Chloride-catalysed Oxidation of Thallium(I) by Manganese(III) in Aqueous Perchlorate

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Manganese(III), in contrast with cobalt(III), does not react with thallium(I), except when manganese dioxide, from decomposition, or added chloride, are present. The observed rates in the presence of chloride are consistent with ' reversible ' reaction of $MnCl^{2+}$ with Cl^- to give Cl_2^-, which oxidises Tl^I slowly and Tl^{II} rapidly. All Tl^{III} appears as $TlCl_4^-$. Curvature of rate plots at >70—80% reaction may be due to the presence of unreactive polynuclear Mn^{III}, in perhaps <10% amounts. With an assumed association constant for $MnCl^{2+}$ of 13·5 l mol^{-1}, the rate constant for $MnCl^{2+}$ + Cl^- is 1·16 l mol^{-1} s^{-1}.

MANGANESE(III) is oxidised by mechanisms different from those of cobalt(III) when the latter is the faster oxidant. With cobalt(III)–mercury(I) $Co^{III} + Hg_2^{2+}$ is rate determining,[1] whereas the manganese(III)–mercury(I) reaction involves a multiple-sequence mechanism.[2] By contrast, in the mechanistically identical oxidations of iron(II),[3,4] manganese(III) is oxidised faster than cobalt(III). Since the oxidation of Hg_2^{2+} involves two-electron transfer it was of interest to investigate another two-electron reductant, thallium(I), with which the cobalt(III) reaction is[5] $Co^{III} + Tl^I$. Contrary to expectation, manganese(III) was found to be unreactive with pure thallium(I) in *ca.* 3M-$HClO_4$, even at 80 °C. This observation, confirming that of Davies,[6] holds despite the favourable 25 °C standard electrode potentials $E°$ of 1·56 V for manganese(III)–(II) and 1·23 V for thallium(III)–(I); this emphasises the contrast with cobalt(III). Oxidation of thallium(I) was found to proceed at an observable rate either after prolonged heating had resulted in visible decomposition to MnO_2 (see Experimental section) or when chloride was present.

Addition of chloride promoted reaction at measurable rates at 25 °C. A comprehensive kinetic investigation was undertaken as follows, the manganese(III) being followed by amperometric titration with iron(II).

EXPERIMENTAL

The manganese(III) (2—4 × 10^{-3}M) was prepared by slow electrolysis of manganese(II) on platinum in 6M-$HClO_4$ at low (*ca.* 10 μA cm^{-2}) current density, in a largely vain attempt to preclude polynuclear manganese(III). The evidence for polynuclear manganese(III) is tenuous but persistent and such species may exceed 10% of total oxidant. All kinetic samples were ' aged ', *i.e.* at approximate equilibrium with respect to polynuclear species, to prevent ageing taking place during sometimes protracted runs. Manganese(III) reaction samples with acidity 4M were allowed to stand prior to reaction for periods in the range 3—36 h, with no kinetic consequences.

For amperometric standardisation[4] against iron(II), and kinetic determinations of manganese(III), we used a cell with a rotating platinum electrode, a perchlorate bridge, and a 10^{-2}M-chloride calomel reference electrode. The iron(II) was run into the Mn^{III} solution, the iron(II) diffusion current being measured on either a Sangamo–Weston microammeter, for the higher currents, or a calibrated 110 Ω Scalamp galvanometer, for the lower. Manganese(II) (from G. Frederick Smith) was standardised by EDTA titration, as was the excess of manganese(II) stabilising (with respect to disproportionation[2]) the manganese(III), after reduction of the latter with hydroxylamine. Thallous carbonate (B.D.H.) was dissolved in $HClO_4$ and the $TlClO_4$ thus obtained was several times recrystallised from water. The solution was standardised against $KBrO_3$ in HCl. Thallic perchlorate (G. Frederick Smith) in solution, was determined, after SO_2 reduction, with bromate, or directly by oxidation of iodide and thiosulphate titration of the iodine thus liberated. Recrystallised AnalaR $NaClO_4$, was determined as solute by evaporation to dryness and weighing of the residue. AnalaR $HClO_4$ and NaCl were employed, and the water was twice distilled, the second time from permanganate.

