reasonable to assume that equilibrium (2) would favour the formation of I^+ more than (1) and hence that the concentration of I^+ would increase with increasing complexity of the negative ion, and therefore with increasing addition of sulphur trioxide. A definite reduction in the apparent moment on addition of potassium hydrogen sulphate may be taken as evidence in favour of equilibrium (1) or (2), and the competing reaction (4) may explain why the reduction was less than expected.

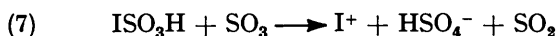
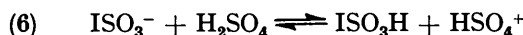
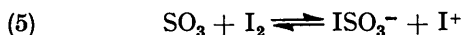
Equilibrium (3) might be considered unlikely since it involves interaction between two very powerful electrophilic reagents. However, the formation of S_2O_3 under very similar conditions, and the fact that ISO_3^+ and S_2O_3 are structurally comparable, support the postulate. The structure of S_2O_3 is unknown. A possible structure would be that of the thiosulphate ion after the removal of two electrons. If two electrons were removed from the structurally equivalent sulphate ion, the molecule SO_4 would almost certainly have two unpaired electrons, since the electrons would be removed from a set of three degenerate molecular orbitals.⁵ However the replacement of one oxygen atom by a sulphur atom or the iodine cation reduces the symmetry of the molecule and would remove the degeneracy of these levels. Thus both S_2O_3 and ISO_3^+ should be diamagnetic.

It is hoped that a study of the temperature-dependence of the spectrum of the blue solutions may shed light on these various possibilities.

⁵ Carrington, Ingram, Schonland, and Symons, *J.*, 1956, 4710.

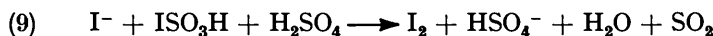
Attempts to study the paramagnetic properties of the blue solutions by electron-resonance methods have so far been inconclusive.⁶ Certainly no resonance absorption is observed in fluid solutions of any concentration, thus showing that strong spin-orbit coupling must occur. In some experiments two small absorption bands were observed at very low magnetic fields when 1.25 cm. radiation at 20° K was used, but these results were irreproducible, and no resonance was observed at this temperature with 8 mm. microwave radiation. No inference can yet be drawn from these results, but if the absorption is due to the iodine cation then the lack of reproducibility may be understood in terms of the extreme sensitivity to conditions expected for an ion with two unpaired electrons.⁵ If an ionic crystalline compound could be isolated containing I⁺ suitably diluted with sodium or potassium ions, then resonance studies might prove extremely fruitful.

Mechanism.—It is suggested that the following reactions are involved in the formation of the iodine cation :

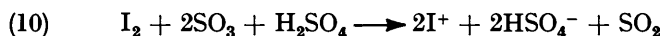


Reaction (5) is written as an S_E2 displacement of the iodine cation by sulphur trioxide. The alternative S_E1 reaction, involving a prior ionisation of I₂ into I⁺ and I⁻, is considered far less likely (see above). Even if this equilibrium is not favoured in the forward direction, the removal of ISO₃⁻ by reactions (6) and (7) will help to build up a high concentration of I⁺, which may, however, be partially removed by reactions (1), (2), and (3).

These reactions are closely related to the oxidation of iodide by sulphuric acid,⁷ which, by analogy, probably follows the course :



The reaction sequence (5), (8), (6), and (9) could conceivably replace (5), (6), and (7) since the overall result (10) would be the same.



On dilution with water the iodine cation would be converted into protonated hypoiodous acid, IOH₂⁺. In sulphuric acid this ion rapidly decomposes to give iodine and iodic acid, probably by the formation of IO⁺.⁸

Reactivity.—It is remarkable that solutions of iodine in oleum have been used for some years to iodinate aromatic compounds which are unaffected by other iodinating reagents, but that, so far as the author is aware, no one has suggested that the iodine cation, which would surely be the most powerful of all iodinating reagents, is the active agent. Thus for example, phthalic anhydride,⁹ pyridine,¹⁰ and picoline¹¹ are iodinated in the positions expected to be attacked by an electrophilic reagent.

Masson¹² found that the addition of iodine to yellow iodous sulphate in sulphuric acid gave brown solutions which, he postulated, contained the ions I₃⁺ and I₅⁺. He found that these solutions were also able to iodinate aromatic compounds readily, and postulated

⁶ Ingram and Symons, unpublished results.

⁷ Bush, *J. Phys. Chem.*, 1929, **33**, 613.

⁸ Masson and Argument, *J.*, 1938, 1702.

⁹ *Org. Synth.*, 1947, **27**, 78.

¹⁰ Rodewald and Plazek, *Ber.*, 1937, **70**, 1159.

¹¹ Plazek and Rodewald, *Roczniki Chem.*, 1947, **21**, 150.

¹² Masson, *J.*, 1938, 1708.

that the free iodine cation was the active agent. It will be shown in Part II that these brown solutions closely resemble the brown solutions formed by the addition of iodine to sulphuric acid containing a very small quantity of sulphur trioxide, and it is most probable that these solutions also contain ions such as I_3^+ and I_5^+ .

Details of Other Evidence.—As was mentioned above, it is considered that previous evidence for the existence of the iodine cation, obtained by transport and conductivity measurements and by kinetic studies, is inconclusive. Thus transport studies on iodine chloride in nitrobenzene¹³ are thought to prove the occurrence of the equilibrium $2ICl \rightleftharpoons I^+ + ICl_2^-$. However, the iodine cation would certainly iodinate nitrobenzene, and the resulting iodonitrobenzene might well act as a proton-acceptor and hence be positively charged. Alternatively the positive ion might be I_2Cl^+ .

Similarly, convincing kinetic evidence in favour of the iodine cation as an intermediate in a reaction has yet to be found, but mention must be made of the interesting studies made by de la Mare, Hughes, and Vernon,^{14,15} who showed that, for a certain range of reactivity, the concentration of the aromatic compound does not enter into the rate equation for chlorination with hypochlorous acid in aqueous perchloric acid. They suggest that the measured rate is the rate of formation of the free chlorine cation from protonated hypochlorous acid $ClOH_2^+$. Further evidence in favour of this interpretation is presented by Swain and Ketley¹⁶ who found that in D_2O the rate of chlorination is reduced to about half the value found in H_2O . An extension of these studies to iodination by hypoiodous acid would be most interesting.

Finally, Eley and Pepper¹⁷ have postulated that the catalysis of vinyl polymerisation by iodine in inert solvents proceeds *via* the free iodine cation formed by the reversible dissociation $2I_2 \rightleftharpoons I^+ + I_3^-$.

Whilst it might appear that this method could be used as a sensitive test for active, free cations, nevertheless many features of the polymerisation can be explained by formulations not involving the free cation.

The work reported in the present paper is incomplete, and further studies are being made. However it was thought that the results might prove to be of sufficient interest to warrant publication at this stage.

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¹³ Sandonnini and Borgello, *Atti R. Accad. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1937, **25**, 46.

¹⁴ de la Mare, Hughes, and Vernon, *Research*, 1950, **3**, 192, 242.

¹⁵ de la Mare, Ketley, and Vernon, *J.*, 1954, 1290.

¹⁶ Swain and Ketley, *J. Amer. Chem. Soc.*, 1955, **77**, 3410.

¹⁷ Eley and Pepper, *Trans. Faraday Soc.*, 1947, **43**, 112.