Evidence for Formation of Free-radical Intermediates in Some Reactions involving Periodate.

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[Reprint Order No. 6333.]

Reactions are described which indicate that photochemical decomposition of periodate, and reaction of periodate with ferrous ion, occur *via* free radicals, but that certain of its thermal reactions do not.

OF the various known reactions involving periodate species, only those in which α-glycols and related compounds participate have received detailed study. Important amongst the remainder are: the rapid oxidations of malonic acid and related compounds (Hubner, Ames, and Bubl, *J. Amer. Chem. Soc.*, 1946, **68**, 1621); photodecomposition of aqueous periodate solutions to give iodate and oxygen (Head and Standing, *J.*, 1952, 1457); photo-oxidation of many simple organic compounds (Head and Hughes, *J.*, 1952, 2046); reactions with certain transition-metal ions, for example, the oxidation of manganous salts to permanganate (Waterbury, Hayes, and Martin, *J. Amer. Chem. Soc.*, 1952, **74**, 15); and the reaction with hydrogen peroxide.

As part of a study of the mechanisms of certain of the above reactions now being undertaken in collaboration with Mr. M. G. Brown and Mr. M. Smith, various tests thought to be diagnostic of the presence of active free radicals have been made. The results are summarised in the Table.

EXPERIMENTAL

pH values were measured on a Cambridge pH meter, ultraviolet and visible spectra on a Hilger Uvispek spectrophotometer, and infrared spectra on a Perkin-Elmer spectrophotometer incorporating a lithium fluoride prism for the 2800—3800-cm.$^{-1}$ region.

Acrylonitrile and methyl methacrylate were purified by washing them with, in turn, dilute sulphuric acid, dilute sodium carbonate, and purified water, drying (Na_2SO_4), and distillation under a reduced pressure of oxygen-free nitrogen. Other reagents were of "AnalaR" grade. Water was doubly distilled from strongly alkaline permanganate, and glass apparatus was cleaned with the same reagent. To avoid inhibition of polymerisation by oxygen, monomer solutions were partially frozen and evacuated until vigorous boiling set in. This procedure was repeated several times and proved necessary for the attainment of consistent results. During irradiation experiments, the reduced pressure was maintained in order to lessen the chance of inhibition of polymerisation by any oxygen formed during the decomposition. The pH was adjusted with perchloric acid or potassium hydroxide solutions. Various light sources were used, the most satisfactory being a 125-w high-pressure mercury arc. The irradiated solutions were cooled by a rapid flow of water, and light of wavelength shorter than 3650 Å was largely removed by passage through three layers of soda glass. The times given in the Table represent approximately the interval between the start of irradiation and the separation of flocculent polymer, when the solution was held 9 in. from the arc. This stage was generally preceded by a uniform turbidity throughout the solution. Non-photochemical initiation experiments were carried out as described previously (*J.*, 1955, 273).

In every case temperature, pH, and initial concentration were varied over a wide range. When reactions resulted in polymerisation the optimum concentration of periodate was found to be approx. 10^{-3}M. For polymerisation with ferrous ion concurrent precipitation of a yellow ferric periodate complex masked the appearance of polymer. However, the complex was soluble in excess of perchloric acid, and in M-perchloric acid only polymer separated. For reactions resulting in hydroxylation of benzoic acid, concentrations of potassium periodate and benzoic acid were of the order of 10^{-2}M, and perchloric acid was added to give a pH of about 2. The concentrations are critical in these experiments, since it is necessary to avoid the preferential formation of ferric benzoate or ferric periodate, both of which mask the colour of the ferric salicylate complex formed when ferric chloride is added to the solution. The purple solutions thus obtained had visible and ultraviolet absorption identical with that of an authentic solution of ferric salicylate. When iodate was used in the rôle of periodate in these experiments neither polymerisation nor hydroxylation resulted.

