Kinetics of Oxidation of Transition-metal Ions by Halogen Radical Anions. Part III.[1] The Oxidation of Manganese(II) by Dibromide and Dichloride Ions Generated by Flash Photolysis

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The radical anions Br_2^- and Cl_2^-, generated by flash photolysis of solutions containing the trihalide ions, oxidize manganese(II) to manganese(III). The reactions are first order in manganese(II) concentration at low concentrations but tend to zero order in manganese(II) at concentrations $>10^{-2}$M. The kinetics are interpreted in terms of the formation of manganese(II)–radical ion complexes, followed by metal-to-ligand electron transfer in the complexes [equations (i) and (ii); X = Br or Cl]. The reaction mechanism can be classified as inner sphere–electron-transfer controlled.

$$X_2^- + Mn^{2+}_{aq} \underset{}{\overset{K}{\rightleftharpoons}} (Mn^{II}X_2^+) \quad \text{(i)}$$

$$(Mn^{II}X_2^+) \xrightarrow{k} Mn^{III} + 2X^- \quad \text{(ii)}$$

At 25 °C and $I = 0{\cdot}25$ mol l^{-1}, the equilibrium constants K are 39 ± 15 (Br_2^-) and 68 ± 30 l mol^{-1} (Cl_2^-) and the rate constants k are $(2{\cdot}3 \pm 0{\cdot}5) \times 10^5$ (Br_2^-) and $(2{\cdot}1 \pm 0{\cdot}5) \times 10^5$ s^{-1} (Cl_2^-). The overall observed activation energies are 36 ± 4 and 34 ± 4 kJ mol^{-1} for the Mn^{II}–Br_2^- and Mn^{II}–Cl_2^- reactions respectively.

IN previous papers [1,2] of this series we have shown that the reactions of Br_2^- with Fe^{2+}_{aq} and of Cl_2^- with Co^{2+}_{aq} are exclusively inner sphere, and that the rate of the redox reaction is controlled by the rate of substitution of the radical anion in the metal ion. The reaction of Cl_2^- with Fe^{2+}_{aq} follows two parallel paths at 25 °C, one an inner sphere–substitution controlled path with a rate constant which is the same as that for the Br_2^-–Fe^{2+}_{aq} reaction, and the other an outer-sphere path. The standard reduction potential of Mn^{3+}_{aq} (+1·55 V) is intermediate between those of Fe^{3+}_{aq} and Co^{3+}_{aq} and the rate of substitution in Mn^{2+}_{aq} is approximately the same (10^6—10^7 l mol^{-1} s^{-1}) as that in Fe^{2+}_{aq} and Co^{2+}_{aq}. The oxidation of Mn^{2+} by the halogen radical anions provides further insight into factors affecting the relative importance of inner- and outer-sphere mechanisms in ligand oxidations of transition-metal aquo-ions.

Manganese(II) was used by Rutenberg and Taube [3] to scavenge halogen radical anions when measuring the primary quantum yields for the photolysis of halogen and trihalide ion in solution, but the scavenging reactions were not investigated. The radical anion Br_2^- has been proposed as an intermediate in the oxidation of Br^- by Mn^{3+}, but no specific information on its reaction with Mn^{2+} has been obtained.[4] The oxidation of Cl^- to Cl by Mn^{3+} is thermodynamically favourable but the high E^0 value (+2·3 V) for reaction (1) makes the initial

$$Cl_2^- + e^- \longrightarrow 2Cl^- \quad (1)$$

one electron-transfer step unfavourable and the reaction has not been observed directly. The production of Cl_2^- from the reaction of Mn^{3+} with Cl^- has been proposed as the initial step in the chloride-catalysed oxidation of thallium(I) by manganese(III).[5]

The present work confirms the preference for the inner-sphere path in the ligand oxidations of labile bivalent transition-metal ions already observed. The rate-determining step in this case is not the rate of substitution of the radical anion on Mn^{2+}_{aq}, but the rate of intramolecular electron transfer in the metal–radical complex. A similar intramolecular electron transfer between radical ligand and metal has recently been observed on pulse radiolysis of the penta-ammine-(*p*-nitrobenzoato)cobalt(III) ion.[6]

EXPERIMENTAL

Solutions of Mn^{II} were prepared from the perchlorate (Fluka) and were standardized by titration with $KMnO_4$. AnalaR sodium halide salts were used to prepare the halide-ion solutions. Acid concentrations and ionic strengths of the solutions were adjusted with perchloric acid (AnalaR) and sodium perchlorate (Fluka). Chlorine used in the preparation of solutions of Cl_3^- was prepared by the oxidation of sodium chloride (AnalaR) and was vacuum distilled. AnalaR bromine was used to prepare Br_3^- solutions. The hydrogen peroxide used was inhibitor-free (Laporte). All other materials were of AnalaR grade purity. Solutions were prepared in water distilled from alkaline potassium permanganate and acidified potassium dichromate.

The flash photolysis apparatus and experimental procedure have been described previously.[1,2] The experiments were performed in aerated solutions as preliminary tests showed that oxygen had no effect on the reactions. In the presence of Mn^{II} reaction (2) (X = Br or Cl) competed with

$$X_2^- + Mn^{II} \longrightarrow Mn^{III} + 2X^- \quad (2)$$

disproportionation (3), and the rate of disappearance of

$$X_2^- + X_2^- \longrightarrow X_3^- + X^- \quad (3)$$

X_2^- was mixed first and second order because the Mn^{II} concentration was very much greater than that of X_2^-. Pseudo-first-order rate constants for the reaction of Mn^{II} with the radical anions were calculated from the time dependence of the X_2^- concentrations.[1,2]

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[1] Part II, A. T. Thornton and G. S. Laurence, preceding paper.

[2] A. T. Thornton and G. S. Laurence, *J.C.S. Dalton*, 1973, 804.

[3] A. C. Rutenberg and H. Taube, *J. Amer. Chem. Soc.*, 1950, **72**, 4426, 5561.

[4] C. F. Wells and D. Mays, *J. Chem. Soc.* (*A*), 1968, 577.

[5] D. R. Rosseinsky and R. J. Hill, *J.C.S. Dalton*, 1972, 715.

[6] M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, 1972, **94**, 1757.

Production of X_2^- *Radical Anions*.—The radical anions Br_2^- and Cl_2^- were produced by flash photolysis of the trihalide ions Br_3^- and Cl_3^- in most of the kinetic experiments, using wavelengths >220 nm. In experiments in which the spectra of the reaction products were measured, OH radicals, produced by flash photolysis of solutions containing H_2O_2, were used to generate the radical anions. This method had been used in the study of the Cl_2^-–Co^{II} reaction [1] and was of particular importance in the present case because the low (*ca.* 100 l mol^{-1} cm^{-1}) absorption coefficients of Mn^{III} species in the 300—500 nm region made accurate measurements impossible in solutions containing free halogen.

