322. *Hypoiodous Cations, and their Action upon an Organic Reagent.*

By Irvine Masson.

In concentrated sulphuric acid, the yellow iodous sulphate I_2O_3,SO_3 takes up elementary iodine to form a deep brown solute. Saturation with excess of iodine gives solutes whose compositions (expressed as oxides) range from $I_{2{\cdot}8}O$ to $I_{8{\cdot}5}O$ according as the acid medium is near H_2SO_4,H_2O or nearer absolute H_2SO_4. The brown liquids react upon chlorobenzene instantly, but quite quietly; and it is shown that, of an initial " oxide " solute I_xO, exactly I_2O is thus consumed, the remaining $(x - 2)$ atoms of iodine being precipitated as element. The organic product is a quantitative yield of chlorotri-iodobenzene (not, in the main, the symmetrical isomer, and including one which is new).

Thus the active iodine in the brown solute is univalent, and the effective absence of tervalent iodine is confirmed by the non-formation of iodonium in the organic reaction (cf. Masson and Hanby, this vol., p. 1699).

The facts are explained by the inorganic equilibria

$$\begin{aligned} IO^+ &+ 2H^+ \rightleftharpoons I^{+++} + H_2O \\ I^{+++} &+ I_2 \rightleftharpoons 3I^+ \\ I^+ &+ nI_2 \rightleftharpoons I^+_{1+2n} \end{aligned}$$

the values of n in the last being 1 and 2; thus, corresponding with the familiar negative ions of univalent iodine I^-, I_3^-, I_5^-, we have here cations I^+, I_3^+, I_5^+. The organic reaction is in accordance with the equation

$$I^+_{1+2n} + RH \longrightarrow RI + H^+ + nI_2$$

successively repeated to complete the observed tri-iodination; and these ionic exchanges are to be compared with those assigned to iodous cations (preceding papers). Other aspects are reviewed.

Elementary iodine is practically insoluble in concentrated sulphuric acids: the saturated solutions, faintly pink, contain 1/5000 g.-atom per litre. Iodine pentoxide is slightly soluble: about 0·05M. When iodine is added to a solution of iodine pentoxide in sulphuric acid, it dissolves rapidly, forming a very dark brown solute; this occurs in concentrations of sulphuric acid lying between H_2SO_4,H_2O and H_2SO_4. (In more dilute acid, there is scarcely any action; in fuming acid, both reagents are directly attacked by the acid instead of by one another, iodine pentoxide being transformed into a white solid iodic–sulphuric complex, while iodine is oxidised to a soluble iodous salt with the formation of a deep blue-green liquid which liberates sulphur dioxide.)

If the relative quantities of the two solid reagents are chosen according to the equation $2I_2 + 3I_2O_5 = 5I_2O_3$, the brown solute is formed at first, but gradually attacks the residual iodine pentoxide, and, in the course of a few hours' shaking, both give place to a faintly yellow solution and a crystalline deposit of the bright yellow compound I_2O_3,SO_3, which is discussed in another communication. If a larger proportion of iodine is used, it forms brown solute at the expense of the yellow product; and if, finally, one uses as the initial reagents the yellow I_2O_3,SO_3 and iodine, they interact in a sulphuric medium to form the brown solute quantitatively.

The maximum quantity of iodine taken up per molecule of dissolved iodous sulphate does not markedly vary when the concentration of the latter is changed, so long as the sulphuric medium remains the same. If, however, the composition of the medium is made to vary within the range from H_2SO_4,H_2O to H_2SO_4, the maximum uptake of iodine per molecule of dissolved iodous sulphate changes considerably. For example, in three parallel experiments, excess of crystalline iodous sulphate was shaken to saturation with $2H_2SO_4,H_2O$, with $3{\cdot}5H_2SO_4,H_2O$, and with H_2SO_4; the filtrates, each containing about 0·02 g.-mol. of I_2O_3 per litre, were then saturated further with excess of solid iodine to yield the brown solutions; the quantities of iodine so taken up per molecule of already-dissolved I_2O_3 were respectively: $3{\cdot}44I_2$, $9{\cdot}68I_2$, and $11{\cdot}07I_2$. These data may without prejudice be expressed as if the product, the brown solute, were a " suboxide " of iodine, in which case the corresponding formulæ are $I_{2{\cdot}96}O$, $I_{7{\cdot}12}O$, $I_{8{\cdot}05}O$. The highest limit so far observed in the course of such experiments is $I_{8{\cdot}5}O$; and the nearness to integrality in the above three examples is fortuitous.