	KIO_4	$CH_2(CO_2H)_2$ or $CHEt(CO_2H)_2$	$(CO_2H)_2$	Fe^{2+}	Cu^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+} *	H_2O_2
	+ $CH_2{:}CH{\cdot}CN$ or $CH_2{:}CMe{\cdot}CO_2Me$					
Dark ...	No P.†	No P.	No P.	Rapid P. pH −1 to 4	No P.	No P. pH −1 to 12
Light ...	P. in 30 min. pH −1 to 12	—	P. in 5 min.	—	—	—
	+BzOH					
Dark ...	No reaction	No S.†	No S.	Rapid S., pH 2	No S.	No S.
Light ...	S. in 2 hr., pH 2	—	No S.	—	—	—

* Small yields of polymer were obtained from solutions containing cobaltous ion when exposed to diffused daylight. † P. = polymerisation; S. = formation of salicylic acid.

Samples of polyacrylonitrile for infrared analysis were prepared by pressing about 5 mg. of the powdered polymer, previously dried at $70°/10^{-4}$ mm. for several hr. over P_2O_5, to give a clear film.

DISCUSSION

There seems to be a close parallel between the behaviour of periodate in these reactions and that of hydrogen peroxide in similar reactions (Bates, Evans, and Uri, *Nature*, 1950, **166**, 869; Baxendale, Evans, and Park, *Trans. Faraday Soc.*, 1946, **42**, 155). By inference, it is probable that hydroxyl radicals are formed both in the reaction with ferrous ion and in the photochemical decompositions. It was hoped that infrared analysis of the polyacrylonitrile formed during these experiments might reveal the presence of hydroxyl end groups (Dainton, *J. Phys. Colloid Chem.*, 1948, **52**, 490), but the results are not conclusive. In all of six analyses, slight, broad, absorption between 3100 and 3400 $cm.^{-1}$ was found, characteristic of hydrogen-bonded hydroxyl groups. In all cases, however, some absorption was also found in the 3600-$cm.^{-1}$ region, indicative of non-hydrogen-bonded hydroxyl groups, and an unidentified band at 1625 $cm.^{-1}$ which might be caused by water. However, since prolonged heating under a high vacuum did not significantly reduce the intensity of the 3600-$cm.^{-1}$ band, this explanation seems unlikely. Definite absorption between 1650 and 1750 $cm.^{-1}$, probably caused by carbonyl groups, was always found. These groups could have been formed either by hydrolysis of cyanide groups, or by oxidation of primary alcoholic end-groups by the irradiated periodate. The former alternative is improbable under the conditions used. In accord with this, it was found that the carbonyl absorption spectrum of a sample of polyacrylonitrile, formed by irradiation of an acidic periodate solution, was unchanged when a portion was left in contact with the parent solution for twelve hours in the dark.

Croutamel, Hayes, and Martin (*J. Amer. Chem. Soc.*, 1951, **73**, 82) found that neutral periodate solutions have a broad absorption peak at 2225 Å, which they assign to the anhydrous ion IO_4^-. This was also found by Head and Standing (*J.*, 1952, 1457), who remarked on the fact that periodate solutions are readily decomposed by light of wavelength far removed from this value. However, in comparison with the absorption curves of other oxy-ions, that of neutral periodate solutions is remarkably broad, with a tail in the near ultraviolet somewhat resembling that of hydrogen peroxide (Symons and Smith, unpublished results). It is tentatively suggested that, whilst the peak at 2225 Å may be characteristic of the IO_4^- ion, being possibly a result of charge transfer to the solvent sheath (Platzman and Franck, *Z. Physik*, 1954, **138**, 411), the long tail may be associated with the hydrated ion $H_4IO_6^-$, which is thought to be the photochemically active species.

