267. *Reactions in Aqueous Solutions of Sodium Metaperiodate exposed to Artificial Light.*

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When dilute solutions of pure sodium metaperiodate are exposed in glass vessels to the enclosed carbon flame-arc they suffer quantitatively complete autoreduction to iodate at a rate convenient for measurement. This is similar to the reaction that occurs much more slowly when metaperiodate solutions are exposed to daylight. When dilute solutions of sodium meta-periodate are exposed in silica vessels to the mercury-in-quartz lamp they suffer autoreduction successively to iodate and iodide. In the presence of air, this is followed by oxidation of iodide ion to iodine, and formation of tri-iodide ion. All these reactions can be followed quantitatively by spectrophotometry.

HEAD (*Nature*, 1950, **165**, 236) reported that dilute solutions of pure sodium metaperiodate are stable in the dark, but suffer autoreduction when exposed to daylight behind glass. The products are sodium iodate and ozonised oxygen, the reaction being eventually quantitatively complete. The absorption spectrum of metaperiodate solutions contains a single band in the wave-length range 200—600 mμ, its maximum being at 220 mμ. Thus the reaction observed by Head occurs under the influence of light of wave-length far removed from that of the absorption maximum. Oertel (*Biochem. Z.*, 1914, **60**, 480) showed that solutions of iodates exposed in silica vessels to the mercury-in-quartz lamp suffer rapid reduction to iodides and oxygen. He did not report results for periodates, but stated that they behave similarly to iodates when similarly irradiated. Presumably, therefore, he observed the reduction of periodates to iodides, but not the formation of iodates as a first stage in the reaction.

The present paper reports more detailed observations of the behaviour of metaperiodate solutions when exposed to artificial light sources richer than daylight in short-wave radiation; these are the enclosed carbon flame-arc and the mercury-in-quartz lamp. The reactions occurring in the system were followed by spectrophotometry.

The carbon flame-arc, enclosed in a glass globe, was surrounded by a heat filter consisting of two concentric glass cylinders forming an annular space through which water circulated. From about 420 mμ upwards the energy distribution in such a source is similar to that in daylight. Owing, however, to the emission bands of the cyanogen radical, which reach their maximum at about 385 mμ, the arc emits radiation of high intensity in the far violet and near ultra-violet that has no counterpart in daylight; much of this radiation is transmitted by the glass globe and heat filter.

The results of exposing 10^{-4}M-sodium metaperiodate solutions, sealed in resistance-glass tubes, at a distance of $9\frac{1}{2}$ inches from the arc centre are shown by the spectral curves of Fig. 1. The upper curve ($\lambda_{max.} = 220$ mμ; $\varepsilon_{max.} = 9\cdot8 \times 10^3$) is the absorption curve of pure 10^{-4}M-sodium metaperiodate solution not irradiated. It is in substantial agreement with the absorption measurements on the metaperiodate ion made by Crouthamel, Meek, Martin, and Banks (*J. Amer. Chem. Soc.*, 1949, **71**, 3031). The lowest

curve in Fig. 1 is the absorption curve of pure 10^{-4}M-sodium iodate, which contains no maximum at wave-lengths above 200 mμ; the absorption is relatively low at 220 mμ ($\varepsilon = 1.3 \times 10^3$), where the metaperiodate curve attains its maximum. The intermediate curves are those obtained for the 10^{-4}M-metaperiodate solution exposed to the arc for various times from 2 to 96 hours. The irradiation produces a rapid fall in the peak density of the solution, and the spectral curve obtained after the longest exposure is nearly identical with that of 10^{-4}M-sodium iodate. Calculated from the peak densities, the amount of reduction of periodate after various times is as follows :

Time of exposure (hours)	1	2	3	5	15	24
Reduction, %	10	17	24	38	79	90

Spectral curves calculated additively for mixtures of periodate and iodate of the above compositions correspond closely to the experimental curves. The data are not suitable for a precise analysis of the reaction kinetics because the radiation from the arc was not
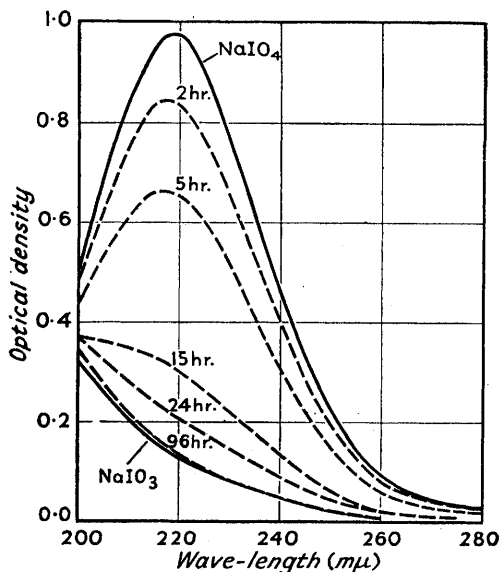

FIG. 1. *Optical densities (1 cm.) of:* 10^{-4}M-NaIO$_4$; 10^{-4}M-NaIO$_3$; *and* 10^{-4}M-NaIO$_4$; *exposed for different times to the enclosed carbon flame arc.*

sufficiently constant; they correspond approximately, however, to a first-order reaction. When a pure 10^{-4}M-solution of iodate was exposed to the arc for 24 hours under the foregoing conditions its absorption spectrum suffered little change.