A clear light upon the nature of these complexes is given by their behaviour as reagents towards an aromatic compound, as follows. To the brown solution is added chlorobenzene from a small burette. An almost instantaneous but perfectly quiet reaction occurs at each addition, solid iodine being thickly precipitated; and the end-point is shown by the vanishing of the brown colour from the liquid, almost as if in a volumetric titration; any excess of the organic reagent shows as droplets coloured pink by dissolved iodine. Dilution, extraction with carbon tetrachloride, and complete analysis show that if the analysed composition of the initial " suboxide " reagent be expressed as I_xO, the chlorobenzene has consumed of this exactly I_2O, leaving unacted upon the residual $(x - 2)$ atoms of iodine, which precipitate as the element. This statement holds good whether x is about 2·8 and the medium $2H_2SO_4,H_2O$, or whether x is about 4·0 or about 7·1 and the medium $3{\cdot}5H_2SO_4,H_2O$ (*i.e.*, 96% H_2SO_4 by weight). Moreover, the quantity of chlorobenzene consumed is normally 2 mols. for every $3I_xO$; and the organic product, which consists when isolated of an almost white, fluffy mass of needles, is essentially a quantitative yield of chlorotri-iodobenzene. Thus, from 3·2 c.c. of chlorobenzene were obtained 15·1 g. of organic product of m. p. (125°)—128°—(140°), of analytical composition $C_6H_{2{\cdot}1}ClI_{3{\cdot}1}$ (Weiler). The fractional crystallisation of this material was not easy, the data suggesting that the constituents may form mixed crystals; but in one fractionation from ether–alcohol, the least soluble part, about 20%, was isolated as a moderately pure fraction of m. p. 165—166° (corr.) and giving on ultimate analysis $C_6H_{2{\cdot}4}ClI_{3{\cdot}3}$ (Weiler), and by our own halogen determination $C_6H_2ClI_{3{\cdot}0}$; whilst in another, the least soluble part, about 25%, had m. p. 130·5—131·5° and gave $C_6H_{2{\cdot}3}ClI_{3{\cdot}3}$ (Weiler), $C_6H_{2{\cdot}3}ClI_{3{\cdot}5}$ (Schoeller), and by our own halogen determinations, $C_6HClI_{2{\cdot}8-3{\cdot}1}$. This was superficially coloured slightly pink, in contrast to the other fractions, which were practically white with a faint trace of yellow; a more soluble fraction, 10%, of silky needles, had m. p. 147° (sharp) and was $C_6H_{2{\cdot}8}ClI_{3{\cdot}0}$ (Weiler), $C_6H_{2{\cdot}1}ClI_{3{\cdot}0}$ (Schoeller).

The remaining fractions were mixtures of the others and were not further treated. Although there is clear evidence that the analyses of these substances by semi-micro-methods and by different workers are liable to aberrations, and our own macro-analyses are seen not exactly to agree with them, it remains proved that the product consists of at least two chlorotri-iodobenzenes, m. p. 165—166° and 147°, with possibly a third, m. p. 130·5—131·5°. Of these, the first is apparently that isolated by Istrati (*Abs.*, 1898, i, 244; but cf. Beilstein) from the products of the prolonged boiling together of concentrated sulphuric acid, iodine, and chlorobenzene, and of m. p. given by him as 162—164°. The second appears to be a new isomer. The third, if not a mixture at a singular point in the fusion diagram of the others, may be the 1-chloro-2 : 4 : 6-tri-iodobenzene obtained by diazotisation from 2 : 4 : 6-tri-iodoaniline and described as melting at 125—126° (Hantzsch, *Ber.*, 1903, **36**, 2071), 119—120° (Green, *Amer. Chem. J.*, 1906, **36**, 600): of the two chlorotri-iodobenzenes hitherto recorded, this is the only one of known orientation; and it is interesting that our crude product mainly consists of the unsymmetrical isomers.

