218. *The Reaction between Mercury*(I) *and Manganese*(III) *in Aqueous Perchlorate Solution.*

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Manganese(III) perchlorate solutions were found to be reasonably stable in the presence of an excess of manganese(II). The reaction follows the kinetic expression,

$$-d[\mathrm{Mn^{III}}]/dt = k_1[\mathrm{Mn^{III}}][(\mathrm{Hg^I})_2]/[\mathrm{Hg^{II}}] + k_2[(\mathrm{Hg^I})_2][\mathrm{Mn^{III}}]^2/[\mathrm{Mn^{II}}],$$

the k_1 term arising from the reaction of manganese(III) with atomic mercury (Hg°) in solution, the k_2 term from that of manganese(IV) with dimeric mercury(I). k_1 and k_2 are composite and include the equilibrium constants for dismutation of $(Hg^I)_2$ and disproportionation of manganese(III), respectively.

Apart from an approximate measurement of isotopic exchange with manganese(II),[1] no investigation has been undertaken of the electron-transfer reactions of manganese(III) perchlorate. This neglect is partly due to the instability of manganese(III) with respect to disproportionation and, unless precautions are taken to prevent it, consequent precipitation of manganese dioxide. Such precautions were taken in the present investigation of the reaction of manganese(III) with mercury(I) at 50°. The reaction was followed by titration, with standard ferrous solution, of manganese(III) in samples withdrawn from the reaction solution.

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[1] Adamson, *J. Phys. Colloid Chem.*, 1951, **55**, 293.

Oxidations involving manganese(III) in the oxalate complex,[2] as a catalytic intermediate,[3] and with ketone reductants [4] have been studied before. Oxidation of mercury(I) by mercury(II) in the isotopic exchange,[5] by thallium(III),[6] cobalt(III),[7] and by cerium(IV) [8] have also been investigated.

Manganese(III) *Perchlorate Solutions*.—Lingane and Selim [9] were able to study the manganese(II)-(III)-(IV) equilibrium by using 4·5—7M-sulphuric acid as the medium; here manganese(IV) was temporarily stabilised by the high acid concentration and by complex formation with sulphate. Though perchlorate has no such stabilising ability, Lingane and Selim's results indicated that stable manganese(III) solutions might be achieved if the concentration of aqueous manganese(IV) was kept low by repression of disproportionation of the former with an excess of manganese(II). Thus, manganese(III) perchlorate solutions of concentration not exceeding about 10^{-3}M were prepared by addition of acid permanganate solution to sufficient acidified manganese(II) to leave finally a 25-fold excess of the latter ion in ~4M-acid. These solutions were usually stable for days, even when subsequently diluted so that the hydrogen-ion concentration became about 1·5M. However, when the solutions were warmed at 50°, after for 90 minutes an appreciable amount of manganese dioxide precipitated. Even at room temperature the manganese(III) solutions are, in fact, metastable.

Reaction in the Presence of Added Mercury(II).—The course of the reaction was consistent with a two-parameter kinetic expression which could be interpreted by assuming two rapid pre-equilibria, (1) and (2), followed by two rate-determining paths, (3) and (5):

$$(\mathrm{Hg^I})_2 \overset{K'}{\rightleftharpoons} \mathrm{Hg^\circ} + \mathrm{Hg^{II}} \qquad (1)$$

$$2\mathrm{Mn^{III}} \overset{K''}{\rightleftharpoons} \mathrm{Mn^{IV}} + \mathrm{Mn^{II}} \qquad (2)$$

$$\mathrm{Mn^{III}} + \mathrm{Hg^\circ} \xrightarrow{k'} \mathrm{Mn^{II}} + \mathrm{Hg^I} \qquad (3)$$

$$\mathrm{Mn^{III}} + \mathrm{Hg^I} \longrightarrow \mathrm{Mn^{II}} + \mathrm{Hg^{II}}\ (\text{Rapid}) \qquad (4)$$

$$\mathrm{Mn^{IV}} + (\mathrm{Hg^I})_2 \xrightarrow{k''} \mathrm{Mn^{II}} + 2\mathrm{Hg^{II}} \qquad (5)$$

