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Kinetics of the Oxidation of Bromide Ions by Bis(2,2′-bipyridine)manganese(III) Ions in Aqueous Perchlorate Media

MALCOLM P. HEYWARD and CECIL F. WELLS*

Department of Chemistry, University of Birmingham, Edgbaston, P.O. Box 363, Birmingham B15 2TT, U.K.

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Abstract

The kinetics of the oxidation of bromide ions by the bis(2,2′-bipyridine)manganese(III) ion have been investigated over a range of acid concentrations for several temperatures. Initial rates of reaction are measured and from their variation with $[Mn^{III}]$ and $[Br^-]$ it is concluded that the observed order in $[Mn(bipy)_2{}^{3+}{}_{aq}]$ is one and that in $[Br^-]$ is intermediate between zero and one. It is shown kinetically that intermediate complexes between Mn^{III} and Br^- ions are involved and from the variation of the rate constant with acidity it is concluded that the decomposition of $Mn(bipy)_2Br^{2+}{}_{aq}$ is definitely involved as a rate controlling step and that the decomposition of the protonated complex $Mn(bipy)(bipy\text{-}H^+)Br^{3+}{}_{aq}$ is also probably involved as a rate controlling step. The kinetics and mechanism for this oxidation are compared with those found for other cations complexed with bipyridine, for aqua-cations and for other complexes of Co^{III}.

Introduction

Transition metal complexes with a high redox potential oxidize bromide ions to molecular bromine. With aqua-cations, the order in $[Br^-]$ is variable, being one for $Co^{III}{}_{aq}$ [1–4], $Co(NH_3)_2{}^{3+}{}_{aq}$ [5], $Co(en)^{3+}{}_{aq}$ [6] and for $Mn^{III}{}_{aq}$ at low $[Br^-]$ [7]; two for $Ce^{IV}{}_{aq}$ [8] and for $Mn^{III}{}_{aq}$ at high $[Br^-]$ [7]; three for $V^V{}_{aq}$ [9]; and with $Ni(bipy)_3{}^{3+}$ the order in $[Br^-]$ is one [10]. In all cases, the order in [cation] is one, and the rate constant varies with $[H^+]$ for all the cases [1–9] except $Ni(bipy)_3{}^{3+}$ [10]. We report here the oxidation of Br^- by $Mn(bipy)_2{}^{3+}{}_{aq}$ to compare with the above oxidations and with the oxidation of other substrate ligands by $Mn(bipy)_3{}^{3+}{}_{aq}$ [11].

Experimental

Solutions of bis(2,2′-bipyridine)manganese(III) ions were prepared by the anodic oxidation of tris(2,2′-bipyridine)manganese(II) ions [12]. Sodium bromide was recrystallized and subsequently dried at 120 °C. Propenonitrile was purified by washing three times with 1 mol dm^{-3} NaOH followed by washing five times with distilled water, drying over anhydrous sodium sulphate and finally distilling under reduced pressure of nitrogen. Solutions of sodium perchlorate were prepared by the neutralization of 12 mol dm^{-3} $HClO_4$ by Analar sodium carbonate followed by boiling to expel CO_2 and filtration to remove trace impurities; solutions of lithium perchlorate were prepared in the same way using lithium carbonate. A.R. perchloric acid was used and water was distilled once in an all-glass still. A.R. benzene was used.

Initial concentrations of $Mn(bipy)_2{}^{3+}$ were determined by sampling into an excess of a solution of Fe^{II} with back-titration with a standard solution of Ce^{IV}. Changes in absorbance with time were followed at 400 nm in the thermostatted cell compartments of either a Unicam SP800 or of a Unicam SP500 Series 2 spectrophotometer with the aid of pen recorders.