RESULTS

Reaction of Br_2^- *with* Mn^{2+}.—In a preliminary study of the reaction between Br_2^- and Mn^{2+} the formation of a transient species absorbing between 400 and 500 nm was reported but not identified.[7] Absorption by Br_2^- and Br_2 prevented measurement of the spectrum of the transient in solutions in which Br_2^- radical ions were produced by flash photolysis of Br_3^-. The spectrum was measured in solutions in which Br_2^- was produced by flash photolysis of H_2O_2–Br^- mixtures (10^{-3}M-H_2O_2, 10^{-1}M-Br^-, and 10^{-1}M-H^+) containing 10^{-1}M-Mn^{2+}. The half-life of the Br_2^- radical ions in these solutions was <10 μs and the spectrum of the transient 100 μs after the flash is shown in Figure 1. The maximum in the spectrum at 470 nm is characteristic of the $T_{2g} \longleftarrow E_g$ transition in manganese(III) species.[8] The absorption coefficient at 470 nm is 150 ± 30 l mol^{-1} cm^{-1}; this was calculated from the yield of Br_2^- (measured at 366 nm), assuming all the Br_2^- reacted with Mn^{2+} to give manganese(III).

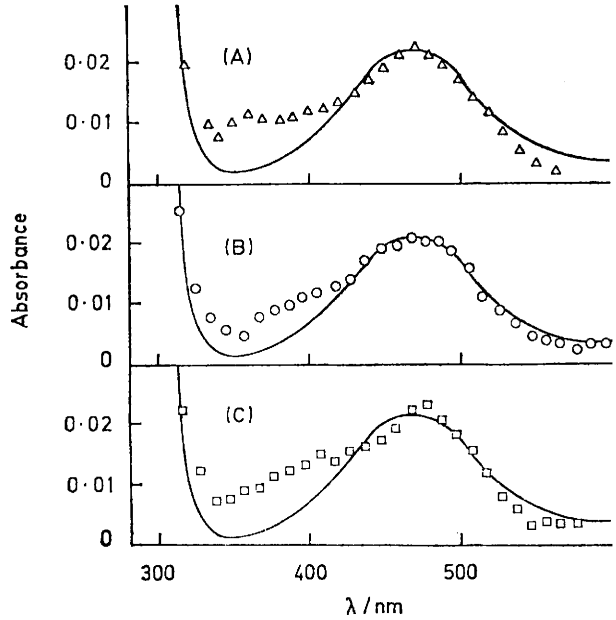

FIGURE 1 Spectra of the products of the reactions of Mn^{2+} with Br_2^- (A), OH (B), and Cl_2^- (C) taken 100 μs after the flash. All the solutions contained 10^{-3}M-H_2O_2, 10^{-1}M-H^+, and 10^{-1}M-Mn^{II}; in addition (A) contained 10^{-1}M-Br^- and (C) 10^{-1}M-Cl^-. The solid line is the spectrum of Mn^{III} in 6M-$HClO_4$ (ref. 11) normalized to our absorbances at 470 nm

Hydroxyl radicals oxidize manganese(II) to manganese(III) [equation (4)] and, in solutions of H_2O_2 (10^{-3}M) and

$$OH + Mn^{2+} \longrightarrow Mn^{III} + OH^- \tag{4}$$

Mn^{2+} (10^{-1}M) alone, a transient manganese(III) species was observed 100 μs after the flash. The spectrum of this transient is also shown in Figure 1. In the experiments in which solutions containing H_2O_2, Br^-, and Mn^{2+} were flashed, the manganese(III) reaction product resulted from oxidation of the Mn^{II} by Br_2^- and not by OH. Rate constants for reaction (4) [9] and for the reaction [10] of OH with Br^- are 2×10^8 and 5×10^9 l mol^{-1} s^{-1} in 10^{-1}M-H^+, and the Br^- effectively scavenged all the OH radicals. Spectra of the manganese(III) species produced by reaction (4), and by reaction of Br_2^- with Mn^{2+} [equation (5)], are

$$Br_2^- + Mn^{2+}_{aq} \longrightarrow Mn^{III} + 2Br^- \tag{5}$$

identical within experimental error (±10%) and are very similar to spectra of manganese(III) aquo- and hydroxo-species measured by Diebler and Sutin.[11]

It was not possible to determine whether Mn^{3+} or $MnBr^{2+}$ was the initial product of reaction (5). Spectra measured 50 or 100 μs after the flash showed no subsequent changes which could be attributed either to anation of Mn^{3+}_{aq} or to aquation of $MnBr^{2+}$. The manganese(III) bromo-complex, $MnBr^{2+}$, has been proposed [4] as an intermediate in the oxidation of Br^- by Mn^{3+}_{aq}, but the spectrum and formation constant of the complex are not known. The Mn^{3+}_{aq} ion is labile, but neither the rate of water exchange nor the rate of ligand substitution in Mn^{3+}_{aq} have been measured. The rate of water exchange has been estimated [12] to be *ca.* 10^6 s^{-1} so that $t_{\frac{1}{2}}$ for equilibrium (6) under our conditions

$$Mn^{3+}_{aq} + Br^- \rightleftharpoons MnBr^{2+} \tag{6}$$

would be *ca.* 1 μs and equilibrium would be maintained during the course of reaction (5) which had a minimum $t_{\frac{1}{2}}$ of *ca.* 10 μs in our experiments.

The reaction product is principally a mixture of Mn^{3+}_{aq} and $MnOH^{2+}$. In 10^{-1}M-Br^- and 10^{-1}M-H^+ we found no evidence of $MnBr^{2+}$ formation. The formation constant [13] of $MnCl^{2+}$ is 13·5 l mol^{-1} and the formation constant of $MnBr^{2+}$ is probably about unity by analogy with the formation constants of $FeCl^{2+}$ and $FeBr^{2+}$. The hydrolysis constant of Mn^{3+}_{aq} is 0·93 l mol^{-1},[14] and in our solutions no more than 5% of the Mn^{III} will be present as $MnBr^{2+}$ even if the formation constant is 10 l mol^{-1}. Our measurements of the spectrum of the reaction products are not accurate enough to identify such a small concentration (<1 μM) of $MnBr^{2+}$ in the presence of Mn^{3+} and $MnOH^{2+}$.

The rate of reaction (5) was studied by measuring the decay of Br_2^- in experiments in which the radical anion was produced by flash photolysis of Br_3^-. Solutions contained *ca.* 3×10^{-5}M-Br_3^- (10^{-1}M-Br^-, 5×10^{-5}M-total Br_2, and 10^{-1}M-H^+) and the manganese(II) concentration was varied from 10^{-3} to 2×10^{-2}M. The kinetics of the Br_2^- disappear-

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[7] A. T. Thornton and G. S. Laurence, *Chem. Comm.*, 1970, **443**.