Evidence supporting the postulation of atomic mercury in steps (1) and (3) is given in ref. 6. $\mathrm{Hg^I}$ represents monoatomic mercury(I) as $\mathrm{Hg^+}$, or in a complex (ion-pair) with perchlorate. $(\mathrm{Hg^I})_2$ exists partly as $\mathrm{Hg_2}^{2+}$ and partly as $\mathrm{Hg_2ClO_4}^+$.[10] $\mathrm{Mn^{IV}}$ is probably present as $\mathrm{Mn^{4+}}$ or $\mathrm{MnO^{2+}}$.[1] The k'' path (5), though written as a single two-equivalent oxidation, may be the sum of two one-equivalent steps involving $(\mathrm{Hg_2})^{\mathrm{III}}$ or $(\mathrm{Hg^I} + \mathrm{Hg^{II}})$ as intermediate species.[7] The kinetic expression, which defines k_1 and k_2, is

$$-\mathrm{d}[\mathrm{Mn^{III}}]/\mathrm{d}t = k_1[\mathrm{Mn^{III}}][(\mathrm{Hg^I})_2]/[\mathrm{Hg^{II}}] + k_2[(\mathrm{Hg^I})_2][\mathrm{Mn^{III}}]^2/[\mathrm{Mn^{II}}] \qquad (6)$$

where $k_1 = k'K'$ and $k_2 = k''K''$. Integration, with $[\mathrm{Mn^{III}}]$ as the only variable, leads to

$$\frac{k_1 t}{2{\cdot}303} \cdot \frac{[(\mathrm{Hg^I})_2]}{[\mathrm{Hg^{II}}]} = \log\left(1 + \frac{k_1[\mathrm{Mn^{II}}]}{k_2[\mathrm{Hg^{II}}][\mathrm{Mn^{III}}]}\right) + \text{Constant}. \qquad (7)$$

In these experiments, species other than manganese(III) unavoidably varied in concentration, by up to 4% usually, and by 12% in two runs. As the kinetic expression becomes prohibitively cumbersome if these variations are included, mean concentrations prevailing

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[2] Ladbury and Cullis, *Chem. Rev.*, 1958, **58**, 403, and refs. therein.

[3] Ogard and Taube, *J. Phys. Chem.*, 1958, **62**, 357.

[4] Littler, *J.*, 1962, 832.

[5] King, *J. Amer. Chem. Soc.*, 1949, **71**, 3553, and references therein.

[6] Armstrong and Halpern, *Canad. J. Chem.*, 1957, **35**, 1020.

[7] Rosseinsky and Higginson, *J.*, 1960, 31.

[8] Higginson, Rosseinsky, Stead, and Sykes, *Discuss. Faraday Soc.*, 1960, **29**, 49.

[9] Lingane and Selim, *Acta Chim. Analyt.*, 1959, **21**, 536.

[10] Hietanen and Sillén, *Arkiv Kemi*, 1956, **10**, 103.

during the reaction were used in the calculation of k_1 and k_2. A value of $(1{\cdot}10 \pm 0{\cdot}10) \times 10^{-4}$M for the ratio k_1/k_2 was found to give a satisfactorily constant value of k_1 from plots of the right-hand side of expression (7) against time t. Values of k_1 so obtained are given in Table 1. Most weight was given to the fourth experiment, in which the derived k_1 value was most sensitive to the choice of k_1/k_2. A typical plot (B) of expression (7) appears in the Figure. A zero-time error of up to 12% with respect to the manganese(III) concentration occurred in some runs, such as that depicted. This arises from incipient precipitation of manganese dioxide, which then vanishes by expremely rapid reaction with mercury(I) on addition of the latter. Subsequently, the rate of formation of manganese dioxide is too low to interfere. Manganese dioxide was readily detectable by the Tyndall effect. Rate constants were apparently unaffected by the zero-time error. Plots of expressions (7) and (9) (below) were linear, after the zero-time point, for at least 80% of reaction.

TABLE 1.

Rate constant k_1, with ratio $k_1/k_2 = 1{\cdot}10 \times 10^{-4}$M.

Temp. 50°; 3·00M-H^+; $[(Hg^I)_2]_0 + [Hg^{II}]_0 + [Mn^{II}]_0 + [Ba^{2+}] = 0{\cdot}20$M; 0·00100 to 0·00091M-$Mn^{III}$ initially; $NaClO_4$ to maintain ionic strength at 4·50 ± 0·01.

$10^2[(Hg^I)_2]_0$	4·76	2·38	0·476	5·16	4·76	5·16	5·16	
$10^2[Mn^{II}]_0$	2·15	2·15	2·15	2·16	2·15	4·37	8·80	
$10^3[Hg^{II}]_0$	8·38	8·28	8·20	41·4	4·29	8·39	8·39	
10^4k_1 (min.$^{-1}$) ...	3·37 *	3·25	3·29	3·44	3·19	3·68	3·80	Mean: 3·43 ± 0·37 †

* Plot B in Figure. † In both Tables, the listed uncertainty is the maximum discrepancy between individual values and the mean.