Results and Discussion

Stoichiometry

Excess of $Mn(bipy)_2{}^{3+}{}_{aq}$ was added to an acidic solution of sodium bromide containing $HClO_4$ and $NaClO_4$. A sample was pipetted into a solution of Fe^{II} which was then back-titrated with a standard Ce^{IV} solution. This was repeated without the presence of sodium bromide. This was done in 0.10 and 1.00 mol dm^{-3} $HClO_4$ at 20 °C whilst maintaining the ionic strength at 1.00 mol dm^{-3} by the addition of $NaClO_4$. The values for the consumption ratio $|\Delta[Mn^{III}]|/|\Delta[Br^-]|$ are collected in Table I. For these experiments with excess Mn^{III} and for others with excess Br^-, the product Br_2 was extracted by shaking the reaction mixture three times with 15 cm^3 samples of benzene which were combined and the concentration of Br_2 determined from the extinction coefficient $\epsilon = 6.88 \times 10^3$ dm^3 mol^{-1} cm^{-1} at 292 nm for the 1:1 Br_2–benzene charge

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*Author to whom correspondence should be addressed.

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TABLE I. Consumption and Product Ratios for the Oxidation of Br^- by $Mn(bipy)_2{}^{3+}{}_{aq}$ at an Ionic Strength of 1.00 mol dm^{-3}

Temperature (°C)	$[H^+]$ (mol dm^{-3})	Initial $[Br^-]$ (10^{-4} mol dm^{-3})	$\lvert\Delta[Mn^{III}]\rvert / \lvert\Delta[Br^-]\rvert$	$\lvert\Delta[Br_2]\rvert / \lvert\Delta[Mn^{III}]\rvert$
5	1.00	8.0		0.38
5	1.00	120		0.40
5	1.00	40		0.40
5	1.00	200		0.45
20	0.10	2.00	0.95	
20	0.10	1.00	1.10	
20	0.50	12.0		0.34
20	1.00	3.00	0.90	0.24
20	1.00	1.00	1.06	0.34
20	1.00	2.00	0.99	0.29
20	1.00	9.6		0.34
20	1.00	14.4		0.32
20	1.00	20.0		0.30
40	1.00	8.0		0.25
40	1.00	40.0		0.24
40	1.00	200		0.28

transfer complex [13]. It was shown that for $[HClO_4] > 0.3$ mol dm^{-3} 2,2′-bipyridine does not interfere with the spectrophotometric examination of benzene extracts. The values for the product yield $\lvert\Delta[Br_2]\rvert/\lvert\Delta[Mn^{III}]\rvert$ at 5, 20 and 40 °C are also given in Table I.

Table I shows that the mean value of $\lvert\Delta[Mn^{III}]\rvert/\lvert\Delta[Br^-]\rvert = 1.00 \pm 0.07$, invariant with acidity, corresponding to an overall reaction (1) which is identical

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

with the stoichiometry found for the oxidation of bromide ions by other oxidizing transition metal cations [1–10]. Unfortunately, the ratio $\lvert\Delta[Br_2]\rvert/\lvert\Delta[Mn^{III}]\rvert$ never reaches the value 0.5 expected for reaction (1); although it approximates to this value at 5 °C, it deviates farther as the temperature rises. As $\lvert\Delta[Br_2]\rvert/\lvert\Delta[Mn^{III}]\rvert = 0.50$ for the oxidation of bromide ions by hexaaquamanganese(III) ions [7], and the deviation becomes greater as the temperature rises, it would appear likely that the $\lvert\Delta[Br_2]\rvert/\lvert\Delta[Mn^{III}]\rvert < 0.5$ found here results from bromine atoms produced in the rate determining step being consumed in a reaction 2,2′-bipyridine rather than dimerizing to give molecular bromine. The production of the bromine atoms is suggested by the observation that these reaction mixtures initiate the polymerization of propenonitrile under anaerobic conditions although the individual reactants separately do not do this.

