Transient Species in the Pulse Radiolysis of Periodate Ion in Neutral Aqueous Solutions

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Summary IO_4^{2-} (ϵ_{360} *ca.* 1000 M^{-1} cm^{-1}) ions and $IO_4^{\bullet}$ ϵ_{520} *ca.* 3000M^{-1} cm^{-1}) radicals are formed by pulse radiolysis of periodate ion in aqueous solution.

WE have investigated the pulse radiolysis of the periodate ion in aqueous solution. Experiments were performed with a Febetron 707 giving pulses of 15 ns duration at half intensity. Doses were measured using aqueous solutions of 0·1 M-potassium ferrocyanide saturated with N_2O, taking ϵ_{440} $[Fe(CN)_6^{3-}] = 600$ M^{-1} cm^{-1} and $G(e_{aq}^-) + G(OH) = 6{\cdot}4$.

The Figure shows the absorption spectrum between 300 and 600 nm of transient species recorded 100 ns and 1 μs after the electron pulse (dose 60 krad) with a $2{\cdot}10^{-2}$M-deaerated periodate solution (pH 5·6).

Two absorption maxima centred around 520 nm (band A) and 360 nm (band B) are observed. The maximum intensity of band A is reached in about 1 μs with a 10^{-2}M-periodate solution. This absorption is weakly enhanced when the solution is saturated with N_2O and decreased when it is saturated with isobutane used as OH radical scavenger. The disappearance of band A is a second-order reaction with $2k/\epsilon = 3{\cdot}10^5$ cm s^{-1}, independent of IO_4^- concentration. This decay is different in the presence of ethanol; then it is a pseudo first-order process with a rate constant of 5×10^5 s^{-1} in presence of 0·1M-ethanol.

This transient species, which has also been observed in our laboratory by flash photolysis of deaerated periodate solution (10^{-4}—10^{-3}M), can be ascribed to $IO_4^{\bullet}$ formed by reaction (1) with OH radicals generated by irradiation of

$$IO_4^- + OH^{\bullet} \xrightarrow{k_1} IO_4^{\bullet} + OH^- \quad (1)$$

water or in a primary photolytic decomposition process of periodate ion.

In the pulse radiolysis experiments, the time taken to reach the maximum concentration of $IO_4^{\bullet}$ varies with the periodate concentration and with the dose because of the recombination reaction of the OH radicals. We have measured these times for IO_4^- concentrations of $2{\cdot}5 \times 10^{-3}$—10^{-1}M at a dose of 50 krad and, using Schmidt's program,[1] have computed the value of k_1 which best fits the collected results. We find $k_1 = (4{\cdot}5 \pm 0{\cdot}5) \times 10^8 M^{-1}$ s^{-1}

Times taken to reach maximum $[IO_4^{\bullet}]$ *concentration as a function of* $[IO_4^-]$ (*dose* 50 *krad*). *Comparison of experimental and computed results for different values*

$[IO_4^-]$	Calculated values (μs) a[a]	b[b]	c[c]	d[d]	Experimental value (μs)
$2{\cdot}5 \times 10^{-3}$M	>2	>2	2	1·9	2
10^{-2}M	>2	2	1·2	0·59	1
2×10^{-2}M	>2	1·2	0·63	0·33	0·6
10^{-1}M	0·60	0·34	0·16	0·08	0·15

[a] $k_1 = 1 \times 10^8$ $M^{-1}s^{-1}$. [b] $k_1 = 2 \times 10^8$ M^{-1} s^{-1}. [c] $k_1 = 4{\cdot}5 \times 10^8$ M^{-1} s^{-1}. [d] $k_1 = 10^9$ M^{-1} s^{-1}.