Kinetics samples were cooled to 0 °C to quench reaction. The analysis was tested at 0 °C over the range 1·5 × 10^{-3}— 5 × 10^{-6}M in manganese(III) in the presence of all species constituting the reaction solution; in all cases the determination was within 1% of the nominal. Negligible reaction was shown to occur at 0 °C in 20 min, well in excess of the few minutes required for titration. No loss of Mn^{III} was detected in 12 h at 25 °C either in a solution of 5 × 10^{-4}-Mn^{III}, 0·1M-Mn^{II}, 0·05M-Cl^-, and 3M-$HClO_4$, or in one of 5 × 10^{-4}M-Mn^{III}, 0·1M-Mn^{II}, 0·01M-Tl^I, and 3M-$HClO_4$. The kinetic experiments were conducted at ionic strength 3·45M at 25 ± 0·02 °C. It was shown that rates were independent of whether Tl^I or Cl^- were added to initiate reaction.

The stoicheiometry of the chloride-catalysed reaction, and also that of MnO_2 with Tl^I, were established by appropriate analyses. The MnO_2 (B.D.H.) was dried at 150 °C for 2 h. Known mmol amounts were added to Tl^I in 3M-$HClO_4$ and after agitation of the suspension for 4—6 h at 80 °C, residual Tl^I was determined with bromate. The stoicheiometry (MnO_2 consumed)/(Tl^I consumed) was 1·05 ± 0·02 (despite the small $E°$ difference at 25 °C, 1·25 and 1·23 V for $Mn^{IV,II}$ and $Tl^{III,I}$).

RESULTS AND DISCUSSION

The stoicheiometry in the presence of chloride, Mn^{III} consumed per Tl^{III} produced, was 2·03—2·08, which, barring the unlikely coincidence of identical losses of Tl^{III} and Mn^{III} by reaction with solvent, confirms the

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[1] D. R. Rosseinsky and W. C. E. Higginson, *J. Chem. Soc.*, 1960, **31**.

[2] D. R. Rosseinsky, *J. Chem. Soc.*, 1963, 1181.

[3] L. E. Bennett and J. C. Sheppard, *J. Phys. Chem.*, 1962, **66**, 1275.

[4] D. R. Rosseinsky and M. J. Nicol, *Trans. Faraday Soc.*, 1968, **64**, 2410.

[5] K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, 1956, 343.

[6] G. Davies, personal communication.

reaction to be almost exclusively $2Mn^{III} + Tl^{I} \longrightarrow 2Mn^{II} + Tl^{III}$. Different determinations showed Mn^{III} consumed per Tl^{I} consumed to be $2 \pm 0{\cdot}04$ indicating no side-reaction of Mn^{III}. Free chlorine was never detectable.

First, initial rates were examined in the form of slopes of log $[Mn^{III}]$ against time, t. In nearly all runs $[Mn^{III}]$ was the only variable, all other participants being in sufficient excess. (Two runs do not quite comply, $[Tl^{I}]$ being slightly low, but deviations of the rate constants were insignificant.) The initial data showed an order close to 2 in Cl^-, *ca.* 1 in Mn^{III}, <1 in Tl^{I}, and a low, apparently inverse, order in Mn^{II}. Some of these features resemble those in the chloride-catalysed oxidation of thallium(I) by cerium(IV),[7] in which the effective oxidant is Cl_2^-. Following Duke and Borchers' scheme [7] for cerium(IV) as oxidant, we tested the following mechanism. Before elaboration, the roles of the chloro-complexes of Tl^{III} have to be reckoned. The species [8,9] $TlCl_n^{(3-n)+}$, with $n = 1$—4 and possibly 6, are established. However, when the ratio $[Cl^-]/[Tl^{III}] > 4{\cdot}5$ the stability constants are such [9] that virtually all of the Tl^{III} is $TlCl_4^-$, which simplifies our task enormously. We have accordingly arranged for the ratio always to be $>4{\cdot}5$ (usually $\gg 4{\cdot}5$).