Kinetics of the Oxidation

The rate of decay of $[Mn^{III}]$ was followed at 400 nm, using an excess of Br^- over Mn^{III}. It was found that $Br_3{}^-$ ions formed by the interaction of the product Br_2 with excess Br^- ions interfere with the spectrophotometric determination of $Mn(bipy)_2{}^{3+}{}_{aq}$ at 400 nm, so initial rates were measured, as done in the oxidation of bromide ions by the hexaaquamanganese(III) ion [7]. The values for these initial rates R_i were determined for a range of initial $[Mn^{III}]$ and initial $[Br^-]$ for varying acidity at 18.1, 21.8, 26.8, 36.0 and 41.8 °C. Plots of R_i against initial $[Mn^{III}]$ for constant $[Br^-]$, $[H^+]$ and temperature were found to be linear and examples of these are shown in Fig. 1. The slopes of such plots provide values for the pseudo first order rate constant k_0 for the oxidative decay of $Mn(bipy)_2{}^{3+}{}_{aq}$ and these are collected in Table II. The ionic strength for the determination of R_i was generally controlled at 1.00 mol dm^{-3} by the addition of sodium perchlorate,

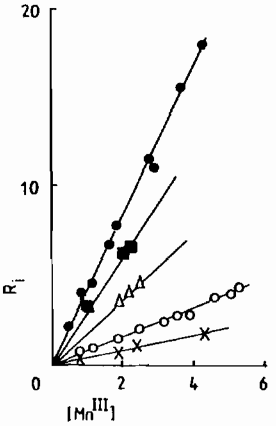

Fig. 1. Plots of R_i (10^{-5} mol dm^{-3} s^{-1}) against initial $[Mn(bipy)_2{}^{3+}]$ (10^{-4} mol dm^{-3}) for the oxidation of bromide ions at $[H^+] = 0.20$ mol dm^{-3} and at an ionic strength = 1.00 mol dm^{-3} and at 21.8 °C with $[Br^-]$ (10^{-3} mol dm^{-3}) as follows: ×, 4.00; ○, 8.00; △, 16.0; ■, 30.0; ●, 40.0.

TABLE II. Values of the First Order Rate Constant k_0 (10^3 s^{-1}) for the $Mn(bipy)_2^{3+}$ + Br^- Reaction at Various Temperatures, [H^+], [Br^-] and Ionic Strengths I

Temperature (°C)	[H^+] (mol dm^{-3})	I (mol dm^{-3})	[Br^-] (10^{-3} mol dm^{-3}) 0.40	0.80	1.20	1.60	2.00	4.00	8.00	12.0	16.0	20.0	30.0	40.0
21.8	0.200	1.00						0.43	0.81	1.33	1.82	2.27	3.05	4.20
21.8	0.500	1.00						0.85	1.33	1.80	1.97	2.28		
21.8	0.70	1.00					0.60	1.05	1.37	1.70	2.07	2.30		
21.8	1.00	1.00	0.18	0.38	0.60	0.63	0.67	1.28	1.55	1.83	2.17	2.33	2.60	
21.8	0.500	2.00							1.25	1.50		1.93		2.50
21.8	1.00	2.00						1.10	1.40			1.75		1.95
21.8	1.50	2.00						1.00	1.18	1.25		1.40		
21.8	2.00	2.00						0.90	1.02	1.07		1.10		
18.1	1.00	1.00					0.60	0.75	1.02	1.13	1.33			
26.8	1.00	1.00	0.40	0.75			1.38	1.75	2.45	2.75	3.07	3.47		
36.0	1.00	1.00			1.97[a]		3.55	4.20	5.8	6.5	7.3	8.6		
41.8	1.00	1.00	1.32	3.38			4.80	5.6	7.8	10.3				

[a] Br^- = 1.00 × 10^{-3} mol dm^{-3}.

but it was shown that replacing Na^+ by Li^+ in the inert salt has no effect on the rate. It was also shown that R_i is unchanged by the addition of an excess [bipy] = 5.14 × 10^{-3} mol dm^{-3} to the reaction mixtures.