These iodinations, each active iodine atom replacing one aromatic hydrogen atom, prove that the effective iodine in the brown solution is univalent. Had it been the tervalent (iodous) radical, merely loosely associated with molecular iodine, the organic product would have been an iodonium salt, as our independent work with iodous sulphate has proved (Masson and Race, J., 1937, 1718; Masson and Hanby, this vol., p. 1699). Iodonium products were carefully sought in the liquor from the action with the brown solutes: they were wholly absent, except in the case where the reagent was so poor in additional iodine as to have the composition "$I_{2\cdot8}O$," in $2H_2SO_4,H_2O$; here a trace of iodonium, less than 1% of the polyiodochlorobenzene formed, was found. This minute quantity is nevertheless not insignificant, since it points to a reversibility in the inorganic reaction: Iodous radical + iodine $\rightleftharpoons$ brown solute. That this reversibility exists, and that it is not only due to the lack of high concentration of the acid above named, is made plain when a brown solute of the exact composition I_2O is prepared in $3\cdot5H_2SO_4,H_2O$; for this solution deposits after a time, in substantial amount, crystals of the yellow I_2O_3,SO_3, while remaining deep brown. In the aromatic reaction, it is only when the ratio I : O is made considerably greater than 2 : 1 that the polyiodo-compound ceases to be accompanied by the trace of iodonium by-product; evidently, the velocity of the iodinating action by the univalent iodine is intrinsically faster than the iodonium-forming action of tervalent iodine; while also the agent responsible for iodination is present in great excess over the other so long as the total iodine content of the liquid much exceeds that of I_2O.

We cannot doubt, having regard to the media in which the brown solutes are stable, that the hypoiodous radicals, which we have up to this point represented non-committally in terms of formal oxides, are in reality cations,* the simplest of which, corresponding with "I_2O," would be I^+. On this hypothesis, all the facts can be brought together as follows.

The inorganic preparative reaction from iodine and iodous salts, whose cation is virtually I^{+++}, is primarily

$$I^{+++} + I_2 \rightleftharpoons 3I^+ \quad . \quad . \quad . \quad . \qquad (a)$$

The reversibility of this, when the reagents are in the above stoicheiometric proportion, has been shown above; and it is further connected with the equilibrium

$$I^{+++} + H_2O \rightleftharpoons IO^+ + 2H^+$$

(cf. preceding papers). With excess of iodine, however, the observed formation of dissociable complexes up to "$I_{8\cdot5}O$" means the formation of cations as complex as I_5^+; so that

$$I^+ + nI_2 \rightleftharpoons I_{1+2n}^+ \quad . \quad . \quad . \quad . \quad . \quad . \qquad (b)$$

where $n = 1$ and 2. Reactions (*a*) and (*b*) are, of course, concomitant; and although we cannot dogmatise on the point, it is not improbable, from considerations of electronic structure, that the simple cation I^+ (with only six external electrons) is intrinsically unstable; that is to say, its equilibrium concentration is always small and it is represented by a mixture of IO^+, I^{+++}, I_3^+, and I_5^+ according to the balance of reactions (*a*) and (*b*).

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* Ionic transport experiments were made, with the brown solution in sulphuric acid buffered from the electrodes with sulphuric acid; but the solvent proved responsible for effectively all the conduction, so that little or no migration of either brown boundary occurred.