Although quantum yields for the photochemical decomposition have not yet been measured, it seems probable that they will be considerably greater than the low values normally found for reactions in solution, owing to the operation of the primary dark back-reaction (Frank and Rabinowitsch, *Trans. Faraday Soc.*, 1934, **30**, 120). A chain mechanism is therefore provisionally postulated, which may, for the $H_4IO_6^-$ ion, be formulated as

$$H_4IO_6^- + h\nu \rightleftharpoons H_3IO_5^{\cdot-} + {\cdot}OH \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$H_3IO_5^{\cdot-} \longrightarrow IO_3^- + H_2O + {\cdot}OH \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$H_4IO_6^- + {\cdot}OH \rightleftharpoons H_2O_2 + H_3IO_5^{\cdot-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$H_4IO_6^- + H_2O_2 \longrightarrow IO_3^- + 3H_2O + O_2 \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

Reaction (2) is a thermal breakdown of the I^{VI} compound, and reactions (2) and (3) represent a chain process for the formation of iodate and hydrogen peroxide. Reaction (4) is a rapid dark reaction, which probably proceeds without the intermediate formation of radicals (see Table). An alternative route, involving the photodecomposition of hydrogen peroxide, and the resulting initiation of further decomposition of the periodate, is considered to be less probable.

In accord with the postulate that it is the hydrated ion which is photochemically active and the source of free radicals is the observation that polymerisation is still induced under acidic and alkaline conditions, when respectively the iodine is largely present as H_5IO_6 and $H_3IO_6^{2-}$ (Croutamel *et al.*, *loc. cit.*).

When oxalic acid is added to periodate solutions, there is a marked shift in the absorption peak at 2225 Å (Brown and Symons, unpublished results) which is thought to be indicative of complex formation. Such a complex, particularly if it is cyclic, could readily break down by a simple electronic shift to give iodate and carbon dioxide, and this may well be the mechanism of the slow thermal decomposition. However, these results show that the relatively rapid photodecomposition is a ready source of active free radicals and does not proceed by the above mechanism. In fact, polymerisation is induced far more readily by irradiation of periodate solutions in the presence of oxalic acid than in its absence, and it therefore seems probable that the photochemically active species is an oxalic acid–periodate complex. However, the photo-oxidation of simple alcohols, aldehydes, etc. (Head and Hughes, *loc. cit.*), may occur by initial formation of hydroxyl radicals.

Again by analogy with hydrogen peroxide, the reaction with ferrous ion is thought to involve hydrated periodate, being pictured as an electron-transfer reaction of the type

$$Fe^{2+} + H_4IO_6^- \rightleftharpoons FeOH^{2+} + H_3IO_5{}^{\cdot -} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$H_3IO_5{}^{\cdot -}$ may break down as in (2), either at the time of electron transfer or later, to give a free hydroxyl radical which can initiate polymerisation or hydroxylate benzoic acid. However, dropwise addition of ferrous sulphate solution to an excess of periodate did not result in oxygen evolution.

Whenever polymerisation did not occur the reductant underwent an overall valency change greater than one, and there is no compelling reason for postulating radical intermediates. Thus, the reaction with hydrogen peroxide may be pictured as involving a peroxy-compound formed by addition of the peroxide to the IO_4^- ion, followed by breakdown to give iodate and oxygen. Thus the rôle of the periodate is that of an acceptor, as is postulated in glycol fission reactions—a rôle for which it is particularly suited because of the ready availability of the outer *d*-orbitals of the iodine for bonding (Symons, *J.*, 1954, 3676).

When malonic acid is oxidised by manganic pyrophosphate, which is a one-electron acceptor only, organic radicals are formed, and can be detected by the polymerisation test (Drummond and Waters, *J.*, 1954, 2456) : thus it can be concluded that such radicals are not involved in periodate oxidations of malonic acid, and therefore that two distinct mechanisms are involved. It is hoped that a kinetic study, now in progress, will shed light on this mechanism.

Thanks are offered to Mr. M. Smith and Mr. M. G. Brown for many helpful discussions, to Dr. C. H. Bamford and Dr. A. Elliott of Courtaulds Ltd., Maidenhead, for their kindness in arranging for the infrared measurements, and for helpful advice on their interpretation, and to Imperial Chemical Industries Limited for a grant.

THE UNIVERSITY, SOUTHAMPTON. [*Received, April* 15*th*, 1955.]