Values for R_i were also determined at 21.8 °C for varying [Mn^{III}], [Br^-] and [H^+] but with the ionic strength adjusted to 2.00 mol dm^{-3} by the addition of $NaClO_4$. The values of k_0 determined from the slopes of the linear plots of R_i *versus* initial [Mn^{III}] at constant [Br^-] and [H^+] are included in Table II. Comparison of these values of k_0 with those found at an ionic strength of 1.00 mol dm^{-3} at the same temperature shows that k_0 decreases as the ionic strength increases.

Plots of k_0^{-1} against $[Br^-]^{-1}$ for constant acidity and constant temperature were found to be linear with an intercept on the ordinate at both ionic strengths and examples of these plots are given in Fig. 2. Values for the slopes and intercepts of these plots, calculated using the least-squares procedure are given with their standard errors in Table III.

Mechanism of the Oxidation

The linear plots of k_0^{-1} against $[Br^-]^{-1}$ show that at least one intermediate complex is involved in the oxidation and the variation of the slopes and intercepts with acidity suggests that either $Mn(bipy)_2{}^{3+}{}_{aq}$ or the intermediate complex or both are involved in acid–base equilibria. Although it is suggested that the bis(2,2′-bipyridine)manganese(III) complex exists predominantly [12] as $Mn(bipy)_2OH^{2+}$, the existence of the aqua-form in solution in equilibrium (2) cannot be excluded.

$$Mn(bipy)_2{}^{3+}{}_{aq} \xrightleftharpoons{K_h} Mn(bipy)_2OH^{2+}{}_{aq} + H^+{}_{aq} \qquad (2)$$

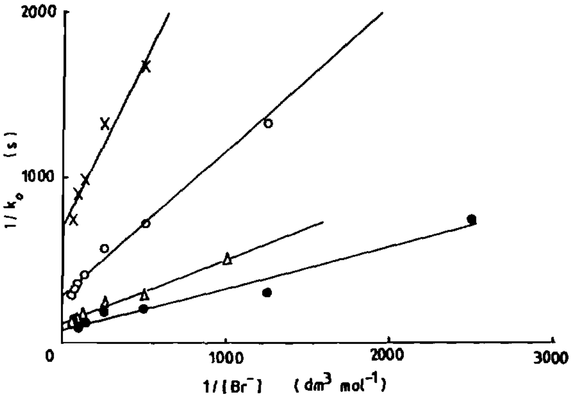

Fig. 2. Plots of k_0^{-1} (s) against $[Br^-]^{-1}$ (dm^3 mol^{-1}) for the $Mn(bipy)_2{}^{3+}$ + Br^- reaction at [H^+] = 1.00 mol dm^{-3} and at an ionic strength = 1.00 mol dm^{-3} at the following temperatures (°C): ×, 18.1; ○, 26.8; △, 36.0; ●, 41.8.

This equilibrium will be established very quickly compared with the rate determining step in the oxidation process, as will also possible pre-equilibria (3)–(5)

$$Mn(bipy)_2{}^{3+}{}_{aq} + Br^- \xrightleftharpoons{\beta} Mn(bipy)_2Br^{2+}{}_{aq} \qquad (3)$$

$$Mn(bipy)_2Br^{2+}{}_{aq} \xrightleftharpoons{K} Mn(bipy)_2OHBr^{+}{}_{aq} + H^+{}_{aq} \qquad (4)$$

$$Mn(bipy)_2OH^{2+}{}_{aq} + Br^- \xrightleftharpoons{\beta'} Mn(bipy)_2OHBr^{+}{}_{aq} \qquad (5)$$

There is more than one route to produce $Mn(bipy)_2OHBr^+$ and these are kinetically indistinguishable. If we assume that the rate determining steps are eqns. (6) and (7)

TABLE III. Slopes and Intercepts of the Plots of k_0^{-1} *vs.* $[\mathrm{Br}^-]^{-1}$ for the $\mathrm{Mn(bipy)_2}^{3+}$ + Br^- Reaction