Alternative mechanisms to explain the retardation by products were considered, both having two-parameter rate expressions. The first involved the reaction of Mn^{III} with $(Hg^I)_2$ and Mn^{IV} with Hg°, the second the omission of reaction step (5) with, instead, a back-reaction in step (3). Neither of these schemes fitted the results. A third mechanism involving the slow formation of manganese(IV) could also be discarded.

An order-of-magnitude estimate of k'' can be made by using Lingane and Selim's value[9] of $K'' = 10^{-3}$ in 4·5M-sulphuric acid at 25° as an upper limit (see Discussion), any temperature correction to K'' being neglected. This gives $k'' \geqslant 3 \times 10^3$ l. mole^{-1} min.$^{-1}$ at 50°.

Reaction with Low Initial Mercury(II) *Concentration.*—For reactions in which no mercury(II) stock solution was added to the reaction mixture the concentration of mercury(II) in the mercury(I) solution was required. The mercury(II) results from the equilibrium in the reaction used to prepare the mercury(I):

$$Hg^{II} + Hg_{(l)} \overset{K_3}{\rightleftharpoons} (Hg^I)_2 \qquad (8)$$

Forsling *et al.*[11] found K_3 at 25° to be 132 at an ionic strength 0·5 in sodium perchlorate solution. In the stock solution the ionic strength was 3·53, of which a large fraction was due to the mercury(I) perchlorate. The value of K_3 at 25° in these conditions, 370 ± 170, was obtained by measurement of the e.m.f. of the cell

$$\begin{array}{c|c|l|l|c} Hg,Hg_2Cl_{2(s)} & KCl(0{\cdot}1M) & Ba(ClO_4)_2(0{\cdot}478M), & Hg_2(ClO_4)_2(M_1),Hg(ClO_4)_2(M_2), & Pt \\ & & HClO_4(2{\cdot}10M) & Ba(ClO_4)_2(0{\cdot}478\text{-}M_1\text{-}M_2),HClO_4(2{\cdot}10M) & \end{array}$$

with the stock solution initially in contact with the platinum electrode. The large scatter in K_3 probably arises from poor establishment of the potential with the oxidised species in such (unavoidably) low concentration. Fortunately the scatter adds only 3—4% to the uncertainty in the rate constant. The change in K_3 from the value in ref. 11 is in the

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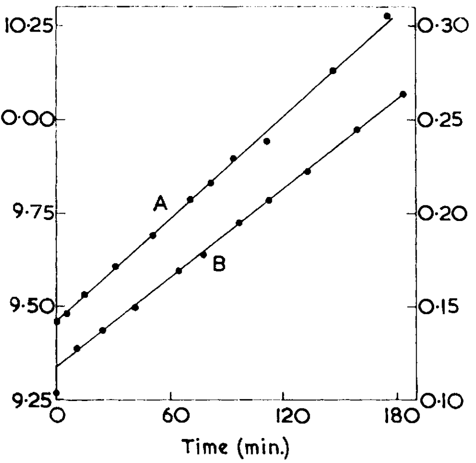
[11] Forsling, Hietanen and Sillén, *Acta Chem. Scand.*, 1952, **6**, 901.

direction to be expected if $Hg_2ClO_4^+$ is formed. Finally, the kinetic analysis gave the most consistent rate constants, in a series of calculations with arbitrary choices of K_3, when the present experimental range was used.

Table 1 shows that with such low mercury(II) concentrations, neglect of reaction step (5) introduces little error. Expression (6) without the k_2 term can be integrated, now with both $[Hg^{II}]$ and $[Mn^{III}]$ as variables, to give

$$k_1[(Hg^I)_2]t = [Mn^{III}] - ([Mn^{III}]_0 + [Hg^{II}]_0) \ln [Mn^{III}]) + \text{Constant}. \qquad (9)$$

In Table 2 are listed values of k_1 obtained from graphs of the right-hand side of expression (9) against time, and a typical plot (A) is shown in the Figure. The values are close to those measured at ionic strength 4·5. The decrease in hydrogen-ion concentration from 2·87M to 1·47M leads to an increase in the rate constant, owing either to the change in medium in the substitution of sodium or lithium for hydrogen ions, or to an increase in concentration of $MnOH^{2+}$, which may be more reactive than Mn^{3+} (compare the greater reactivity of $TlOH^{2+}$ than of Tl^{3+} in reaction[5] with Hg°).