(Table). This value is greater than that given in a recent publication concerning γ-irradiation of periodate ion.[2]

With a dose of 80 krad, the scavenging of OH radicals is quite complete in a 0·3M-periodate solution and the molar extinction coefficient of the $IO_4^{\bullet}$ radical has been determined as ϵ_{520} ($IO_4^{\bullet}$) *ca.* 3000 M^{-1} cm^{-1} taking $G(OH) = 3{\cdot}2$. The rate of disappearance of $IO_4^{\bullet}$ radicals is $2k = 9 \times 10^8$ M^{-1} cm^{-1}.

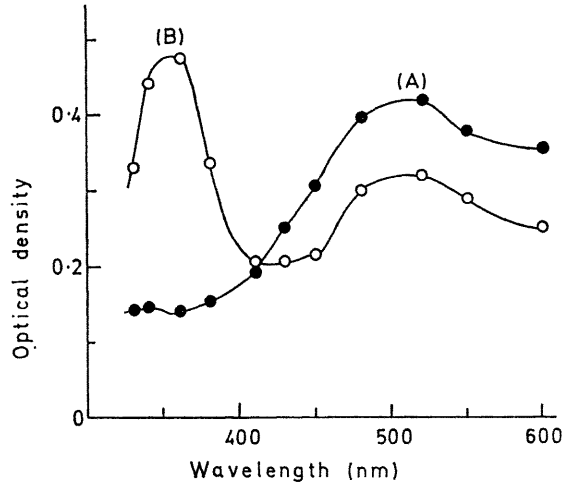

FIGURE. *Absorption spectrum of the transient species observed at* 300—600 nm *in the pulse radiolysis of a deaerated solution* (IO_4^- = 2×10^{-2}M, *dose* 60 *krad*, pH 5·6) —○—, 100 *ns after the electron pulse*, —●—, 1 μs *after the electron pulse.*

The intensity of band B decreases by 80% when the solution of KIO_4 ($2{\cdot}5 \times 10^{-3}$M) is saturated with N_2O ($2{\cdot}5 \times 10^{-2}$M) and remains unchanged on addition of alcohols. It is reasonable to assume, therefore, that it is formed by reaction of periodate ions with solvated electrons. Band B is formed immediately after the pulse ($\tau_{\frac{1}{2}} \leqslant 50$ ns, $[IO_4^-] = 2{\cdot}5 \times 10^{-3}$M) and this is in good agreement with the value k ($IO_4^- + e_{aq}^-$) = $(1{\cdot}1 \pm 0{\cdot}15) \times 10^{10} M^{-1}$ s^{-1} as determined by Anbar and Hart[3] at pH 7.

Band B disappears by a second-order reaction with $2k = 2{\cdot}5 \times 10^{10} M^{-1}$ s^{-1} at $[IO_4^-] = 2{\cdot}5 \times 10^{-3}$M. The effect of ionic strength on its rate of decay measured in the range $2{\cdot}5 \times 10^{-3}$M $< [KIO_4] < 2{\cdot}10^{-2}$M, shows the product to have a charge of + 4. We assume that the reactions (2a), (2b), and (3) take place. The salt effect does not

$$IO_4^- + e^-aq \rightarrow IO_4^{2-} \quad (2a)$$

$$\text{or } IO_4^- + e^-aq \rightarrow IO_2^{2-} + O_2 \quad (2b)$$

$$2\ (IO_4^{2-} \text{ or } IO_2^{2-}) \rightarrow \text{product} \quad (3)$$

distinguish between reaction (2a) and (2b): however, in the pulse radiolysis of the iodate ion in alkaline aqueous solution[4] we have observed a transient species formed by the reaction of O^- with IO_3^- which also has a maximum absorption at 360 nm and which we have tentatively attributed to IO_4^{2-}.

The "product" of reaction (3) may be a dimer such as the species observed by Buist *et al.*[5] at pH $\geqslant$ 7·9. The molar extinction coefficient of IO_4^{2-} as determined immediately after the pulse (< 100 nsec) is ϵ_{360} (IO_4^{2-}) *ca.* 1000M^{-1} cm^{-1}, taking $G(e_{aq}^-) = 3{\cdot}2$.

(*Received, March* 29*th*, 1971; *Com.* 440.)

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