Temperature (°C)	Ionic strength (mol dm^{-3})	[H$^+$] (mol dm^{-3})	Slope (mol dm^{-3} s)	Intercept (s)
21.8	1.00	0.200	9.4 ± 0.3	9 ± 31
21.8	1.00	0.500	3.69 ± 0.13	265 ± 17
21.8	1.00	0.700	2.64 ± 0.12	338 ± 29
21.8	1.00	1.00	1.99 ± 0.06	316 ± 38
21.8	2.00	0.500	4.00 ± 0.33	313 ± 26
21.8	2.00	1.00	1.74 ± 0.09	481 ± 13
21.8	2.00	1.50	1.36 ± 0.14	667 ± 21
21.8	2.00	2.00	1.02 ± 0.02	856 ± 4
18.1	1.00	1.00	2.02 ± 0.25	712 ± 65
26.8	1.00	1.00	0.88 ± 0.02	285 ± 16
36.0	1.00	1.00	0.39 ± 0.02	115 ± 10
41.8	1.00	1.00	0.25 ± 0.03	79 ± 33

$$\mathrm{Mn(bipy)_2Br^{2+}{}_{aq}} \xrightarrow{k_1} \mathrm{Mn^{II}{}_{aq}} + 2\mathrm{bipy} + \mathrm{Br}\cdot \qquad (6)$$

$$\mathrm{Mn(bipy)_2OHBr^{+}} \xrightarrow{k'_1} \mathrm{Mn^{II}{}_{aq}} + 2\mathrm{bipy} + \mathrm{Br}\cdot \qquad (7)$$

to produce bromine atoms as the free radical detected by the polymerization test which then dimerize very rapidly as in eqn. (8) to give the product, molecular bromine.

$$\mathrm{Br}\cdot + \mathrm{Br}\cdot \xrightarrow[\text{fast}]{\text{very}} \mathrm{Br_2} \qquad (8)$$

As $K_h h^{-1} \gg 1$ [11, 12], where $h = [\mathrm{H^+{}_{aq}}]$, eqn. (9) can be deduced

$$\frac{1}{k_0} = \frac{K_h}{(k_1 h + k'_1 K)\beta[\mathrm{Br}^-]} + \frac{h + K_1}{(k_1 h + k'_1 K)} \qquad (9)$$

This equation would explain the linear plots of k_0^{-1} against $[\mathrm{Br}^-]^{-1}$ with slopes and intercepts which vary with acidity.

If eqn. (9) applies quantitatively, the slopes of these plots will vary with h according to eqn. (10).

$$\frac{1}{(\mathrm{slope})} = \frac{\beta(k_1 h + k'_1 K)}{K_h} \qquad (10)$$

However, as the example in Fig. 3 shows, the linear plot obtained for $(\mathrm{slope})^{-1}$ against h appears to pass through the origin and, indeed, as this implies, a plot of (slope) against h^{-1} (cf. Fig. 4) should be linear passing through the origin. In this case, $k_1 h \gg k'_1 K$, and the intercepts of the plots of k_0^{-1} against $[\mathrm{Br}^-]^{-1}$ should vary linearly with h^{-1}. However, as Fig. 5 shows, a plot of the intercept against h for an ionic strength = 1.00 mol dm^{-3} is linear with an intercept on the ordinate. As R_i is independent of [bipy], an additional rapid pre-equilibrium (11) followed by the rate determining step (12) are suggested.

$$\mathrm{Mn(bipy)_2Br^{2+}{}_{aq}} + \mathrm{H^+{}_{aq}} \overset{K_2}{\rightleftharpoons} \mathrm{Mn(bipy)(bipyH^+)Br^{3+}{}_{aq}} \qquad (11)$$

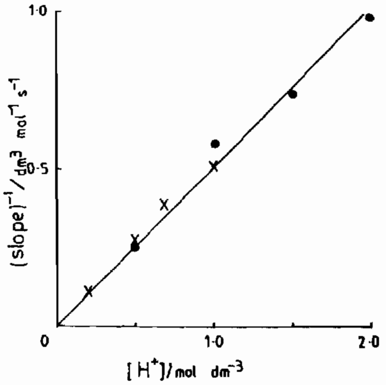

Fig. 3. Plots of the $(\mathrm{slope})^{-1}$ (dm^3 mol^{-1} s^{-1}) against [H$^+$] (mol dm^{-3}) for k_0^{-1} *vs.* $[\mathrm{Br}^-]^{-1}$ at ionic strengths of 1.00 (X) and 2.00 (●) (mol dm^{-3}) at 21.8 °C.

