Kinetics of the Oxidation of Bromide Ions by Tris(2,2′-bipyridine)nickel(III) Ions in Aqueous Perchlorate Media: Comparison with Oxidation by Aqua-cations

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The rate of oxidation of bromide ions by $[\text{Ni(bipy)}_3]^{3+}$ is first order in $[\text{Ni(bipy)}_3{}^{3+}]$ and first order in $[\text{Br}^-]$. The second-order rate constant is independent of acidity in the range 1—5 mol dm^{-3} HClO_4 at a constant ionic strength of 5.00 mol dm^{-3}, and the slow step is a simple interaction of $[\text{Ni(bipy)}_3]^{3+}$ with Br^- without removal of any co-ordinated 2,2′-bipyridine from the Ni atom before the electron transfer. Intermediate complexes between the reactants are not detected. This is contrasted with the oxidation of Br^- by aqua-cations and is compared with the oxidation of H_2O_2 by $[\text{Ni(bipy)}_3]^{3+}$.

THE kinetics of the oxidation of bromide ions by several aqua-cations have been investigated. For Mn^{III}(aq),[1] V^{V}(aq),[2] and Ce^{IV}(aq) [3] the order in $[\text{Br}^-]$ is greater than one, and it is difficult to interpret this without assuming the establishment of rapid pre-equilibria for complex formation between the cation and Br^- ions. The subsequent slow oxidative step involves either the interaction of a (cation + Br^-) complex with more Br^- ions or the first-order decomposition of a (cation + Br^-) complex. At an ionic strength $I \leqslant 3.0$ mol dm^{-3} the oxidation [4–6] of Br^- by Co^{III}(aq) is first order in $[\text{Co}^{\text{III}}\text{(aq)}]$ and first order in $[\text{Br}^-]$, and the rate constant is proportional to $a + b[\text{H}^+]^{-1}$ with $a \ll b$;[6] but at $I = 8.0$ mol dm^{-3} the rate [7] is proportional to $[\text{Co}^{\text{III}}][\text{Br}^-][\text{H}^+]$. From a comparison of the rate of this reaction at $I \leqslant 3.0$ mol dm^{-3} with the rate of oxidation of other ligands by Co^{III}(aq) and with rates of substitution at Co^{III}(aq), it has been suggested that the slow step in the oxidation of Br^- is the substitution of Br^- for water in the co-ordination shell of Co^{III}(aq):[4,5] *i.e.* that the mechanism for Co^{III}(aq) (first order in $[\text{Br}^-]$) is of a different type from that for Mn^{III}(aq), V^{V}(aq), and Ce^{IV}(aq) where the order in $[\text{Br}^-]$ is >1 and requires [1–3] the existence of rapid pre-equilibria between the cation and Br^- ions. Moreover, this suggestion of a rate-controlling substitution of Br^- for Co^{III}(aq) at $I \leqslant 3.0$ mol dm^{-3} conflicts with the observations on Co^{III}(aq) at $I = 8.00$ mol dm^{-3}, where rate is proportional to $[\text{H}^+]$ and is first order in $[\text{Br}^-]$ at high $[\text{Br}^-]$, requiring intermediate ($\text{Co}^{\text{III}} + \text{Br}^-$) complexes to be formed in rapid pre-equilibria with a slow oxidative step: as these complexes decompose only slowly relative to the rate of substitution at $I = 8.00$ mol dm^{-3}, it is unlikely that this situation is reversed at $I = 3.00$ mol dm^{-3}. Further, the suggestion of a rate-controlling substitution is based on a comparison of rates and transition-state parameters for oxidation with those for substitution at Co^{III}(aq) with oxidatively inert ligands; but for two of the oxidized ligands, H_2O_2 and HN_3, the existence of rapid pre-equilibria between Co^{III}(aq) and the ligand before the slow oxidation has been demonstrated.[8,9] It has also been suggested [10] that the oxidation of Br^- by $[\text{Co(NH}_3)_2(\text{OH}_2)_2]^{3+}$ and $[\text{Co(NH}_3)(\text{OH}_2)(\text{OH})]^{2+}$ is controlled by a slow substitution of Br^- for water, even though here there is considerable difference [10] between the empirical heat $\Delta H^\ddagger$ (kJ mol^{-1}) and entropy $\Delta S^\ddagger$ (J K^{-1} mol^{-1}) of activation for the oxidation of Br^- ($\Delta H^\ddagger = 33$, $\Delta S^\ddagger = -192$; $\Delta H^\ddagger = 121$, $\Delta S^\ddagger = 88$; respectively) and those for substitution of the oxidatively inert Cl^- for water ($\Delta H^\ddagger = 117$, $\Delta S^\ddagger = 92$; $\Delta H^\ddagger = 71$, $\Delta S^\ddagger = -88$; respectively).

