The Kinetics of the Oxidation of Halide Ions by Bismuth(V) in Aqueous Solution: Evidence for Bi^{IV} as a Reactive Intermediate

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Summary The fact that the rates of oxidation of I^-, Br^-, and Cl^- by Bi^V are identical and are zero-order with respect to halide ion concentration suggests that the rate-determining step is the production of the reactive intermediates Bi^{IV} and the hydroxy-radical.

BISMUTH(V) oxidises halide ions in aqueous perchloric acid according to the equation $Bi^V + 2X^- \rightarrow Bi^{III} + X_2$. The kinetics of the oxidation of Cl^-, Br^-, and I^- by Bi^V have been investigated using a Durrum–Gibson stopped-flow spectrophotometer, the reactions being followed by measuring the increasing absorption due to product $Bi^{III}–X^-$ complexes. Halide ion was present in an excess of at least ten-fold in all runs and excellent straight lines were obtained when $\log_{10}(A_\infty - A_t)$ was plotted against time for up to 90% reaction. (Where A_t and A_∞ are absorbancies at time $= t$ and time $= \infty$). The reactions are thus accurately first-order with respect to Bi^V concentration.

Values of k_1 (the pseudo-first-order rate constant) were measured over a range of halide ion concentrations and the results are illustrated in the Figure. Orders of reaction with respect to $[X^-]$ were determined from the slopes of plots of $\log_{10}k_1$ versus $\log_{10}[X^-]$ and results are listed in the table.

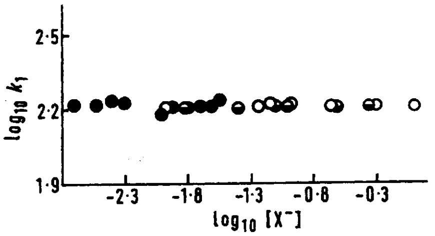

FIGURE. *The dependence of the first-order rate constant on halide ion concentration.* *Temp.* $= 25{\cdot}0 \pm 0{\cdot}1°$ C; $I = 2{\cdot}0$ M; $[H^+] = 0{\cdot}5$ M; $[Bi^V]_0 = 1{\cdot}0 \times 10^{-4}$ M. I^-; *filled circles.* Br^-; *half-filled circles.* Cl^-; *open circles.*

It is seen that each reaction is zero-order with respect to $[X^-]$ over the range of $[X^-]$ employed, and that k_1 is identical for the three reactions, with an average value of $k_1 = 161{\cdot}4 \pm 8{\cdot}0$ sec.$^{-1}$ As far as we know, this is the first example in which three different redox reactions proceed at identical rates, and of a redox reaction which has a rate independent of the concentration of one of the reactants.

TABLE

Temp. $= 25{\cdot}0 \pm 0{\cdot}1°$ C; $I = 2{\cdot}0$ M; $[H^+] = 0{\cdot}5$ M; $[Bi^V]_0 = 1 \times 10^{-4}$ M

Halide ion	γ_{max} (Product)	Order with respect to $[X^-]$	k_1 (sec.$^{-1}$)
I^-	460 nm	$0{\cdot}032 \pm 0{\cdot}030$	$162{\cdot}1 \pm 11{\cdot}6$
Br^-	365 nm	$-0{\cdot}001 \pm 0{\cdot}003$	$160{\cdot}2 \pm 1{\cdot}6$
Cl^-	325 nm	$-0{\cdot}007 \pm 0{\cdot}012$	$161{\cdot}2 \pm 4{\cdot}2$

The probable mechanism of the reaction is:

$$\begin{aligned} Bi^V + H_2O &\overset{k_1}{\rightleftharpoons} Bi^{IV} + OH\cdot + H^+ && (1) \\ \left.\begin{aligned} Bi^{IV} + X^- &\rightarrow Bi^{III} + X\cdot \\ OH\cdot + X^- &\rightarrow OH^- + X\cdot \\ 2X\cdot &\rightarrow X_2 \end{aligned}\right\} & \text{ fast} \end{aligned}$$

which leads to $d[Bi^{III}]/dt = k_1[Bi^V]$. An alternative mechanism involving the production of oxygen atoms in which Bi^V would undergo a two- rather than a one-electron reduction would fit the observed facts but is less probable for energetic reasons.

The kinetics of the $Bi^V–X^-$ reactions are in marked contrast to those of the $Sb^V–I^-$ reaction[1] when rate $\propto [Sb^V][I^-]^2$ and where there is presumably no oxidation of water by Sb^V.

Mechanisms involving the oxidation of water by strong oxidising agents to yield hydroxy-radicals as intermediates have been invoked[2,3] for a number of reactions in which oxygen is the product (*e.g.* $Xe^{VIII} + H_2O$, $Ag^{II} + H_2O$) but it is surprising that this mechanism has not been observed[4-6] in other halide ion oxidations by oxidising agents equally as powerful as Bi^V, such as $S_2O_8^{2-}$, IO_4^-, and Ce^{IV}.

The likelihood of a mechanism such as is postulated for Bi^V will be related to the energetics of reaction (1). It has been estimated[7] that the electrode potential for $OH\cdot + e + H^+ \rightleftharpoons H_2O$ is $+2{\cdot}4$ V, and we have obtained an approximate value of $+2{\cdot}0 \pm 0{\cdot}2$ V for the $Bi^V + 2e \rightleftharpoons Bi^{III}$ electrode potential from potentiometric titrations of Bi^V with I^- in $0{\cdot}5$ M-$[H^+]$ and $I = 2{\cdot}0$ M. (This is much higher than the value of $1{\cdot}6$ V obtained by Latimer[8] by extrapolating from measurements in alkaline solution.) That reaction (1) proceeds at a measurable rate suggests that the $Bi^V + e \rightleftharpoons Bi^{IV}$ electrode potential cannot be very much smaller than $+2{\cdot}0$ V, and this implies that Bi^{IV} in acid solution is not very unstable thermodynamically with respect to disproportionation, $2Bi^{IV} \rightleftharpoons Bi^V + Bi^{III}$.

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