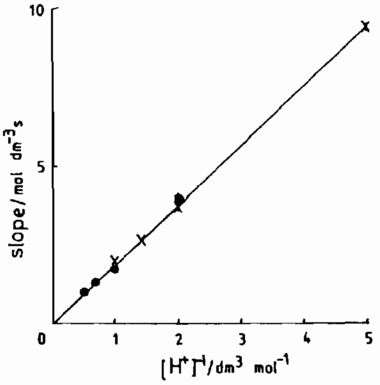

Fig. 4. Plot of the slope (mol dm^{-3} s) against $[\mathrm{H^+}]^{-1}$ (dm^3 mol^{-1}) for k_0^{-1} *vs.* $[\mathrm{Br}^-]^{-1}$ at ionic strengths of 1.00 (X) and 2.00 (●) (mol dm^{-3}) at 21.8 °C.

$$\mathrm{Mn(bipy)(bipyH^+)Br^{3+}{}_{aq}} \xrightarrow{k_2} \mathrm{Mn^{II}} + 2\mathrm{bipy} + \mathrm{Br}\cdot \qquad (12)$$

With the inclusion of these two steps, eqn. (13) can be deduced.

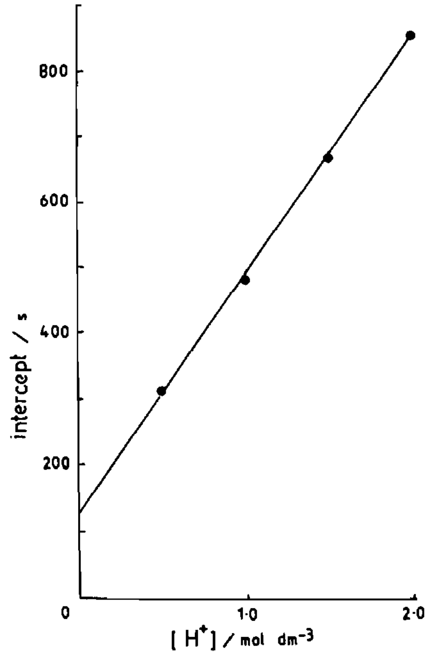

Fig. 5. Plot of the intercept (s) of k_0^{-1} *vs.* $[\mathrm{Br}^-]^{-1}$ against $[\mathrm{H}^+]$ (mol dm^{-3}) at an ionic strength of 2.00 mol dm^{-3} at 21.8 °C.

$$\frac{1}{k_0} = \frac{K_h}{(k_1h + k'_1K + k_2K_2h^2)[\mathrm{Br}^-]} + \frac{h + K + k_2h^2}{k_1h + k'_1K + k_2K_2h^2} \qquad (13)$$

If $k_1h \gg k'_1K + k_2K_2h^2$ and $K_2h^2 + h \gg K$, slope = $K_h/k_1\beta h$, as found in Fig. 4, and eqn. (14) should apply for the intercept.

$$\text{intercept} = \frac{K_2h}{k_1} + \frac{1}{k_1} \qquad (14)$$

This predicts that the intercept will vary linearly with h with an intercept on the ordinate, as found in Fig. 5: the value for $K_2 = 2.88$ dm^3 mol^{-1} at an ionic strength = 2.00 mol dm^{-3} and at 21.8 °C. There is too much scatter on the data at ionic strength = 1.00 mol dm^{-3} to test eqn. (14). From the values for the slopes of the plots of (slope) against h^{-1}, similar to that in Fig. 4, the least-squares procedure applied to a range of temperatures produces $\Delta H^* = 69 \pm 5$ kJ mol^{-1} and $\Delta S^* = -15 \pm 17$ J K^{-1} mol^{-1} for the function $k_1\beta K_h^{-1}$.

