228. *Oxides and Oxyions of the Non-metals. Part I. Iodine Heptoxide.*

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The effect of strong acids on periodic acid has been studied, mainly by spectrophotometry. In strong aqueous acids there is good evidence for the cation $I(OH)_6^+$, but in 100% sulphuric acid there is vigorous reaction to give quinquevalent iodine. In 65% oleum an orange solid is precipitated which corresponds closely in analysis to the unknown heptoxide.

We are extending our studies of the structure and reactivity of oxyanions of the transition metals[1] to the comparable oxy-compounds of non-metals. The present paper concerns the oxy-anions of iodine.

The reaction between periodic acid and strong acids has been studied in order first to check the possibility that the cation IO_3^+ is formed when septivalent iodine compounds are dissolved in concentrated sulphuric acid. No evidence for this cation has been obtained, but two new species, protonated periodic acid, $I(OH)_6^+$, and iodine heptoxide, I_2O_7, are thought to be formed under specific conditions.

The chemistry of aqueous solutions of periodates is confused by the ability of septivalent iodine to exist in tetrahedral and octahedral forms, but whatever may be the true interpretation of results for solutions containing only mononegatively charged species, we conclude that the equilibria (1) and (2) are established rapidly, and that addition of a

$$IO_4^- + H_2O \rightleftharpoons H_2IO_5^- \quad (1)$$

$$H_2IO_5^- + H_2O \rightleftharpoons H_4IO_6^- \quad (2)$$

strong acid results in conversion of all the iodine into periodic acid, H_5IO_6. An attempt to calculate a " true " p*K* value for this acid depends on conclusions relating to the equilibria (1) and (2), which are still poorly understood.

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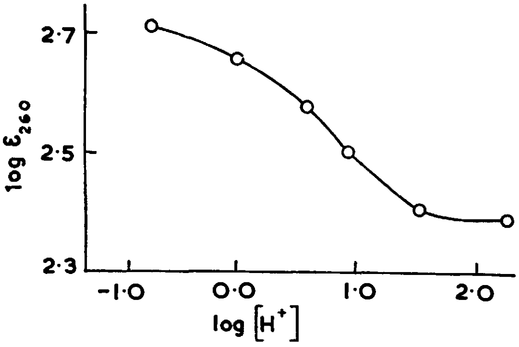
[1] Lott and Symons, *J.*, 1960, 973 and earlier Parts of that Series; cf. Bailey, Carrington, Lott, and Symons, *J.*, 1960, 290.

Crouthamel, Hayes, and Martin[2] estimated the p*K* value on the basis of spectrophotometric and potentiometric data and the incompletely justified assumption that periodate, IO_4^-, is the major component in neutral aqueous solutions at room temperature and the only component at high temperatures. They give an " apparent " p*K* value for periodic acid at 25° of +1·6, and a " true " value of +3·3, based on the above assumption and relating to the equilibrium:

$$H_4IO_6^- + H^+ \rightleftharpoons H_5IO_6 \qquad (3)$$

We do not wish to draw firm conclusions regarding the structure of periodate in neutral solutions, but only to mention some results which are not readily understandable in terms of the conclusions of Crouthamel *et al.*[2] (i) Sodium periodate trihydrate has been shown by infrared studies[3] to have the composition NaH_4IO_6,H_2O not $NaIO_4,3H_2O$, and saturated solutions certainly contain large concentrations of the ion $H_4IO_6^-$ in addition to IO_4^- (see, however, ref. 4). (ii) Various periodates in aqueous solution and in the solid state have weak bands in the 300—340 mμ region which are not readily explicable in terms of an electronic transition for a regular tetrahedral ion such as IO_4^-.[5] (iii) The spectra of periodates in anhydrous alcohol are remarkably similar to those of aqueous solutions, but some properties of the former solutions indicate complete conversion into the corresponding esters, $R_4IO_6^-$, when R is alkyl.[6] By analogy one might conclude that the spectra of aqueous solutions are due to octahedral $H_4IO_6^-$.

The effect of aqueous perchloric acid on the extinction coefficient (ε) of periodic acid at 260 mμ.



In view of these results we conclude that no accurate p*K* value can be assigned to H_5IO_6, but that it is probably in the region of +2 to +3.

Protonated Periodic Acid.—If no further reaction occurred, the spectrum of septivalent iodine in strong aqueous acids should not vary with pH for solutions having a negative pH. In fact, both the results of Crouthamel *et al.*[2] and those of Smith[7] show that this is not the case. By extrapolation of Smith's data in the 300—320 mμ region the molar extinction coefficient of septivalent iodine species is found to be zero at pH ~ —2·5, whilst at 260 mμ the variation of extinction coefficient with pH, shown in the Figure, is characteristic of an acid–base reaction. In 10·0M-perchloric acid the spectrum is simply a curve rising steadily from about 300 mμ, with no sign of the characteristic shoulder found for periodic acid and octrahedrally bonded periodates. We postulate that further protonation occurs to give $I(OH)_6^+$, which has p*K* ~ —0·8. That this result is reasonable can be seen by application of Ricci's empirical equation,[8] from which a p*K* of —1·0 is deduced for $I(OH)_6^+$.

[2] Crouthamel, Hayes, and Martin, *J. Amer. Chem. Soc.*, 1951, **73**, 82.
[3] Keen and Symons, *Proc. Chem. Soc.*, 1960, 383.
[4] Chantry and Plane, *J. Chem. Phys.*, 1961, **34**, 1268.
[5] Griffiths, Lott, and Symons, *Analyt. Chem.*, 1959, **31**, 1338.
[6] Kläning and Symons, *J.*, 1960, 977.
[7] Smith, Ph.D. Thesis, Southampton, 1958.
[8] Ricci, *J. Amer. Chem. Soc.*, 1948, **70**, 109.