Quantitatively complete autoreduction of metaperiodate to iodate ion may thus be observed in exposures both to daylight and to the carbon arc. The time necessary for a reduction of 90% when metaperiodate solutions are exposed to direct summer daylight is of the order of 2—3 months. The much higher rate observed in exposures to the arc is no doubt due, not merely to the difference in intensity, but to the fact that the arc emits radiation of wave-length nearer to that of the absorption maximum.

It has been shown in a similar way that complete reduction to iodate occurs when 10^{-4}M-sodium metaperiodate, contained in a closed silica tube, is exposed to the mercury-in-quartz lamp under suitable conditions, and that the reaction is then relatively rapid. The source was a commercial high-pressure mercury lamp deprived of its glass bulb (Mercra, 125 watts). The change from the spectrum of metaperiodate to that of iodate was practically complete in 15 minutes at $3\frac{1}{2}$ inches from the source. When, however, the duration and intensity of the irradiation were greatly increased, further changes occurred in the spectral absorption curve of the solution, and these were partly due to the further reduction of iodate to iodide. This is the reaction reported by Oertel, who did not observe the first stage in the reduction of the periodate ion, which occurs at a much greater rate

than the subsequent reduction to iodide. It is unlikely that he could have done so by means of the chemical methods of analysis employed by him. As will be shown, spectro-photometric methods are particularly suitable for revealing the complicated series of successive reactions occurring in aqueous metaperiodate solutions exposed to short-wave radiation in the presence of air. These are :
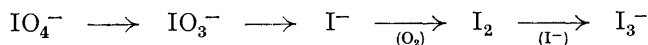
$$IO_4^- \longrightarrow IO_3^- \longrightarrow I^- \xrightarrow[(O_2)]{} I_2 \xrightarrow[(I^-)]{} I_3^-$$

Fig. 2 shows the effect on its absorption spectrum of exposing 10^{-4}M-potassium iodate contained in a closed silica tube to the high-pressure mercury lamp for 1 and for 5 hours. The lowest curve is the absorption curve of the original iodate solution, and the highest is that of pure potassium iodide ($\lambda_{max.} = 224$ mμ, $\varepsilon_{max.} = 12\cdot7 \times 10^3$; cf. Scheibe *et al.*, *Z. physikal. Chem.*, 1928, *A*, **139**, 22; 1929, *B*, **5**, 355). On irradiation, the iodate solution develops an absorption band with a maximum close to that in the spectrum of the iodide. The curves show, however, that reduction of iodate to iodide is not the sole reaction, since

FIG. 2. *Optical densities (1 cm.) of:* 10^{-4}M-KIO$_3$; 10^{-4}M-KI; *and* 10^{-4}M-KIO$_3$; *exposed to the high-pressure mercury lamp (125 watts, 2 ins.).*
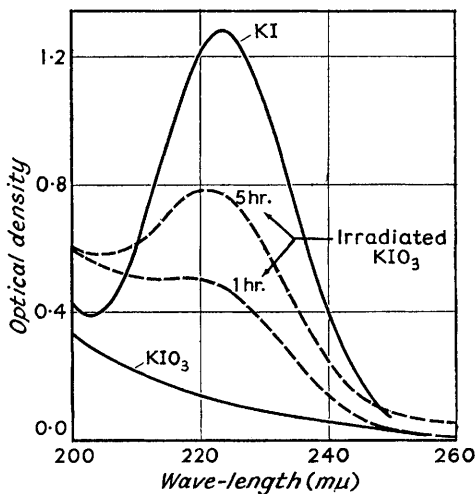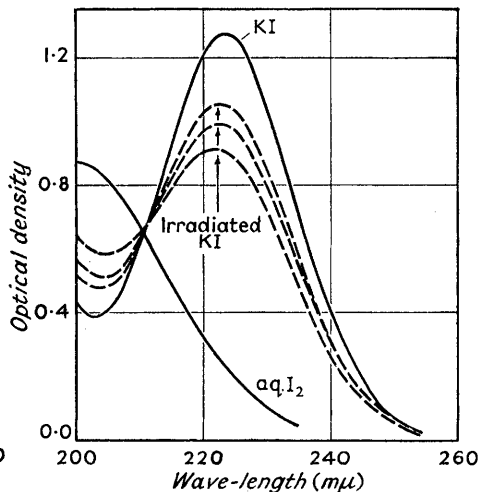
FIG. 3. *Optical densities (1 cm.) of:* 10^{-4}M-KI; 10^{-4}M-KI; *exposed to the high-pressure mercury lamp (125 watts, 5 hours, 2 ins.); and* $0\cdot5 \times 10^{-4}$M-I$_2$ aq.

the irradiated iodate solutions have higher absorptions at wave-lengths below 210 mμ than either the pure iodate or the pure iodide. The further reaction responsible for this is the oxidation of iodide ion to iodine, which is known to occur in the presence of air under the influence of short-wave radiation (Oertel, *loc. cit.*).