We therefore decided to investigate the oxidation of Br^- by a complex where there is no water in the inner-co-ordination sphere, $[\text{Ni(bipy)}_3]^{3+}$ (bipy = 2,2′-bipyridine). We have already shown [11] that this complex oxidizes H_2O_2 without substitution of the latter into the inner-co-ordination sphere of Ni^{III}.

EXPERIMENTAL

Materials.—Solutions of the lime-green tris(2,2′-bipyridine)nickel(III) ion,[11,12] sodium perchlorate, and tris(2,2′-bipyridine)iron(II) sulphate were prepared as in the preceding paper. Sodium bromide was recrystallized from distilled water and the crystals were dried at 120 °C: solutions were made up by weight. Water was distilled once in an all-glass still. Nickel(III) concentrations were determined as previously.[11]

Kinetic Measurements.—The rates were all followed using a Durrum–Gibson stopped-flow spectrophotometer. Reaction traces were photographed on the storage screen of a Tektronix oscilloscope. The temperature was maintained constant by the circulation of water from a thermostat. The spectral characteristics of $[\text{Ni(bipy)}_3]^{3+}$ have already been described.[11] A wavelength of 350 nm was used in these experiments. Preliminary rate measurements have shown that the rate of oxidation of water by $[\text{Ni(bipy)}_3]^{3+}$ is too slow at the acidities used in these experiments to interfere with the stopped-flow traces for the oxidation of Br^-

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ions.[11,12] The product of the oxidation, $[Ni(bipy)_3]^{2+}$, is slowly solvolyzed, but the errors in the stopped-flow traces from this cause never exceeded 2%.

RESULTS AND DISCUSSION

Stoicheiometry.—The consumption of Ni^{III} was determined in solutions containing excess of $[Ni^{III}]$ (*ca.* 2.5×10^{-5} mol dm^{-3}) over $[Br^-]$ (1.00×10^{-5} mol dm^{-3}) with varying concentrations of perchloric acid. Table 1 shows that, assuming that all the Br^- is oxidized, $|\Delta[Ni^{III}]|/|\Delta[Br^-]| = 1.0$ in the range 1—5 mol dm^{-3} $HClO_4$. It is therefore concluded that the overall reaction is as in (1).

TABLE 1

Stoicheiometry at various acidities

$[HClO_4]$ / mol dm^{-3}	$\lvert\Delta[Ni^{III}]\rvert$ / $\lvert\Delta[Br^-]\rvert$
1.00	0.91
2.00	1.04
	0.98
	0.94
	1.00
3.00	0.94
	1.04
4.00	0.94
5.00	0.95

Mean 0.97 ± 0.05

$$2Ni^{III} + 2Br^- \longrightarrow 2Ni^{III} + Br_2 \qquad (1)$$

Rates at 25 °C.—Rates were investigated with an initial $[Ni^{III}] \sim 1 \times 10^{-4}$ mol dm^{-3}. At 4 mol dm^{-3} $HClO_4$ with $I = 5.00$ mol dm^{-3} maintained by the addition of sodium perchlorate, rates were determined with the excess of $[Br^-]$ varying from 1.0×10^{-3} to 0.5 mol dm^{-3}. Linear plots were obtained for log(optical density) against time, and Figure 1 shows that a plot of the pseudo-first-order rate constant k_0 obtained from their gradients varies linearly with $[Br^-]$ and passes through the origin. It is concluded, therefore, that the reaction is first order in $[Ni^{III}]$ and first order in $[Br^-]$: the second-order rate constant k_2 at 4.00 mol dm^{-3} $HClO_4$ and $I = 5.00$ mol dm^{-3} was 115 dm^3 mol^{-1} s^{-1} at 25.4 °C.