The mechanism to be tested is:

$$Mn^{3+} + Cl^- \overset{K}{\rightleftharpoons} MnCl^{2+} \text{ (rapid)}$$

$$MnCl^{2+} + Cl^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Mn^{2+} + Cl_2^-$$

$$Tl^{I} + Cl_2^- \xrightarrow{k_3} Tl^{II} + 2Cl^-$$

$$Tl^{II} + Cl_2^- \xrightarrow{k_4} Tl^{III} + 2Cl^-$$

$$Tl^{III} + 4Cl^- \rightleftharpoons TlCl_4^- \text{ (rapid and virtually complete)}$$

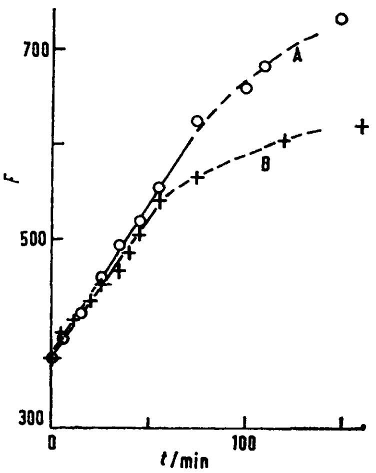
Here $[Cl^-]_t = [Cl^-]_0 - 4[Tl^{III}]_t$. Participation of Tl^{II} in a variety of reactions has been listed by Benson.[10] The stationary state assumption for this and the other intermediate, Cl_2^-, gives the rate law (1). $[Mn^{II}]$ and

$$-\frac{d[Mn^{III}]}{dt} = k_1K[Mn^{III}][Cl^-]^2\left(1 - \frac{k_2[Mn^{2+}]}{2k_3[Tl^{I}] + k_2[Mn^{2+}]}\right) \quad (1)$$

$[Tl^{I}]$, but not $[Cl^-]$, being constant in each experiment, we write the parenthesised factor as $(1 - k')$, and obtain $dx/dt = k''x(a + 2x)^2$ by putting $[Tl^{III}]_0 = 0$, $[Mn^{III}]_t = x$, and $[Cl^-]_0 - 2[Mn^{III}]_0 = a$, with $k'' = k_1K(1 - k')$. Hence on integration:

$$([Cl^-]_0 - 2[Mn^{III}]_0)^{-2} \ln [Mn^{III}]^{-1}([Cl^-]_0 + 2[Mn^{III}] - 2[Mn^{III}]_0) - \{([Cl^-]_0 + 2[Mn^{III}] - 2[Mn^{III}]_0)([Cl^-]_0 - 2[Mn^{III}]_0)\}^{-1} = k''t$$

This function has been plotted for 10-fold changes in $[Mn^{III}]_0$ (and so *ca.* 100-fold in $[Mn^{III}]$), 50-fold in Tl^{I}, 12-fold in Cl^-, and in 1—3M-$HClO_4$. Four separate stock solutions of manganese(III) were employed. The plots for three of these stock solutions were linear to *ca.* 70 or 80% reaction, but for one the curvature started sooner, usually between 65 and 70%. This deviation is discussed below, but we emphasise the linearity of the major part of the runs, as illustrated in the Figure for two runs of virtually identical composition, but one comprising the more deviant stock manganese(III). In Table 1, when k' (depending on $[Tl^{I}]$ and $[Mn^{II}]$) is constant, then $k_1K(1 - k')$ from the linear slope remains satisfactorily constant with extensive change of $[Mn^{III}]$ and $[Cl^-]$, underlining the close correspondence of the observations to the assumed mechanism. Values of $k_1K(1 - k')$ are given in the second column of the Table. Where expected (*i.e.* at fixed $[HClO_4]$) they are constant, to *ca.* 10% at worst and to 3% on average.



Plots of function F of the integrated rate equation against time, t, for the two different stock solutions indicated in Table 1. F is the function $([Cl^-] - 2[Mn^{III}]_0)^{-1} \ln [Mn^{III}]^{-1}([Cl^-]_0 + 2[Mn^{III}] - 2[Mn^{III}]_0) - ([Cl^-]_0 + 2[Mn^{III}] - 2[Mn^{III}]_0)$. Linearity: A, 80% reaction; B, 60% reaction

Since $1 - k' = (2k_3/k_2)/\{(2k_3/k_2) + [Mn^{2+}]/[Tl^{I}]\}$, several guesses of $(2k_3/k_2)$ were made and the constancy of k_1K checked, for reactions with differing $[Tl^{I}]$ and $[Mn^{II}]$, for each choice. The result is shown in Table 2, where $2k_3/k_2 = 30 \pm 5$ is clearly indicated. This value was used to obtain the quoted k_1K results in the third column of Table 1. Using an estimate [11,12] of $K = 13{\cdot}5 \pm 0{\cdot}5$ l mol^{-1}, from a fit of rate data for the Mn^{II}-catalysed oxidation of oxalic acid by bromine in the presence of chloride (ionic strength 2M, 25 °C), one obtains, for k_1, $1{\cdot}16 \pm 0{\cdot}05$ l mol^{-1} s^{-1}, the standard deviation of the 36 individual values (from Table 1) being quoted.