Comparison with Oxidation by Other Cations

The inverse plots of k_0^{-1} against $[\mathrm{Br}^-]^{-1}$ for this oxidation show that intermediate $\mathrm{Mn^{III}{-}Br^-}$ complexes are involved with $\mathrm{Mn(bipy)_2}^{3+}$ as the oxidant. The plots such as Fig. 4 suggest that the intermediate complex $\mathrm{Mn(bipy)_2Br^{2+}}_{\mathrm{aq}}$ is involved, and although the scatter on the numerical values of the intercepts of the plots of k_0^{-1} *versus* $[\mathrm{Br}^-]^{-1}$ at an ionic strength = 1.00 mol dm^{-3} is too great to confirm that this is the complex involved, this is strongly supported by the intercepts found at an ionic strength = 2.00 mol dm^{-3}. With $\mathrm{Mn^{3+}}_{\mathrm{aq}}$ the order in $[\mathrm{Br}^-]$ of two at high $[\mathrm{Br}^-]$ shows [7] that intermediate complexes are involved also with the hexaaquamanganese(III) ion. Similarly, the orders in $[\mathrm{Br}^-]$ higher than unity found for the oxidations by $\mathrm{Ce^{4+}}_{\mathrm{aq}}$ [8] and $\mathrm{V^{V}}_{\mathrm{aq}}$ [9] show that cation + Br^- intermediate complexes are involved also in these cases. However, when sufficient bipyridine is present in the coordination sphere to exclude water molecules from contact with the cation, as with $\mathrm{Ni(bipy)_3}^{3+}$ [10], intermediate complexes are not detected. For the oxidation of Br^- by $\mathrm{Co^{III}}_{\mathrm{aq}}$ at high ionic strengths it has been shown [4] that the observed order [3] in h requires the involvement of intermediate complexes, but these have not been detected at lower ionic strengths [1, 2, 4]. Davies and Watkins have argued [2] that a comparison of rate constants at 25 °C with $\mathrm{Co^{III}}_{\mathrm{aq}}$ for the oxidation of Br^- and the substitution by Cl^- is evidence that a similar rate controlling process, namely substitution, is involved in both cases. However, a similar conclusion [2] drawn on the same type of evidence for the oxidation of $\mathrm{H_2O_2}$ by $\mathrm{Co^{III}}_{\mathrm{aq}}$ has been shown [14] to be spurious, as intermediate $\mathrm{Co^{III}}_{\mathrm{aq}} + \mathrm{H_2O_2}$ complexes have been detected kinetically and spectrophotometrically for this oxidation [15]. Similarly, rate controlling substitution for the $\mathrm{Co(NH_3)_2}^{3+}{}_{\mathrm{aq}}{-}\mathrm{Br}^-$ [5, 16] and the $\mathrm{Co(en)^{3+}}_{\mathrm{aq}}{-}\mathrm{Br}^-$ [6] redox reactions has been adduced from a comparison of rate constants at one temperature. However, deductions based on comparisons of rate constants at one temperature only must be approached with caution. With $\mathrm{Co(NH_3)_2}^{3+}{}_{\mathrm{aq}}$, ΔH^* and ΔS^* for the reactions with Br^- and Cl^- compare well [5, 16] but for the reactions with $\mathrm{H_2O_2}$ ΔS^* does not compare well with ΔS^* for substitution by Cl^- even though the rate constants are similar [16]; but for the reactions of $\mathrm{Co(en)^{3+}}_{\mathrm{aq}}$, no comparison of ΔH^* and ΔS^* is made [6]. An analysis of the possible individual processes involved in the approach of the reactants and in the activation steps has been made [14] for cation–ligand redox reactions.

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