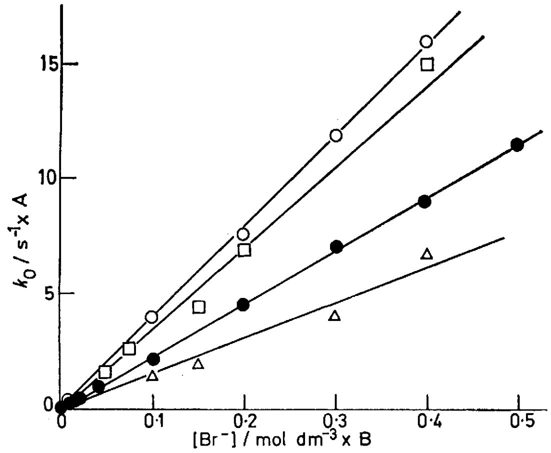

FIGURE 1 Plots of the pseudo-first-order rate constant against $[Br^-]$ at 4.00 mol dm^{-3} $HClO_4$, $I = 5.00$ mol dm^{-3}, and various temperatures: (○), 15.0 °C, A = B = 1.00; (●), 25.4 °C, A = 0.25, B = 1.00; (△) 32.3 °C, A = 10, B = 100; (□), 40.0 °C, A = 5, B = 100

Linear plots of log(optical density) against time were obtained for varying $[HClO_4]$ with $[Br^-] = 8.0 \times 10^{-3}$ and 2.00×10^{-2} mol dm^{-3}, and Figure 2 shows that these plots at $I = 5.00$ mol dm^{-3} are all parallel at constant $[Br^-]$. This shows that the rate of oxidation is insensitive to changes in acidity in the range 1—5 mol dm^{-3} $HClO_4$ at constant ionic strength: the values for k_2 are given in Table 2.

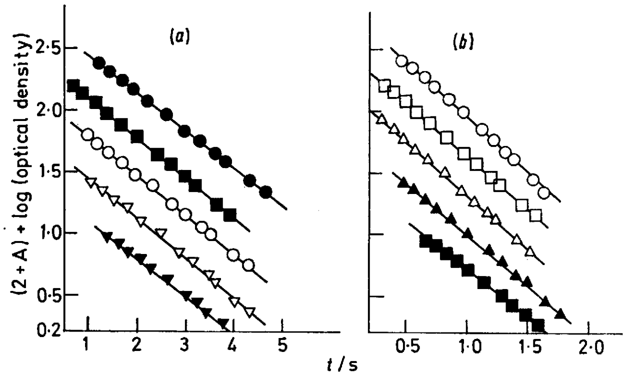

FIGURE 2 Plots of log(optical density) against time for various acidities at constant $[Br^-]$, $I = 5.00$ mol dm^{-3}, and 25.4 °C. (*a*) $[Br^-] = 8.0 \times 10^{-3}$ mol dm^{-3} with $[HClO_4]$/mol dm^{-3} as follows: (●), 5.00, A = 1.00; (■), 4.00, A = 0.80; (○), 3.00, A = 0.40; (▽), 2.00, A = 0; (▼), 1.00, A = 0. (*b*) $[Br^-] = 2.00 \times 10^{-2}$ mol dm^{-3} with $[HClO_4]$/mol dm^{-3} as follows: (○), 5.00, A = 1.00; (□), 4.00, A = 0.80; (△), 3.00, A = 0.50; (▲), 2.00, A = 0; (■), 1.00, A = 0

Rates at Various Temperatures.—Rates were determined with various $[Br^-] \gg [Ni^{III}]$ at 4.00 mol dm^{-3} $HClO_4$ with $I = 5.00$ mol dm^{-3} at 15.0, 32.3, and 40.0 °C. Linear plots of log(optical density) against time were always obtained, and Figure 1 shows that plots of k_0 against $[Br^-]$ are linear at constant temperature. The gradients of these lines give k_2 = 40, 155, and 355 dm^3 mol^{-1} s^{-1} at the three temperatures, for 4.00 mol dm^{-3} $HClO_4$ and $I = 5.00$ mol dm^{-3}. The linear plots of log(optical density) against time for varying $[HClO_4]$ at constant $[Br^-] = 1.00 \times 10^{-3}$ mol dm^{-3} are all parallel at constant temperature: Table 2 confirms that k_2 is insensitive to changes in $[HClO_4]$ at constant temperature.