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[7] F. R. Duke and C. E. Borchers, *J. Amer. Chem. Soc.*, 1953, **75**, 5186.

[8] M. J. M. Woods, P. K. Gallagher, Z. Z. Hugus, jun., and E. L. King, *Inorg. Chem.*, 1964, **3**, 1313.

[9] T. G. Spiro, *Inorg. Chem.*, 1965, **4**, 731.

[10] D. Benson, ' Mechanisms of Inorganic Reactions in Solution,' McGraw-Hill, London, 1968, pp. 110, 126.

[11] H. Taube, *J. Amer. Chem. Soc.*, 1948, **70**, 1216, 3928.

[12] G. Davies and K. Kustin, *Inorg. Chem.*, 1969, **8**, 1196.

The deviations from linearity in the rate plots, perhaps ascribable to error in Mn^{III} analyses (systematic over-estimates of 10—20% accounting for most of the deviation) are more likely the result of slight, irreversible polymer–Mn^{III} formation since there is the clear difference in extents of linearity between different stocks. The requisite unreactive nature of the polymer and its persistence is possibly a consequence of resonance, for example Mn^{III}–$Mn^{III} \longleftrightarrow Mn^{II}$–$Mn^{IV}$, all three oxidation states being viable in solution and hence of accessible energy in the indicated wavefunction combination of the multi-ion species. We do not pursue the kinetic complication quantitatively both because of its irreproducibility and also because of the further possibility of the formation of mixed Tl^{I}–Tl^{III} chloro-complexes during the run. These are known in the solid [13] but are not detected in solution by Raman spectroscopy.[14] They may still be present at concentrations $<10^{-2}$M, which may be sufficient to affect kinetic results.

TABLE 1

Variation of rate constants (l^2 mol^{-2} s^{-1}) with composition, for four stock manganese(III) solutions

Composition *	$k_1K(1 - k')$	k_1K
As footnote *†	12·3	16·4
1mM-Mn^{III}, 10mM-Cl^-	12·6	16·7
50mM-Tl^{I}	14·4	15·4
6mM-Tl^{I}	9·72	15·1
3mM-Tl^{I}	7·22	15·2
1mM-Tl^{I}	3·83	16·6
10mM-Mn^{II}	14·6	15·1
2M-$HClO_4$	8·33	11·1
1M-$HClO_4$	5·28	7·04
	For 3M-$HClO_4$, mean:	15·8
As footnote *	12·5	16·7
7·5mM-Cl^-	11·8	15·7
7·5mM-Cl^-	12·1	16·1
7·5mM-Cl^-, 5mM-Tl^{I}	8·55	14·3
10mM-Cl^-	11·7	15·6
50mM-Cl^-, 10mM-Tl^{III}	12·9	17·2
2mM-Cl^-	11·3	15·1
7·5mM-Cl^-, 2M-H^+	9·0	12·0
7·5mM-Cl^-, 1·5M-H^+	6·44	8·6
	For 3M-$HClO_4$, mean:	15·6
As footnote *	13·1	17·4
1mM-Mn^{III}	11·1	14·8
7·5mM-Cl^-, 1mM-Mn^{III}	12·1	16·1
10mM-Cl^-	11·1	14·8
45mM-Cl^-, 10mM-Tl^{III}	12·8	17·0
	Mean:	16·0
As footnote *	10·6	14·1
As footnote *†	13·3	17·8
0·1mM-Mn^{III}	11·4	15·2
1mM-Mn^{III}	11·8	15·7
0·25mM-Mn^{III}	11·9	15·9
2mM-Mn^{III}	11·7	15·6
10mM-Cl^-	11·7	15·6
7·5mM-Cl^-	11·4	15·2
7·5mM-Cl^-	12·2	16·3
7·5mM-Cl^-	11·1	14·8
3·75mM-Cl^-	11·1	14·8
7·5mM-Cl^-, 1mM-Tl^{I}	3·78	16·4
7·5mM-Cl^-, 3mM-Tl^{I}	6·39	13·5
6mM-Tl^{I}	9·31	14·5
12mM-Mn^{II}	14·7	15·3
20mM-Mn^{II}	12·8	13·6
200mM-Mn^{II}	9·72	16·2
	Mean:	15·3