[8] J. P. Fackler and I. D. Chawla, *Inorg. Chem.*, 1964, **3**, 1130; C. F. Wells, D. Mays, and C. Barnes, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1341.

[9] D. M. Brown, F. S. Dainton, D. C. Walker, and J. P. Keene, 'Pulse Radiolysis,' eds. M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London, 1965, p. 221.

[10] H. C. Sutton, G. E. Adams, J. W. Boag, and B. D. Michael, 'Pulse Radiolysis,' eds. M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London, 1965, p. 61.

[11] H. Diebler and N. Sutin, *J. Phys. Chem.*, 1964, **68**, 174.

[12] G. Davies, *Co-ordination Chem. Rev.*, 1969, **4**, 199.

[13] G. Davies and K. Kustin, *Inorg. Chem.*, 1969, **7**, 1196.

[14] C. F. Wells and G. Davies, *J. Chem. Soc.* (*A*), 1967, 1858.

ance were mixed first and second order because of competition between the pseudo-first-order reaction (5) ($[Mn^{2+}] \gg [Br_2^-]$) and the second-order disproportionation of Br_2^-. Pseudo-first-order rate constants k_5' for reaction (5) at several temperatures are plotted against the manganese(II) concentration in Figure 2. The linear relation between k_5' and the manganese(II) concentration reported previously[7] was not maintained at higher concentrations and temperatures.

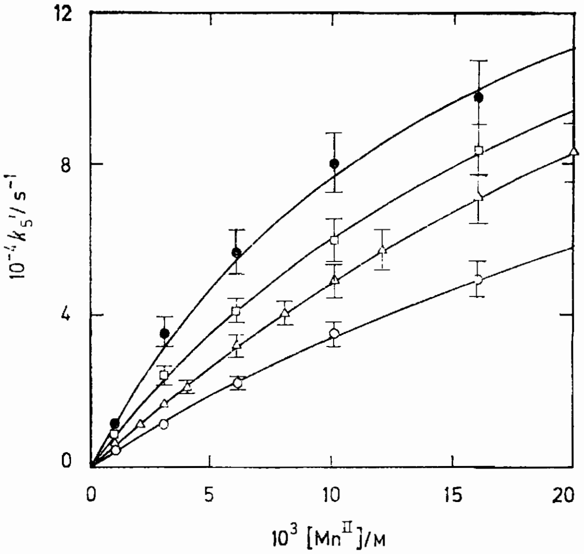

FIGURE 2 Dependence of the pseudo-first-order rate constant, k_5', on $[Mn^{II}]$ for the reaction of Mn^{2+} and Br_2^- at several temperatures: (○), 16; (△), 25; (□), 31; and (●), 40 °C. The solutions contained *ca.* 3×10^{-5}M-Br_3^- (10^{-1}M-Br^-, 5×10^{-5}M-total Br_2, and 10^{-1}M-H^+)

For a reaction between oppositely charged ions, a decrease in rate constant with increasing ionic strength is expected, but the ionic strength increased only from 0·2 to 0·25M over the range of Mn^{II} concentration employed. For the reaction between Cl_2^- and Mn^{2+} we found the rate constant to be independent of ionic strength in this range.

The curvature of the plots of k_5' against Mn^{II} concentration is most simply interpreted in terms of a rapid bimolecular equilibrium step (7) (X = Br or Cl) in which a manganese(II)-radical ion intermediate ($Mn^{II}X_2^+$) is formed followed by a rate-determining step which leads to the products (Mn^{III} and X^-) either directly or through subsequent fast steps (8). If equilibrium (7) is maintained during the reaction, the rate of disappearance of X_2^- is given by equation (9). In our experiments, where $[Mn^{II}] \gg [X_2^-]$, the observed pseudo-first-order rate constant k' is as in equation (10) and for the Mn^{II}–Br_2^- reaction $1/k'$ should be a linear function of $1/[Mn^{II}]$, with intercept $1/k_8$ and gradient $1/k_8K_7$. Reciprocal plots of the experimental data are shown in Figure 3; the expected linear relation apparently holds over the range of Mn^{II} concentration employed. The value of k_8 (25 °C) for the Mn^{II}–Br_2^- reaction, obtained from the intercept in Figure 3, is $(2{\cdot}3 \pm 0{\cdot}5) \times 10^5\ s^{-1}$ and the apparent value of K_7 is 27 ± 10 l mol^{-1}. Values of K_7k_8, K_7, and k_8 at several temperatures are given in Table 1. The errors in the values of K_7 and k_8 are larger than the error in the product K_7k_8 and the observed temperature dependence of the latter cannot sensibly be split into an enthalpy term for K_7 and an activation enthalpy term for k_8. Observed activation parameters for K_7k_8 are included in Table 2.

$$X_2^- + Mn^{II} \underset{}{\overset{K_7}{\rightleftharpoons}} (Mn^{II}X_2^+) \qquad (7)$$

$$(Mn^{II}X_2^+) \xrightarrow{k_8} Mn^{III} + 2X^- \qquad (8)$$

$$-\,d[X_2^-]/dt = k_8K_7[X_2^-][Mn^{II}]/(1 + K_7[Mn^{II}]) \qquad (9)$$

$$k' = k_8K_7[Mn^{II}]/(1 + K_7[Mn^{II}]) \qquad (10)$$

Reaction of Cl_2^- *with* Mn^{2+}.—Flash photolysis of Cl_3^- in the presence of Mn^{2+} showed that the Cl_2^- produced reacted with Mn^{2+}. The rate of disappearance of Cl_2^- was increased and an absorbance in the 400—500 nm region was observed after the Cl_2^- absorbance had decayed. The spectrum of the reaction product was measured in solutions in which the Cl_2^- was produced by flash photolysis of H_2O_2–Cl^- mixtures (10^{-3}M-H_2O_2, 10^{-1}M-Cl^-, and 10^{-1}M-H^+). The Mn^{II} concentration in the solutions was 10^{-1}M and the half-life of Cl_2^- was <10 μs. The spectrum taken 100 μs after the flash is shown in Figure 1. It is the same as that of the products of the reactions of OH and Br_2^- with Mn^{2+}, and the absorption coefficient at the maximum (470 nm) is 150 ± 30 l mol^{-1} cm^{-1}. The Cl^- and H^+ concentrations were large enough for more than 99% of the OH radicals produced by the photolysis of H_2O_2 to react to give Cl_2^-.