TABLE 2

Second-order rate constants k_2 at $I = 5.00$ mol dm^{-3}

θ_c / °C	$[HClO_4]$ / mol dm^{-3}	$10^3[Br^-]$ / mol dm^{-3}	k_2 / dm^3 mol^{-1} s^{-1}
15.0	4.00	8.0—400	39.9 ± 1.6
25.4	1.00—5.00	1.00—500	101 ± 9
32.3	4.00	1.00—4.00	145 ± 18
40.0	2.00—5.00	1.00—8.00	321 ± 29

A plot of log k_2 for 4.00 mol dm^{-3} $HClO_4$ and $I = 5.00$ mol dm^{-3} against the reciprocal of the absolute temperature was linear. From the gradient of this plot, determined by the least-squares procedure, the energy of activation $\Delta H^\ddagger = 60 \pm 4$ kJ mol^{-1}; the entropy of activation $\Delta S^\ddagger = -3 \pm 11$ J K^{-1} mol^{-1}.

Mechanism of the Oxidation of Bromide Ions by Cations. —The oxidation of Br^- by $[Ni(bipy)_3]^{3+}$ is first order in $[Ni^{III}]$ and first order in $[Br^-]$, but zero order in $[H^+]$. The last order contrasts with the oxidation of Br^- by aqua-cations, where, whatever the order in $[Br^-]$, the rate varies with acidity.[1-7] Similarly, we found[11] that the rate of oxidation of hydrogen peroxide by $[Ni(bipy)_3]^{3+}$ is first order in $[Ni^{III}]$ and first order in $[H_2O_2]$ but zero order in $[H^+]$, although the rates of oxidation of H_2O_2 by aqua-cations that vary with $[H_2O_2]$ also vary with $[H^+]$.[8,13] The absence of any variation with $[H^+]$ for these two oxidations by $[Ni(bipy)_3]^{3+}$ where there is no water in the inner-co-ordination sphere confirms the assignment of the $[H^+]$ dependences for reactions with aqua-cations to the participation of hydrolytic species of the aqua-cations and of the intermediate (cation + Br^-) and (cation + H_2O_2) complexes.

The oscilloscope traces for the $Ni^{III} + Br^-$ reaction show no evidence for intermediate complexes, like those for the $Ni^{III} + H_2O_2$ reaction, supporting the conclusion from the observed kinetic orders. The acid independence of the rate also supports this, as the removal of 2,2'-bipyridine from cations is acid-catalyzed.[14] This is also supported by the observed stability of $[Ni(bipy)_3]^{3+}$ at high acidities, its stability in the absence of added substrate decreasing with decreasing acidity due to the oxidation of water.[11,12] It is concluded, therefore, that this oxidation of Br^- occurs in a bimolecular encounter of solvated $[Ni(bipy)_3]^{3+}$ and solvated Br^- as in (2). This

$$[Ni(bipy)_3]^{3+} + Br^- \xrightarrow{k_2} [Ni(bipy)_3]^{2+} + Br^{\bullet} \qquad (2)$$

$$Br^{\bullet} + Br^{\bullet} \xrightarrow{\text{fast}} Br_2 \qquad (3)$$

will be followed by a rapid dimerization of the bromine atoms to give molecular bromine as in (3).

This simplicity contrasts with the oxidation of Br^- by aqua-cations $M^{z+}(aq)$ where the $[H^+]$ dependence shows that hydrolytic species are involved. If complexes $M^{z+}Br^-{}_n(aq)$ are involved as intermediates, with K_h and K_n' as the first-hydrolysis equilibrium constants of $M^{z+}(aq)$ and $M^{z+}Br^-{}_n$ respectively and β_n as the formation-equilibrium constant of the latter, the rate of disappearance of total M^{z+}, $[M^{z+}]_T$, is given by equation (4) where

$$-\frac{d[M^{z+}]_T}{dt} = \frac{[M^{z+}]_T \sum_n m\beta_n[Br^-]^n(k_n + k_n'K_n'h^{-1})}{1 + K_h h^{-1} + \sum_n [Br^-]^n\beta_n(1 + K_n'h^{-1})} \qquad (4)$$