Further evidence for this formulation comes from a comparison of the spectrum assigned to $I(OH)_6^+$ with those of other periodate ions and of the corresponding tellurates. In all spectra except those assigned to $I(OH)_6^+$ and $Te(OH)_6$, weak bands are detected, as shoulders, having molar extinction coefficients close to 100.[5,7,9] Approximate wavelengths are $H_3IO_6^{2-}$ 335, H_5IO_6 285, $H_4TeO_6^{2-}$ 260, and $H_5TeO_6^-$ 240 mμ.

Without assigning these bands to a particular electronic transition, we suggest that the transition is similar in principle for all these ions, and that it is allowed only when there is considerable deviation from octahedral symmetry. Thus no band would be expected for $I(OH)_6^+$ or $Te(OH)_6$.

Septivalent Iodine in Sulphuric Acid.—Although solutions in aqueous acids, thought to contain $I(OH)_6^+$, are stable, solutions in 100% sulphuric acid decompose rapidly, affording iodine in the quinquevalent state, with evolution of oxygen and ozone.

When discussing the decomposition of septivalent manganese and sexivalent chromium in oleum we postulated that sulphation of permanganic acid and chromic acid occurred, and that the powerful electron-attraction of the resulting sulphate groups resulted in the extrusion of molecular oxygen:[10]

$$O_2Mn(O{\cdot}SO_3H)_2^+ \longrightarrow O_2 + Mn(O{\cdot}SO_3H)_2^+ \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

In these decompositions ozone was never detected as a product. We suggest that the formation of ozone under such conditions is diagnostic of the formation of oxygen atoms as intermediates and we are thus led to postulate an initial sulphation followed by decomposition of the type:

$$OI(OH)_x(O{\cdot}SO_3H)_{5-x} \longrightarrow H_2IO_3^+ + O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Spectrophotometric and conductimetric studies favour the formulation $H_2IO_3^+$ for the resulting quinquevalent iodine species.

Septivalent Iodine in Oleum.—Remarkably, periodic acid reacts with 65% oleum without the iodine's passing to the quinquevalent state. An orange solid is formed which dissolves slightly in oleum to give yellow solutions. The iodine remains in the septivalent state, the new species is neutral, and the solid is not a sulphato-complex. In view of the high reactivity of the solid, analyses are only approximate, but we conclude from them that this solid is the previously unknown heptoxide, I_2O_7. We tried to check this formulation by infrared analyses but have been unable to prepare a specimen suitable for measurement.

The diffuse reflectance spectrum is characterised by a broad band in the 400 mμ region. This may be linked to the weak transitions discussed above for unsymmetrically substituted periodates, though why it appears at lower energies is not clear. It is noteworthy that, although tellurates and telluric acid are colourless, the trioxide is yellow.

The heptoxide is our preference to an unstable sulphato-complex of the type formulated in reaction (5) and thought to be a necessary precursor to spontaneous decomposition; it seems to be in accord with other results that we have obtained with 65% oleum. Thus the dehydrating power of the medium often manifests itself in preference to its sulphating power when the dehydration product is sparingly soluble.

EXPERIMENTAL

Materials.—Sulphuric acid and oleums were prepared and purified as described previously.[11] "AnalaR" potassium periodate was dried *in vacuo* over magnesium perchlorate.

Iodine Heptoxide.—The solid thought to be iodine heptoxide was obtained by treating periodic acid with 65% oleum. The precipitated orange solid was washed repeatedly with liquid sulphur trioxide in an atmosphere of dry nitrogen, and residual sulphur trioxide was removed *in vacuo*. Nitromethane or dry ether was also used to remove traces of sulphur

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[9] Earley, Fortnum, Wojeicji, and Edwards, *J. Amer. Chem. Soc.*, 1959, **81**, 1295.

[10] Mishra and Symons, unpublished work.

[11] Arotsky, Mishra, and Symons, *J.*, 1961, 12.

trioxide, and analyses were identical for solids purified by the two procedures. However, the latter procedure is not recommended since decomposition sometimes occurred with explosive violence.

Analyses.—The oxidation state of iodine in the orange solid was estimated by dissolving a known weight of it in water, and either adding an excess of potassium iodide and determining the liberated iodine, or adding a slight excess of arsenite to reduce the iodine to iodate and determining the excess with iodine. The results of several estimations were in close agreement and showed that all the iodine was present in the septivalent state. This was confirmed by measuring the ultraviolet spectra of neutral aqueous solutions, which had maxima at 222·5 mμ, characteristic of neutral aqueous periodate,[2] and, by using an extinction coefficient of 10^4 at this wavelength,[2] it was found that all the iodine was present as periodate. Because of the possibility that a sulphato-complex of septivalent iodine was formed, a sulphur estimation was also performed for this *oxide* (Found: S, 0; I, 69·0 ± 0·5. I_2O_7 requires I, 69·3%). These results are thus in accord with the empirical formula I_2O_7 and, in view of its insolubility and very low vapour pressure, we conclude that it is polymeric.

Reflectance Spectra.—Ultraviolet spectra were obtained with the precautions described earlier,[5] potassium sulphate being used as diluent and reference surface. Because of the high reactivity of the heptoxide, spectra measured at room temperature were irreproducible. However, by using a modified tray, in which samples were cooled to 77° K, better resolved and reproducible spectra were obtained.[12]

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[12] Travalion and Symons, *Spectrovision*, 1961, **10**, 8.