Once again the two possible products of reaction (11), $Mn^{3+}{}_{aq}$ and $MnCl^{2+}$, could not be distinguished because of the lability of $Mn^{3+}{}_{aq}$. The formation constant[13] of $MnCl^{2+}$ is 13·5 l mol^{-1} and in our solutions (10^{-1}M-Cl^- and 10^{-1}M-H^+) only a small fraction of the Mn^{III} was in the form of $MnCl^{2+}$. The final reaction products are mainly Mn^{3+} and $MnOH^{2+}$.

$$Cl_2^- + Mn^{2+}{}_{aq} \longrightarrow Mn^{III} + 2Cl^- \qquad (11)$$

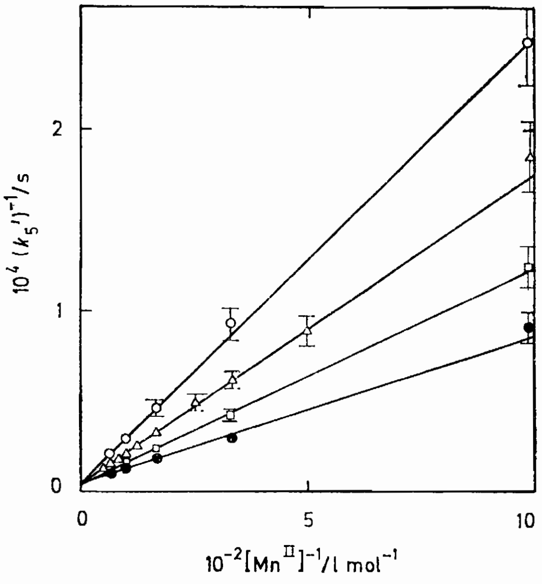

FIGURE 3 Dependence of the reciprocal of the pseudo-first-order rate constant, $1/k_5'$, on $1/[Mn^{II}]$ for the Mn^{2+}–Br_2^- reaction: (○), 16; (△), 25; (□), 31; and (●), 40 °C

The rate of reaction (11) was studied in solutions containing *ca.* 10^{-4}M-Cl_3^- (10^{-1}M-Cl^-, 5×10^{-3}M-Cl_2, and 10^{-1}M-H^+).

TABLE 1

Rate constants for Mn^{II}–halogen radical ion reactions

	$Br_2^- + Mn^{II} \rightarrow Mn^{III} + 2Br^-$			$Cl_2^- + Mn^{II} \rightarrow Mn^{III} + 2Cl^-$		
t/°C	K_7k_8 [$\equiv k_fk_{et}/(k_b + k_{et})$] [a] / $l\ mol^{-1}\ s^{-1}$	k_8 ($\equiv k_{et}$) / s^{-1}	K_7 [$\equiv k_f/(k_b + k_{et})$] [b] / $l\ mol^{-1}$	K_7k_8 [$\equiv k_fk_{et}/(k_b + k_{et})$] [a] / $l\ mol^{-1}\ s^{-1}$	k_8 ($\equiv k_{et}$) / s^{-1}	K_7 [$\equiv k_f(k_b + k_{et})$] [c] / $l\ mol^{-1}$
16	$(4{\cdot}1 \pm 0{\cdot}2) \times 10^6$	$(2{\cdot}1 \pm 0{\cdot}7) \times 10^5$	20 ± 10	$(5{\cdot}6 \pm 0{\cdot}3) \times 10^6$	$(1{\cdot}6 \pm 0{\cdot}6) \times 10^5$	35 ± 15
25	$(6{\cdot}0 \pm 0{\cdot}3) \times 10^6$	$(2{\cdot}2 \pm 0{\cdot}7) \times 10^5$	27 ± 10	$(8{\cdot}3 \pm 0{\cdot}4) \times 10^6$	$(2{\cdot}1 \pm 0{\cdot}6) \times 10^5$	40 ± 15
31	$(8{\cdot}4 \pm 0{\cdot}5) \times 10^6$	$(3{\cdot}0 \pm 0{\cdot}7) \times 10^5$	28 ± 15	$(1{\cdot}08 \pm 0{\cdot}1) \times 10^7$	$(2{\cdot}5 \pm 0{\cdot}6) \times 10^5$	43 ± 20
40	$(1{\cdot}2 \pm 1{\cdot}0) \times 10^7$	$(2{\cdot}2 \pm 0{\cdot}7) \times 10^5$	55 ± 20	$(1{\cdot}7 \pm 0{\cdot}2) \times 10^7$	$(2{\cdot}7 \pm 0{\cdot}7) \times 10^5$	63 ± 20

The data refer to acid and halide-ion concentrations of 10^{-1}M. The ionic strength varied from 0·21 to 0·25M.

[a] The significance of the term $k_fk_{et}/(k_b + k_{et})$ is explained in the Discussion section. [b] If k_f is assumed to be $2 \times 10^7\ l\ mol^{-1}\ s^{-1}$, then k_b is $5 \times 10^5\ s^{-1}$ and the real value of K_7 ($= k_f/k_b$) is $39 \pm 15\ l\ mol^{-1}$ at 25 °C. [c] If k_f is assumed to be $2 \times 10^7\ l\ mol^{-1}\ s^{-1}$, then k_b is $3 \times 10^5\ s^{-1}$ and the real value of K_7 ($= k_f/k_b$) is $68 \pm 30\ l\ mol^{-1}$ at 25 °C.

TABLE 2

Rates and mechanisms of M^{2+}–X_2^- reactions

Reaction	Mechanism [a]	ΔG^0 / kJ mol^{-1}	k (25 °C) / $l\ mol^{-1}\ s^{-1}$	ΔH^* / kJ mol^{-1}	ΔS^* / J $K^{-1}\ mol^{-1}$
$Fe^{2+} + Cl_2^-$ [b]	Outer sphere	−147	$1{\cdot}0 \times 10^7$	20·2	−44
$Fe^{2+} + Cl_2^-$ [b]	I.s.–substitution	−147	$4{\cdot}0 \times 10^6$	29·0	−23
$Fe^{2+} + Br_2^-$ [b]	I.s.–substitution	−97	$3{\cdot}6 \times 10^6$	22·7	−45
$Mn^{2+} + Cl_2^-$ [c]	I.s.–electron transfer	−71	$8{\cdot}5 \times 10^6$	32 ± 4	-4 ± 6
$Co^{2+} + Cl_2^-$ [d]	I.s.–substitution	−43	$1{\cdot}4 \times 10^6$	29·0	−31
$Mn^{2+} + Br_2^-$ [c]	I.s.–electron transfer	−21	$6{\cdot}3 \times 10^6$	$33{\cdot}6 \pm 4$	-3 ± 6

[a] I.s.–substitution and i.s.–electron transfer refer to inner sphere–substitution controlled and inner sphere–electron-transfer controlled mechanisms respectively. [b] Ref. 2. [c] Data refer to the overall reactions. Rate constants are equivalent to $k_fk_{et}/(k_b + k_{et})$ as discussed in the text. [d] A. T. Thornton and G. S. Laurence, preceding paper.