$h = [H^+(aq)]$, k_n and k_n' are the respective rate constants for the oxidative decomposition of $M^{z+}Br^-{}_n(aq)$ and $M^{z+}(OH^-)Br^-{}_n(aq)$; $m = 1$ for $n = 1$ and the product is $Br^{\bullet}$, $m = 2$ for $n \geqslant 2$ and $[Br_2]^{-\bullet}$ is the product. $Br^{\bullet}$ dimerizes as in (3) and $[Br_2]^{-\bullet}$ is oxidized to Br_2 by more M^{z+}.[1] With the dominance of appropriate terms in the numerator and denominator, equation (4) covers all the orders in reactants[1-3,6,7] found for $Mn^{III}(aq)$, $V^V(aq)$, and $Ce^{IV}(aq)$ and for $Co^{III}(aq)$ at $I = 8.00$ mol dm^{-3}. In the last case it is difficult[6] to formulate any other mechanism which will account for the order of unity in $[H^+]$ at $I = 8.00$ mol dm^{-3}; equation (4) can also account for the observations with $Co^{III}(aq)$ at $I \leqslant 2.0$—3.0 mol dm^{-3},[4-6] providing a uniform mechanism involving $M^{z+}Br^-{}_n$ formed in rapid pre-equilibria, with merely n and the hydrolysis varying with I. This general mechanism can be expanded to cover further hydrolysis of $M^{z+}(OH^-)Br^-{}_n(aq)$ and the bimolecular oxidative interaction of all the bromo-complexes with Br^- without invalidating these conclusions.

Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for such redox reactions are involved in achieving the configurational changes in the transition state, including those of the solvent molecules, sufficient to facilitate the tunnelling of the electron from the ligand to the cation. A major contribution arises from the changes in the solvent molecules adjacent to M^{z+} and Br^- attendant on the charge changes occurring with the electron transfer. For $M^{z+} = Mn^{III}$, V^V, and Ce^{IV}, paths with $n \geqslant 2$ are preferred, as the transition state is stabilized by a contribution from ΔH for $Br^{\bullet} + Br^- \longrightarrow [Br_2]^{-\bullet}$ (compare that[15] for $I^{\bullet} + I^- \longrightarrow [I_2]^{-\bullet}$, $\Delta H = -23$ kJ mol^{-1} with $\Delta S \sim 0$): additionally for $Co^{III}(aq)$, if the active species is a dimer,[16] $[Br_2]^{-\bullet}$ may be produced and consumed at the same cation. In M^{z+}-$Br^-{}_n(aq)$ varying degrees of penetration of the aqua-shell of $M^{z+}(aq)$ by Br^- may occur, provided that it is sufficient to ensure a kinetically identifiable species.[17] As all the changes involve the movement of water molecules in the vicinity of $M^{z+}(aq)$ it is not surprising that in some cases[4,5] there is a close similarity of the rates and transition-state parameters with those for substitution reactions which are also mainly controlled by the movement of water molecules.

Such stabilizations from the participation of $[Br_2]^{-\bullet}$ and hydrolytic species cannot occur with $[Ni(bipy)_3]^{3+}$ as Br^- does not penetrate the bipy shell and hydrolysis does not occur. The higher $\Delta H^{\ddagger}$ for the oxidation of Br^- compared with that (37.5 kJ mol^{-1}) for the oxidation[11,12] of H_2O_2 by $[Ni(bipy)_3]^{3+}$ reflects the higher redox potential of Br^- (1.807 V)[18] compared with that of H_2O_2 (0.682 V).[18] The high negative $\Delta S^{\ddagger}$ for H_2O_2 (−126 J K^{-1} mol^{-1}) has been attributed[11] to the dominance of the restriction imposed on the solvent in the transition state by the product $H^+(aq)$ over the solvation changes accompanying the charge change in the nickel complex: it is not surprising, therefore, that $\Delta S^{\ddagger} \sim 0$ for Br^-, where the overall change in charge in the transition state is small and no proton is produced.

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