(A) Left ordinate: Plot of $10^3 \{[Mn^{III}] - ([Mn^{III}]_0 + [Hg^{II}]_0) \ln [Mn^{III}]\}$ against t (min.) (see Table 2).
(B) Right ordinate: Plot of $\log (1 + k_1[Mn^{II}]/k_2[Hg^{II}][Mn^{III}])$ against t (min.) (see Table 1).

TABLE 2.

Rate constant k_1, with low $[Hg^{II}]_0$.

Temp. 50°; $[Hg^{II}]_0 = [(Hg^I)_2]/370$; $[Mn^{II}]_0 = 0{\cdot}0254$M; ionic strength 3·00 ± 0·04; 2·87M-H^+ except where indicated.

$10^2[(Hg^I)_2]_0$	1·40	1·40	1·41	1·94	2·35	0·94	1·42	1·42	1·42
$10^3[Mn^{III}]_0$	0·81	1·19	0·58	1·16	1·16	1·16	0·84	0·25	0·79
10^4k_1 (min.$^{-1}$)	3·00	3·33 *	3·06	3·08	3·24	2·92	3·76 †	3·95 ‡	4·13 ‡

Mean of first six results, $k_1 = 3{\cdot}10 \pm 0{\cdot}23 \times 10^{-4}$ min.$^{-1}$.

* Plot A in Figure. † 1·47M-H^+, 1·40M-Na^+. ‡ 1·47M-H^+, 1·40M-Li^+.

A very approximate value of k' can be obtained by making use of K_3 and the measured solubility of mercury[12] at 25° ($3{\cdot}1 \times 10^{-7}$M). When mercury(I) and mercury(II) are in contact with liquid mercury, $K' =$ (Hg solubility)$/K_3$.* Thus, k' at 50° is 3×10^5 l. mole^{-1} min.$^{-1}$. For the reaction Tl^{III} + Hg° the rate constant (here[6] corrected for both hydrolysis and complex formation with perchlorate) is $6{\cdot}0 \times 10^7$ l. mole^{-1} min.$^{-1}$ at 25°.

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* $K' = 8{\cdot}4 \times 10^{-10}$ mole l.$^{-1}$ at 25°, so obtained, may be compared with $K' = 2{\cdot}2 \times 10^{-8}$ mole l.$^{-1}$ at 50°, calculated from ΔH and K' at 25° ($5{\cdot}5 \times 10^{-9}$ mole l.$^{-1}$), given in ref. 6. Because of the enhanced formation of $Hg_2ClO_4^+$ expected in present reaction conditions, K' at 50° should be somewhat lower than the value $2{\cdot}2 \times 10^{-8}$ mole l.$^{-1}$. The first value has therefore been taken, without temperature correction, and it may thus be too low by about one power of ten.

[12] Moser and Voigt, *J. Amer. Chem. Soc.*, 1957, **79**, 1837.

Discussion.—Adamson [1] suggested that at $\ngtr 25°$ the reverse step of (2) was slow, and that the equilibrium (favouring predominant reactant concentrations in his conditions),

$$3Mn^{II} + Mn^{VII} \rightleftharpoons 3Mn^{III} + Mn^{IV} \qquad (10)$$

was rapid. In the present investigation equilibrium (2) was taken to be rapid at 50°, and the overall process (see Experimental)

$$4Mn^{II} + Mn^{VII} \longrightarrow 5Mn^{III} \qquad (11)$$

was found to be slow at room temperature. The apparent discrepancies may be explained by the assumption of a very high activation energy for the reverse step of (2), which would then allow this step to be rapid at 50°. Reaction (11) differs from (10) by the reverse of reaction (2), which at lower temperatures ($<25°$) may then be the slow step in the sequence which when summed leads to (11). [However, K'' in perchlorate medium would have to be rather smaller than Lingane and Selim's value [9] for sulphate medium, to allow reaction (11) to go to the completion found in our conditions, and further experimental evidence is necessary.]