The Mn^{II} concentration was varied from 10^{-3} to 2×10^{-2}M. The Cl_2^- produced by the flash disappeared by a combination of first-order [the pseudo-first-order kinetics of reaction (11)] and second-order (the Cl_2^- disproportionation) processes. Pseudo-first-order rate constants k_{11}' for reaction (11) at several temperatures are shown in Figure 4, and show the same type of non-linear dependence on manganese(II) concentration found for the reaction of Br_2^- with Mn^{2+}. The ionic strength of the reactant solutions varied from 0·20 to 0·25M as the Mn^{II} concentration was increased, but the effect of this change in ionic strength was negligible. For 2×10^{-3}M-Mn^{II} in 10^{-1}M-H^+ at 25 °C, the pseudo-first-order rate constants were $(1{\cdot}6 \pm 0{\cdot}1) \times 10^4$ and $(1{\cdot}5 \pm 0{\cdot}1) \times 10^4\ s^{-1}$ at ionic strengths of 0·21 and 0·30M respectively.

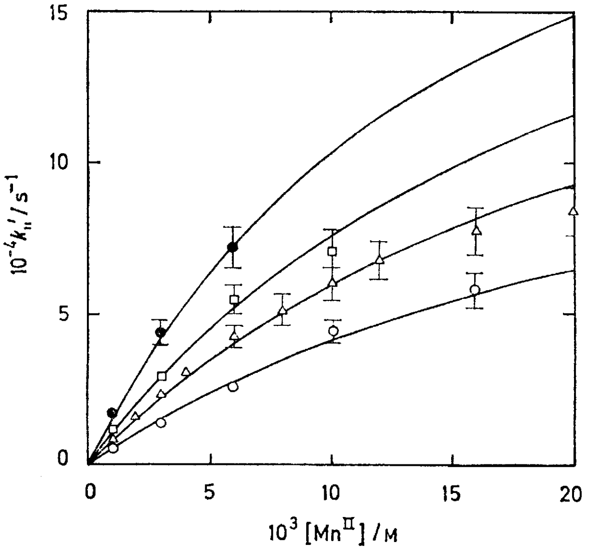

FIGURE 4 Dependence of the pseudo-first-order rate constant, k_{11}', on $[Mn^{II}]$ for the reaction of Mn^{2+} and Cl_2^- at several temperatures: (○), 16; (△), 25; (□), 31; and (●), 40 °C. The solutions contained *ca.* 10^{-4}M-Cl_3^- (10^{-1}M-Cl^-, 5×10^{-3}M-Cl_2, and 10^{-1}M-H^+)

The non-linear dependence of k_{11}' on $[Mn^{II}]$ can be attributed to the same scheme as that for reaction (5). The rapid equilibrium reaction (7) (X = Cl) is followed by a rate-determining step, reaction (8), which ultimately gives the products Mn^{III} and Cl^-. Reciprocal plots of $1/k_{11}'$ against $1/[Mn^{II}]$ are shown in Figure 5. From the intercept, the value of k_8 (25 °C) is $(2{\cdot}1 \pm 0{\cdot}5) \times 10^5\ s^{-1}$ and the apparent value of K_7 is $40 \pm 20\ l\ mol^{-1}$. Values of

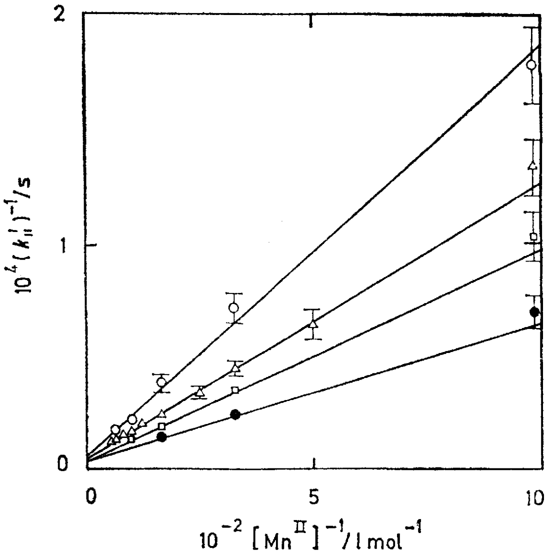

FIGURE 5 Dependence of the reciprocal of the pseudo-first-order rate constant, $1/k_{11}'$, on $1/[Mn^{II}]$ for the Mn^{II}–Cl_2^- reaction: (○), 16; (△), 25; (□), 31; and (●), 40 °C

K_7k_8, K_7, and k_8 for the Mn^{II}–Cl_2^- reaction at several temperatures are given in Table 1 and the observed activation parameters for the overall reaction are given in Table 2.

DISCUSSION

The kinetics suggest that the reactions of Br_2^- (5) and Cl_2^- (11) with Mn^{2+}_{aq} have the same mechanism, but we cannot observationally distinguish between inner- and outer-sphere mechanisms for the reactions because of the lability of Mn^{3+}_{aq}. The complex dependence of the observed rates of reaction on the Mn^{II} concentration, which we have attributed to equilibrium formation of a Mn^{II}–radical ion intermediate followed by a rate-determining step leading to the products, does not uniquely define the reaction mechanism. The equilibrium step may be either formation of an outer-sphere complex (or solvent-separated ion-pair) or formation of an inner-sphere complex. If the intermediate, which we have formally written as ($Mn^{II}X_2^+$) ($X = Br$ or Cl), is an outer-sphere complex the reaction mechanism may be either outer or inner sphere, depending on the nature of the rate-determining step.

For an outer-sphere mechanism the rate-determining step will be electron transfer across the water molecules in the first co-ordination sphere of the manganese ion, and the reaction scheme is as in equations (12) and (13)

$$X_2^- + Mn^{2+}_{aq} \overset{\text{Fast}}{\rightleftharpoons} (Mn^{2+}H_2OX_2^-) \quad (12)$$

$$(Mn^{2+}H_2OX_2^-) \xrightarrow{\text{Slow}} Mn^{3+}_{aq} + 2X^- \quad (13)$$

($X = Cl$ or Br). The formation constants for the outer-sphere complexes will be K_7 and the outer-sphere electron-transfer rate constants will be k_8. The values of K_7 of 27 (Br_2^-) and 40 l mol^{-1} (Cl_2^-) are somewhat larger than would be expected for outer-sphere formation constants between ions with a charge product of 2—, and are also larger than formation constants for the inner-sphere complexes $MnBr^+$ (*K ca.* 5·5 l mol^{-1}) and $MnCl^+$ (*K ca.* 4 l mol^{-1}).[15] Within experimental error the values of k_8 [$(2{\cdot}3 \pm 0{\cdot}5) \times 10^5$ (Br_2^-) and $(2{\cdot}1 \pm 0{\cdot}5) \times 10^5$ s^{-1} (Cl_2^-)] are the same despite the difference of 50 kJ mol^{-1} in the free-energy changes for reactions (5) and (11), and the evidence does not favour an outer-sphere mechanism for the reactions.