For 3M-$HClO_4$, mean for all four stock Mn^{III} solutions (± av. dev.): $k_1K = 15{\cdot}61 \pm 0{\cdot}17$

* 0·50mM-Initial Mn^{III}, 5mM-Cl^-, 100mM-Mn^{II}, 10mM-Tl^{I}, 3M-$HClO_4$, unless otherwise stated; 25 °C, 3·45M ionic strength; $(1 - k')$ as from Table 2. † Plotted in Figure.

TABLE 2

Relative sums of deviations from mean k_1K for various choices of $2k_3/k_2$ *

$2k_3/k_2$	20	25	30	35	40
Residuals	6·25	5·60	5·50	5·80	6·25
Chosen $2k_3/k_2$			30 ± 5		

* From the 12 reactions in Table 1 where $[Mn^{II}]$ and $[Tl^{I}]$ differ from the values given in the footnote.

The order of reaction in $[H^+]$ (Table 1), from 1M to 3M, is apparently 0·7—0·8 if the rate law is written in terms of total oxidant, $[Mn^{III}]$. There is no simple explanation for this, since the extensive hydrolysis of Mn^{III} gives appreciable amounts of both Mn^{3+} and $MnOH^{2+}$. If only the former reacts, the apparent order in $[H^+]$ would be 0·5—0·6, just less than the value quoted. The only other hydrolysed species is Tl^{III} which, however, as $TlCl_4^-$, would be essentially unaffected by the $[H^+]$ changes. Further marginal effects as activity coefficient changes with composition (possibly more marked with both cationic and anionic reactants), or slight increases in amount of unreactive polymer at lower acidity, also require consideration. We do not, however, consider that the $[H^+]$ dependence casts any doubt on the mechanism favoured.

The assumption implicit hitherto, that only a small fraction of Mn^{III} is present as $MnCl^{2+}$, is not quite exact, introducing a maximum error in one case of 7% and an average error of 3%. The chloro-complexes of Tl^{I} and Mn^{II} may be assumed weak, and so neglected.

The species Cl_2^- has been invoked in the reaction of H_2O_2 with O_3 in chloride solution, and it presumably arises also in the Mn^{II}-catalysed oxidation of oxalic acid by chlorine,[11] as well as in the Ce^{IV}–Tl^{I}–Cl^- reaction. The halogen species X_2^- is now quite widely established as a reactive intermediate in redox reactions.[14]

Our mechanism differs from that for Ce^{IV}–Tl^{I}–Cl^- in that the rate for the latter is independent of $[Tl^{I}]$, and several Ce^{II} chloro-complexes are involved; the rate laws thus differ.

Silver(I) catalyses the (chloride free) oxidation of thallium(I) by cerium(IV),[15] but not by manganese(III),

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[13] H. Remy, 'Treatise on Inorganic Chemistry,' vol. I, Elsevier, London, 1956, p. 385.

[14] A. McAuley, *Co-ordination Chem. Rev.*, 1970, **5**, 245.

[15] W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discuss. Faraday Soc.*, 1960, **29**, 49.

even in 0·1M concentration; our observation accords with that of Davies.[6] The difference does not depend on oxidation strength, E° values being 1·56 V ($Mn^{III,II}$) and 1·5 V ($Ce^{IV,III}$).[16] Further trial catalysts for the Mn^{III} reaction, Co^{II} and Cu^{II} in the absence of Cl^-, were also without effect.

The reaction of Co^{III} with Tl^I in the presence of chloride can be confidently predicted to be fast sinc cobalt(III) reacts rapidly with Cl^- to give Cl_2, *via* Cl_2^-.[1] This result would not conform with the Mn^{III}–Co^{II} pattern which we have remarked; it is noteworthy tha a clear first order in H^+ is asserted for the Co^{III}–Cl reaction.[17]

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[16] L. G. Sillén and A. E. Martell, 'Stability Constants,' *Chem. Soc. Special Publ.* No. 17, 1964.

[17] B. Šrámková, J. Zýka, and J. Doležal, *J. Electroanalyt Chem. Interfacial Electrochem.*, 1971, **30**, 185.