It will be noted that the equilibrium of reaction (*a*) should be characterised by the constancy of the ratio $(I^+)^3/(I^{+++})$, whilst that of reaction (*b*) requires, in a given medium, a constant ratio between the concentrations of I^+, I_3^+, and I_5^+; for the reagent iodine is so insoluble, as such, that its concentration is an invariable quantity. These requirements mean, qualitatively, that the solubility of iodine per molecule of dissolved iodous sulphate in a given medium should change only slightly with the concentration of the iodous salt; and as far as these experiments have gone, this is so. With a change of acid medium from less to more anhydrous, however, reaction (*b*) moves to the right.

As regards the organic reaction, the effective cations can be generalised as I_{1+2n}^+, and the iodination of chlorobenzene consists quantitatively in the ionic exchange, successively repeated for polyiodination,

$$I_{1+2n}^+ + RH \longrightarrow H^+ + RI + nI_2 \quad . \quad . \quad . \qquad (c)$$

thus bringing it into line with the ionic exchanges, described by Masson and Hanby (*loc. cit.*), between aromatic hydrogen and the cations of iodous (tervalent) iodine.

It is right to point out that a hypothesis alternative to that embodied in equations (*a*) and (*b*) could be put forward for the formation of the brown solute in the inorganic reaction. This is a "micelle" hypothesis, wherein the triply-charged iodous cation takes up an iodine molecule (or more) but without then dividing into univalent ions: that is,

$$I^{+++} + nI_2 \rightleftharpoons I_{1+2n}^{+++}$$

This hypothesis meets the observed fact that the solubility of iodine per iodous molecule does not much vary with the iodous concentration; but as an alternative to the hypothesis of (*a*) and (*b*) it appears to involve a very complicated and artificial mechanism for the aromatic iodinations which are simply represented by (*c*); one therefore disregards the idea of micelle formation except as a conceivable but quite unproved half-way step towards reactions (*a*) and (*b*).

As long ago as 1862 Lenssen and Löwenthal (*J. pr. Chem.*, **86**, 216), in their work on aqueous hypoiodous acid, concluded that in dilute acid it forms a brown complex with iodine which, in modern symbols, would be HI_3O (on our hypothesis, I_3^+); and Skrabal and Buchta (*Chem. Z.*, 1909, **33**, 1193) extended and confirmed the work, with the same conclusion. The experiments were upon the oxidation of iodide or iodine by mixtures of aqueous permanganate and manganous sulphate in quite dilute (5N) sulphuric acid. Dushman (*J. Physical Chem.*, 1904, **8**, 453) also inferred from kinetic studies the existence of HI_3O. These facts connect the region of dilute acids with that of concentrated acid in respect of the facts given in the present paper, and in conjunction with them can be held to show that the hypoiodous radical, especially when stabilised by co-ordination with iodine, is the strongest of the inorganic cations formed by the element; this is to be expected from its univalency as contrasted with the tervalency of iodine in its other cations.

Attention should be drawn to electronic problems: for instance, the cation I_3^+ would *a priori* be given, in a static model, an inert-gas structure $:\ddot{\underset{..}{I}}:\ddot{\underset{..}{I}}:\ddot{\underset{..}{I}}:$; but such a model is neither in accord with the solute's being brown, nor with the fact that towards an organic reagent one alone of the iodine atoms becomes reactive. Absorption photometry is also desirable. Counterparts to these problems, both optical and electronic, already exist in the familiar anionic iodides and polyiodides; we may, indeed, formulate for comparison the two series, which illustrate several properties of amphoteric, univalent iodine:

Cations:	I^+	I_3^+	I_5^+
Anions:	I^-	I_3^-	I_5^-

The remarkable potency of the hypoiodous cation in concentrated sulphuric acid, whereby such a compound as chlorobenzene is as easily tri-iodinated as is phenol in dilute aqueous bicarbonate, seems to deserve further application by organic chemists; and the fact that the unsymmetrical isomers preponderate is to be noted. The few additional trials which the author has made show that nitrobenzene, as well as chlorobenzene, undergoes a reaction involving I^+, and even more refractory substances have given similar indications. There are obvious limitations, such as appeared during attempts at partition experiments, in which carbon tetrachloride was decomposed, forming iodine trichloride; moreover, compounds like xylene undergo complex and drastic decompositions.

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