The mechanism of the reactions may be inner sphere, even if the intermediate is the outer-sphere complex ($Mn^{2+}H_2OX_2^-$), provided that substitution on Mn^{2+}_{aq} is determined by the rate of loss of water from the solvent-separated outer-sphere complex and that electron transfer between metal and radical ligand in the inner-sphere complex formed in the slow step is fast (inner sphere–substitution controlled mechanism) [equations (12), (14), and (15)]. Because of the relatively large values of K_7 and the slowness of the substitution step (k_8 *ca.* 2×10^5 s^{-1}), we do not think the reactions are inner sphere–substitution controlled. We have found[1,2] that the rates of the inner-sphere oxidation reactions of Fe^{2+}_{aq} and Co^{2+}_{aq} by Br_2^- and Cl_2^- are the same as the rates of substitution in the metal ions. The rate of formation[16] of $MnCl^+$ is $1{\cdot}5 \times 10^7$ l mol^{-1} s^{-1} which is close to the water-exchange rate[17] for Mn^{2+}_{aq} of $2{\cdot}3 \times 10^7$ s^{-1}, as expected for a substitution process largely controlled by loss of water from the outer-sphere complex, but our values of k_8 are only 1/50th of the expected substitution rates.

$$(Mn^{2+}H_2OX_2^-) \xrightarrow{\text{Slow}} Mn^{II}X_2^+ \quad (14)$$

$$Mn^{II}X_2^+ \xrightarrow{\text{Fast}} Mn^{III}X^{2+} + X^- \quad (15)$$

If the intermediate [formally ($Mn^{II}X_2^+$)] is an inner-sphere complex formed by Mn^{2+} and the radical ion, the reaction mechanism is inner sphere–electron-transfer controlled. The formation of the inner-sphere complex [equation (16)] ($X = Cl$ or Br) is followed by rate-determining intra-complex electron transfer [equation (17)]. The equilibrium constants K_7 now refer to formation of the inner-sphere complexes and the rate of the equilibrium step will be governed by the rates of formation and aquation, k_f and k_b. The rate constant, k_{et}, for the electron-transfer reaction will be equivalent to k_8.

$$X_2^- + Mn^{2+}_{aq} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Mn^{II}X_2^+ \quad \text{Fast} \quad (16)$$

$$Mn^{II}X_2^+ \xrightarrow[\text{Slow}]{k_{et}} Mn^{III}X^{2+} + X^- \quad (17)$$

In deriving the rate equations from which K_7 and k_8 were obtained, it was assumed that the equilibrium was rapid compared with the subsequent rate-determining step; the specific assumption was that $k_b \gg k_{et}$. If the equilibrium step is formation of the inner-sphere complex, then k_f will be of the same order of magnitude as the rate of formation of other Mn^{II} complexes and as the rate of water exchange for Mn^{2+}_{aq}, *i.e.* k_f *ca.* 2×10^7 l mol^{-1} s^{-1}. From the values of K_7, we estimate the value of k_b to be *ca.* 5×10^5 s^{-1}; k_{et} ($\equiv k_8$) is 2×10^5 s^{-1} and k_b is *not* very much larger than k_{et}. For the inner sphere–electron-transfer controlled mechanism we have therefore fitted the experimental data to the reaction scheme by means of a computer program which simulates coupled successive reactions by numerical integration.†

After a short induction period (<10 μs) the system comes to a pseudo-equilibrium state in which the ratio $d[X_2^-]/dt : d[Mn^{II}X_2^+]/dt$ is constant. Reciprocals of the observed pseudo-first-order rate constants are not linear in $1/[Mn^{II}]$ in this case, but over the range of Mn^{II} concentration covered in our experiments the departure from linearity is within experimental error (±10%). If k_{obs} is the observed pseudo-first-order rate constant

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† The program is a modification of Program WR16 by K. H. Schmidt, Argonne National Laboratory Report ANL-7199 (TID-4500), Argonne, 1966.

[15] L. G. Sillen and A. E. Martell, 'Stability Constants of Metal-ion Complexes,' Chem. Soc. Special Publ. No. 17, 1964; No. 25, 1969.

[16] R. G. Hayes and R. J. Myers, *J. Chem. Phys.*, 1964, **40**, 877.

[17] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307; M. Grant, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1971, **10**, 71.

approximation (18) can be made. The intercepts of

$$\frac{1}{k_{\text{obs}}} = \frac{k_{\text{b}} + k_{\text{et}}}{k_{\text{f}}k_{\text{et}}[\text{Mn}^{\text{II}}]} + \frac{1}{k_{\text{et}}} \qquad (18)$$

plots of $1/k_{\text{obs}}$ against $1/[\text{Mn}^{\text{II}}]$ (Figures 3 and 5), are unchanged by this treatment, and k_8 is equivalent to k_{et}. From the gradients we obtain not K_7 but $k_{\text{f}}/(k_{\text{b}} + k_{\text{et}})$ and true equilibrium constants for reaction (7) cannot be evaluated. If we assume a value for k_{f} of 2×10^7 l mol^{-1} s^{-1} for both reactions (7) (X = Br or Cl), we find the values for K_7 of 39 ± 15 (Br_2^-) and 68 ± 30 l mol^{-1} (Cl_2^-) at 25 °C. These values are larger than formation constants of manganese(II) halogeno-complexes and of MnNCS^+ (*K ca.* 17 l mol^{-1}),[15] perhaps because of the greater polarizability of the radical anions. Electron transfer between a radical ligand and the metal ion in a metal ion–radical complex has been reported in the pulse radiolysis of penta-ammine(*p*-nitrobenzoato)-cobalt(III) ion.[6] The intermediate cobalt(III)–radical complex decays by ligand-to-metal electron transfer, producing Co^{2+} and free ligand.

The temperature dependence of the overall reaction (Table 2) must refer to the temperature dependence of the function $k_{\text{f}}k_{\text{et}}/(k_{\text{b}} + k_{\text{et}})$ and is not simply the sum of the enthalpy changes for the equilibrium and electron-transfer steps. Activation enthalpies for k_{f} and k_{b} are not known and experimental errors in the values of $k_{\text{et}}(\equiv k_8)$ are too large for a realistic evaluation of the activation enthalpies for electron transfer, so that the observed temperature dependence cannot be related to those of the individual terms in the function $k_{\text{f}}k_{\text{et}}/(k_{\text{b}} + k_{\text{et}})$. For an inner sphere–electron-transfer controlled reaction the observed activation energy must be larger than ΔH^* for formation of the intermediate complex. The ΔH^* value for formation[16] of MnCl^+ is 39 ± 4 kJ mol^{-1} and that for water exchange[17] on $\text{Mn}^{2+}{}_{\text{aq}}$ is 36 ± 4 kJ mol^{-1}. Observed activation energies for reactions (5) and (11) are 36 ± 4 and 34 ± 4 kJ mol^{-1}, suggesting that the electron-transfer reaction is only just rate limiting for these reactions, in agreement with the rate constants k_8 which are only about a factor of 10^{-2} smaller than the probable rates of Mn^{II}–radical ion complex formation.