The difference found in the kinetic paths for cobalt(III) [7] ($Co^{III} + Hg_2^{2+} \longrightarrow$) on the one hand, and manganese(III) and thallium(III) [6] ($M^{III} + Hg° \longrightarrow$) on the other, does not appear to be explicable in terms of the oxidation potentials of the 3+ ions, though the last two are weaker oxidants than cobalt(III) [$E°$ values being $-1{\cdot}84$ v for cobalt(III), $-1{\cdot}51$ v for manganese(III), $-1{\cdot}25$ v for thallium(I)-(III), and $-1{\cdot}0$ v for thallium(II)-(III) [13]]. If the extent of orbital overlap between reactants is an important factor in the formation of the transition state, the difference in $3d$-electron structure may be relevant for cobalt and manganese. t_{2g}-Orbital overlap extending between oxidant ligands would be more easily achieved than e_g-orbital overlap where ligand obstruction would compel a greater inter-reactant distance. Cobalt(III) may react *via* the thermally accessible high-spin species,[14] thereby achieving t_{2g}-overlap with Hg_2^{2+}. The required overlap with the manganese(III) e_g-orbital may be attainable only with Hg°, either because of the larger radial extension of its mononuclear $6s$-orbital in comparison with that of the dinuclear $6s\sigma$-orbital in Hg_2^{2+}, or because the greater desolvation possible with Hg° allows a closer approach of reactants. Thus overlap requirements and a diminished Franck–Condon barrier (associated with transfers to e_g-orbitals) appear capable of forcing the Hg° path. The overlap requirements of manganese(IV) and thallium(III) are not apparent, owing to current ignorance of the hydrational structures of these ions; the former may be enabled to react directly as MnO^{2+} with Hg_2^{2+} by oxygen bridging.

EXPERIMENTAL

Mercury(II) perchlorate was prepared from "AnalaR" materials by dissolution of mercury in nitric acid and precipitation of the oxide by sodium carbonate; the oxide was washed ten times by decantation, then dissolved in perchloric acid. Mercury(I) perchlorate was prepared by shaking mercury(II) solution with mercury. Both solutions were standardised by titration with chloride. Lithium perchlorate from G. Frederick Smith was used. Sodium and barium perchlorate solutions were prepared by neutralisation of perchloric acid with the carbonates. These solutions were standardised by titration of the acid liberated by passage through a cation-exchange resin in the acid form. Manganese perchlorate from G. Frederick Smith, and that prepared by double decomposition of manganous sulphate with barium perchlorate, were standardised complexometrically with EDTA. No difference in reactivity was found. "AnalaR" potassium permanganate solution was boiled for an hour, filtered through a thick layer of clean glass wool and stored in the dark. It was constantly examined for Tyndall effect, which would indicate the presence of manganese dioxide.

The e.m.f. of the given cell when stable was measured on a pH meter, first with 15 ml. of the stock solution [containing $0{\cdot}478\text{M}$-$(Hg^{I})_2$, $2{\cdot}10\text{M}$-perchloric acid, and an unknown amount

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[13] Hush, *Discuss. Faraday Soc.*, 1960, **29**, 134; Higginson, *ibid.*, p. 135.

[14] Rosseinsky, *Discuss. Faraday Soc.*, 1960, **29**, 128.

of mercury(II)], then 20—30 min. after addition of standard mercury(II) solution [2 ml.; 0·00963M-mercury(II), 0·468M-barium perchlorate, and 2·10M-perchloric acid]. The changes of e.m.f. after each addition, and corresponding values of K_3, were: 13 mv, 210; 16 mv, 840; 8 mv, 220; 7 mv, 370; 5 mv, 210.

For each kinetic investigation, a solution was prepared consisting of all the manganese(II) and medium salt, and most of the perchloric acid, necessary to give ultimately the required reaction concentrations. Sufficient permanganate solution to give the required manganese(III) concentrations was acidified with the remaining acid necessary, and this was quickly added to the manganese(II) solution. Formation of manganese(III) was slow and the solution was usually left overnight. Then 5·0 or 10·0 ml. were removed by pipette for the determination of initial manganese(III) concentration. After being warmed to 50°, mercury(I) solution was added to the manganese(III) in a thermostat-bath (50°), to start the reaction. For the reactions recorded in Table 1, mercury(II) was added in the first step of the preparation sequence.

Samples from the reaction solution were quenched by being cooled to room temperature. Manganese(III) was titrated with a 10^{-3}N-solution of ferrous ammonium sulphate in M-perchloric acid, ferroin indicator being present in the lowest convenient concentration. Mercury-(I) and -(II) were shown not to interfere in the conditions used. The hydrogen-ion concentration in the titration was kept between 2·1 and 2·7M, as outside this range the titration was sluggish. The end-point, if overshot, could be found by back-titration with 10^{-3}M-cerium(IV), as this ion reacted with ferrous much more rapidly than with mercury(I) and, in the low concentration used, not at all with manganese(II).

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