Fig. 3 shows the absorption curves of potassium iodide solutions, initially 10^{-4}M, before and after exposure in closed silica vessels to the high-pressure mercury lamp in three different experiments. The figure also shows the absorption of an equivalent solution of iodine ($0\cdot5 \times 10^{-4}$M-I$_2$) free from iodide ion; at the lower limit of our working range the absorption is high and still rising ($\varepsilon = 17\cdot5 \times 10^3$ at 200 mμ). The five curves in the figure show an isosbestic point at about 210 mμ. The compositions of the irradiated solutions can therefore be expressed in terms of the two components, iodide ion and molecular iodine. This result shows that most of the free iodine in solution is present in the molecular state, and not in combination with iodide, as tri-iodide ion. The conclusion was confirmed by the observation that the absorption of the irradiated solutions was very low over the whole wave-length range from 250 to 400 mμ, whilst the spectral absorption curve of the tri-iodide ion contains two bands in the ultra-violet with very high maxima, one at about 290 mμ ($\varepsilon_{max.} = 40 \times 10^3$), and the other at about 350 mμ ($\varepsilon_{max.} = 26\cdot4 \times 10^3$; Awtrey and Connick, *J. Amer. Chem. Soc.*, 1951, **73**, 1842). The absence of tri-iodide ion

in measurable concentration from the irradiated solutions of 10^{-4}M-potassium iodide is due to unfavourable equilibrium conditions. The dissociation constant of the tri-iodide ion-complex obtained by Jones and Kaplan from electrometric measurements is 1.4×10^{-3} at 25° (*J. Amer. Chem. Soc.*, 1928, **50**, 1845). Calculated from this, the concentration of tri-iodide ion when a solution originally 10^{-4}M in potassium iodide is oxidized to the extent of 20% is about 5×10^{-7}M, which is too low to be observed with certainty by the methods used. When 10^{-3}M-potassium iodide was exposed to the high-pressure mercury lamp under conditions similar to those employed with the more dilute solution, the irradiated solution showed strong absorption at the wave-lengths corresponding to the tri-iodide bands. From the optical density at 290 mμ, and the known extinction coefficient of the tri-iodide ion at this wave-length, the concentration of tri-iodide ion could be obtained; and, from the dissociation constant of the tri-iodide ion, and the known sum of the concentrations of all the iodine species (10^{-3} equiv. per l.), the concentrations of molecular iodine and of iodide ion in the irradiated solution could then be calculated. The latter agreed, within the experimental error, with that obtained from the optical density at 220 mμ, where the absorption is due chiefly to the iodide ion.

EXPERIMENTAL

Sodium metaperiodate was prepared by conventional methods, and was purified before use by several recrystallizations from water. Manganese was a known impurity in the crude material. It could not be detected in the purified salt, and the addition of small quantities of manganese was without effect on the rate of autoreduction of periodate to iodate in light. Iodates and iodides were of " AnalaR " quality.

The spectrophotometric measurements were made at room temperature with a Unicam SP 500 quartz spectrophotometer. The results illustrated graphically are expressed in the form of optical densities as measured, usually in 1-cm. cells; numerical results are quoted as molecular extinction coefficients, ε.

Measurements of the absorption of iodine in aqueous solution free from iodide ion were made with 1.5×10^{-4}M-solutions over the ranges 200—240 and 400—600 mμ. The iodine solution was prepared from an aqueous mixture originally 0.5×10^{-4}M in pure potassium iodate, 2.5×10^{-4}M in pure potassium iodide, and 10^{-2}N in mineral acid (both hydrochloric and sulphuric acids were used in different experiments). The mixture, contained in a closed vessel, was kept for a day at 25°, and it was assumed that both iodate and iodide had then been converted quantitatively into iodine according to the equation $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$; the control solution used in the photometric measurements was 10^{-2}N-hydrochloric or -sulphuric acid. In these experiments the iodide and iodate were present in equivalent concentrations. In a further experiment made in the same way, iodate was used in 50% excess of the iodide; the control solution was then a 10^{-2}N-solution of the acid, 0.25×10^{-4}M in iodate (the excess iodate concentration). The curves obtained in these different ways were in fair agreement, and a mean curve was used for the calculation of molecular extinction coefficients. The measurements made in the visible region were in reasonable agreement with the value reported by Awtrey and Connick (*loc. cit.*) at the absorption maximum; we have found no values in the literature with which to compare our measurements in the range of shortest wave-lengths.

In some of the exposures described, the temperature of the irradiated solutions rose appreciably. It was confirmed that the thermal decomposition was negligible compared with the observed photo-chemical effect.