The simple square-root relation between the rate of an outer-sphere electron-transfer reaction, the electron-exchange rates, and the equilibrium constant for the reaction, derived by Marcus[18] for a weak-interaction model, is well established.[19] The model has been applied with some success[19,20] to inner-sphere reactions involving common oxidants or reductants on the assumption that the contribution of the work terms to $\Delta G^‡$ will be approximately constant for reactions involving similar reactants. Rates of reduction of some Co^{III} complexes by Fe^{2+} and Cr^{2+} are fitted by the model, but calculated rates of reduction by V^{2+} are too high. The inner-sphere V^{2+} reduction reactions are probably substitution controlled and Marcus theory can be applied even approximately only to inner sphere–electron-transfer controlled reactions. For inner sphere–electron-transfer controlled reactions involving metal–radical ligand electron transfer a weak-interaction model is probably inappropriate.

The relevant relations are (19) and (20),[18] and for the

$$\ln f_{ij} \simeq (\ln K_{ij})^2/4\ln(k_{ii}k_{jj}/Z^2) \qquad (19)$$

$$k_{ij} \simeq (k_{ii}k_{jj}K_{ij}f_{ij})^{\frac{1}{2}} \qquad (20)$$

Mn^{II}–X_2^- reactions k_{ii} and k_{jj} are the electron-exchange rates for Mn^{II}–Mn^{III} and X_2^-–X^-, and K_{ij} and k_{ij} are the equilibrium and rate constants for reaction (2). The constant k_{ii} has been estimated[11] to be *ca.* 10^4 l mol^{-1} s^{-1}; k_{jj} is unknown but, as the rates of reaction (21) (X = Cl or Br) are *ca.* 10^{10} l mol^{-1} s^{-1}, it must be *ca.* 10^{10} l mol^{-1} s^{-1}.

$$\text{X} + \text{X}^- \rightleftharpoons \text{X}_2^- \qquad (21)$$

The equilibrium constant K_{ij} can be calculated from the E^0 values for Br_2^- and Cl_2^-.[1] Calculated values of k_{ij} are 5×10^4 and 5×10^7 l mol^{-1} s^{-1} [the experimental values are 6×10^6 (k_5) and 8×10^6 l mol^{-1} s^{-1} (k_{11})]. The agreement between the calculated and experimental values is remarkably good for $k_{11}(\text{Mn}^{\text{II}}\text{–Cl}_2^-)$ but the values for $k_5(\text{Mn}^{\text{II}}\text{–Br}_2^-)$ emphasise the independence of the rates on ΔG^0 for the reaction.

For the outer-sphere path of the reaction between Cl_2^- and Fe^{2+} the model is even less successful. The experimental rate constant is 10^7 l mol^{-1} s^{-1} and the calculated value is 10^{12} l mol^{-1} s^{-1}. It is apparent that the work and reorganizational terms in the Marcus theory, which take into account the work required to bring reactants and products to the separation distances and configuration required in the transition state, cannot be neglected even for this outer-sphere reaction with $\Delta G^0 - 147$ kJ mol^{-1}. The failure of the simple form of the theory for some electron-transfer reactions which involve a change of spin state in going from Co^{II} to Co^{III} is due to the neglect of the work terms and to the possible requirement of an initial spin-excitation equilibrium. For the halogen radical anion oxidations of Mn^{II} to Mn^{III} there are also special factors likely to make the organizational energies large. The major factor is the relatively large change in bond length and configuration on going from Mn^{2+} ($t_{2g}{}^3e_g{}^2$) to Mn^{3+} ($t_{2g}{}^3e_g{}^1$) due to Jahn–Teller distortion associated with the $t_{2g}{}^3e_g{}^1$ electronic configuration for Mn^{3+}. Bond-length changes of *ca.* 0·2 Å could readily account for a contribution of 40 kJ mol^{-1} to the energy required to reach the transition state[21] and therefore for the observation that the Mn^{II} oxidation reactions are electron-transfer controlled.*

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* Reliable bond lengths for corresponding Mn^{II} and Mn^{III} complexes are not widely available, but the Mn–O bond lengths in $[\text{Mn}^{\text{II}}(\text{acac})_2(\text{H}_2\text{O})_2]$[22] and $[\text{Mn}^{\text{III}}(\text{acac})_3]$[23] (acac = acetylacetonato) are 2·13 and 1·87 Å.

[18] R. A. Marcus, *J. Phys. Chem.*, 1963, **67**, 853; *ibid.*, 1968, **72**, 891.

[19] N. Sutin, *Ann. Rev. Phys. Chem.*, 1966, **17**, 119.

[20] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, 1966, **88**, 434; D. P. Fay and N. Sutin, *Inorg. Chem.*, 1970, **9**, 1291.

[21] H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 2304.

[22] H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, 1968, **B24**, 1127.

[23] B. Morison and J. R. Brathovde, *Acta Cryst.*, 1964, **17**, 705.

The kinetic and thermodynamic data and observed mechanisms for the reactions of Br_2^- and Cl_2^- with Mn^{2+}, Fe^{2+}, and Co^{2+} are summarized in Table 2. The different mechanisms prevent a detailed discussion of the factors influencing rates of electron transfer to the radical anions but the diverse mechanisms can be understood qualitatively. For all three metal ions the rates and activation enthalpies for substitution are approximately the same. Only for Mn^{2+} are the reactions inner sphere–electron-transfer controlled and only for the Fe^{2+}–Cl_2^- reaction does the outer-sphere path compete effectively with the inner-sphere path. As expected for the reaction with the largest ΔG^0 value, the Fe^{2+}–Cl_2^- reaction has the highest outer-sphere electron-transfer rate.

For a halogen radical anion bound in the inner sphere of the metal ion, electron transfer from a t_{2g} orbital of the metal to a π orbital of the radical anion will be most probable on symmetry grounds. For the inner-sphere reactions the change in electronic configuration on oxidation will be $t_{2g}^4e_g^2 \longrightarrow t_{2g}^3e_g^2$ for the ground-state change $Fe^{2+} \longrightarrow Fe^{3+}$, and for the outer-sphere reaction attack by Cl_2^- on the face of the octahedron will also favour t_{2g} electron transfer from Fe^{2+}. For Co^{2+} and Mn^{2+} a $t_{2g} \longrightarrow \pi$ electron transfer will result in excited states of Co^{3+} ($t_{2g}^4e_g^2$) and Mn^{3+} ($t_{2g}^2e_g^2$). The change in spin state from Co^{2+}_{aq} to Co^{3+}_{aq} is not a significant barrier to electron transfer in the Co^{2+}_{aq}–Co^{3+}_{aq} electron exchange (activation enthalpies and entropies for the Co^{2+}_{aq}–Co^{3+}_{aq} and Fe^{2+}_{aq}–Fe^{3+}_{aq} exchanges are almost identical),[24] and is probably not important for the substitution controlled Co^{2+}–Cl_2^- reaction. It is possible however that the increased energy requirements which make the Mn^{2+}–X_2^- reactions inner sphere–electron-transfer controlled are due not only to Jahn–Teller effects but also to the barrier to $t_{2g} \longrightarrow \pi$ electron transfer.

The oxidation reactions of Br^- to Br_2^- and of Cl^- to Cl_2^- by Mn^{3+} proceed *via* the halogeno-complexes MnX^{2+} [equations (22) and (23)] followed, in the case of

$$Mn^{3+} + X^- \overset{K_{22}}{\rightleftharpoons} MnX^{2+} \qquad (22)$$

$$MnX^{2+} + X^- \underset{k_{-23}}{\overset{k_{23}}{\rightleftharpoons}} Mn^{II} + X_2^- \qquad (23)$$

Br^-, by the further reaction (24). The reactions of

$$Mn^{3+} + Br_2^- \longrightarrow Mn^{II} + Br_2 \qquad (24)$$

MnX^{2+} with X^- (23) must have the same reaction profiles as those we have observed for the reverse reactions of Mn^{2+} with X_2^- and the inner sphere–electron-transfer controlled mechanism we have established is compatible with the reaction of MnX^{2+} with X^- to give X_2^-, but not with the formation of X by direct reaction (25).

$$Mn^{3+} + X^- \longrightarrow Mn^{II} + X \qquad (25)$$

Wells and Mays [4] observed no specific retardation by Mn^{II} of the oxidation of Br^- by Mn^{III} and, in fitting a reaction scheme to their observed kinetics, assumed that reaction (26) was very much slower than reaction (24).

$$Mn^{II} + Br_2^- \longrightarrow Mn^{III}Br^- + Br^- \qquad (26)$$

Our observations on the mechanism of reaction (5) account for the failure to observe an inverse dependence on $[Mn^{II}]$ for the rate of oxidation of Br^- by Mn^{III}. Wells and Mays used a minimum concentration of Mn^{II} in their reaction mixtures of 0·3M in order to reduce the disproportionation of Mn^{III}. The equilibrium constant K_7 for the formation of the manganese(II)–radical ion complex $Mn^{II}Br_2^+$ is 39 l mol^{-1} and at Mn^{II} concentrations greater than 0·3M more than 90% of the Br_2^- will be complexed. The rate of reaction (5) will then be independent of the Mn^{II} concentration.

It is possible to estimate the standard reduction potential of Br_2^- by combining Wells and Mays' data for reactions (22) and (23) (X = Br) with our value for k_{-23} ($\equiv k_5$). The product $K_{22}k_{23}$ at 25 °C and an ionic strength of 4·0M was $3\cdot6 \times 10^5$ l^2 mol^{-2} s^{-1}. The constant K_{22} is probably close to unity and k_{23} is therefore *ca.* $3\cdot6 \times 10^5$ l mol^{-1} s^{-1}, so that K_{23} is *ca.* 6×10^{-2}. The latter value and the standard reduction potential of Mn^{3+} (1·55 V) give +1·62 V for the standard reduction potential of Br_2^-. In view of the difference in the ionic strengths of the solutions, and the assumed value of K_{22} the agreement with the previously calculated value, +1·77 V,[1] is reasonable.

The oxidation of Cl^- by Mn^{3+} has not been investigated directly. Solutions of Mn^{3+} containing Cl^- are effectively stable, and this is not surprising in view of the unfavourable free-energy change, +77 kJ mol^{-1}, for reaction (23) (X = Cl). The reaction has been proposed by Rosseinsky and Hill [5] to account for the chloride-ion catalysed oxidation of Tl^I by Mn^{III}. They obtained a value of 1·16 l mol^{-1} s^{-1} for k_{23}, which combined with our k_{11} value, 8×10^6 l mol^{-1} s^{-1}, leads to a value for the standard reduction potential of Cl_2^- of +1·9 V, considerably less than the value of +2·29 V calculated previously from thermodynamic data and confirmed by kinetic data for the oxidation of Cl^- by Co^{3+} and the OH–Cl^- equilibrium.[1] The difference is too great to be accounted for by the difference in the acidity and ionic strength of the two sets of measurements. It is probable that the course of the Cl^- catalysed reaction between Mn^{III} and Tl^I is more complex than Rosseinsky and Hill assumed.

The radical anion Cl_2^- was proposed as the active oxidant not only of Tl^I [equation (27)], but also of Tl^{II}

$$Cl_2^- + Tl^I \longrightarrow Tl^{II} + 2Cl^- \qquad (27)$$

[equation (28)]. From the data of Rosseinsky and

$$Cl_2^- + Tl^{II} \longrightarrow Tl^{III} + 2Cl^- \qquad (28)$$

Hill [5] and our value of k_{11}, the stationary-state concentration of Cl_2^- can be calculated. For typical reactant conditions (10^{-3}M-Mn^{III}, 10^{-1}M-Mn^{II}, 10^{-2}M-Tl^I, and

[24] H. S. Habib and J. P. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 1668.

10^{-2}M-Cl^-), the stationary-state concentration of Cl_2^- is $<10^{-11}$ mol l^{-1}, and even if the rate of the Cl_2^-–Tl^{II} reaction is $>10^9$ l mol^{-1} s^{-1}, 10^{-3}M-Mn^{III} can compete for Tl^{II} as in (29) provided the rate of reaction is 10 l mol^{-1} s^{-1}. The reaction of Tl^{II} with Co^{3+} has been studied by flash photolysis.[25] The rate constant is $9{\cdot}5 \times 10^6$ l mol^{-1} s^{-1} and it is therefore probable that the reaction of Mn^{III} with Tl^{II} has a rate constant $\gg 10$ l mol^{-1} s^{-1}. A direct measurement of this rate is being undertaken in order to resolve the problem. We have also found in this laboratory that Mn^{II} reacts with Tl^{II} [equation (30)]

$$Mn^{III} + Tl^{II} \longrightarrow Mn^{II} + Tl^{III} \qquad (29)$$

$$Mn^{II} + Tl^{II} \longrightarrow Mn^{III} + Tl^{I} \qquad (30)$$

with a rate constant of $1{\cdot}9 \times 10^4$ l mol^{-1} s^{-1} and therefore Mn^{II} may also be an effective competitor for Tl^{II}.

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[25] B. Falcinella and G. S. Laurence, unpublished work.