

# Kinetics and Mechanism of the Formation of Manganese(III) from Manganese(II) and (VII) in Aqueous Perchlorate Solution

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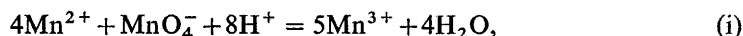
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Received 1st March, 1965

The reaction  $4\text{Mn}^{\text{II}} + \text{Mn}^{\text{VII}} = 5\text{Mn}^{\text{III}}$  obeyed the rate equation,  $\text{rate} = k[\text{Mn}^{\text{II}}]^2[\text{Mn}^{\text{VII}}]$ . In lithium perchlorate media the  $[\text{H}^+]$ -dependence was found to be  $k = k_{\text{H}}[\text{H}^+] + k_0$ . Activation energies and entropies were compared with standard values for formation of intermediate species in an examination of possible mechanisms.

The  $\text{Mn}^{\text{II}} + \text{Mn}^{\text{VII}}$  reaction has often been studied in conditions where  $\text{MnO}_2$  is the final product<sup>1-3</sup> or where  $\text{Mn}^{\text{III}}$  as product is complexed.<sup>4</sup> Our study employs simplifying conditions where  $\text{Mn}^{\text{III}}_{\text{aq}}$  is stable, viz., excess  $\text{Mn}^{\text{II}}$  and  $[\text{H}^+] \gg 0.5 \text{ M}$ <sup>5</sup> (cf. ref. (6); Latimer's<sup>7</sup> calculated free energy for  $\text{Mn}^{\text{III}}$  disproportionation, being too negative by a factor of two relative to the electrode potentials used,<sup>7</sup> exaggerates the instability of  $\text{Mn}^{\text{III}}$ ). In these conditions the overall stoichiometry may be represented by the reaction,



together with the corresponding reaction producing  $\text{MnOH}^{2+}$ .<sup>8</sup> Precise rates (cf. ref. (3)) were determined from recordings of the diminution of the permanganate absorbance at 525  $\text{m}\mu$  with time.

## EXPERIMENTAL

Reactant solutions were prepared from analytical grade reagents and standardized by established methods.<sup>17</sup> Ionic strength media were prepared by the dissolution of hydroxides or carbonates in A.R. perchloric acid, or (aluminium perchlorate) by fuming the chloride with perchloric acid. Manganese(III) was prepared by the reaction  $4\text{Mn}^{\text{II}} + \text{Mn}^{\text{VII}}$  and standardized amperometrically against electrogenerated iron(II). Reactions were conducted in optical cells in a holder thermostatted by water circulation, temperature constancy of the reaction solution to within  $0.1^\circ$  being established. After a small volume of solution containing the final reactant, manganese(VII), previously kept at the required temperature, was squirted in from a syringe pipette, the solution was stirred vigorously for 2-3 sec with a mechanical stirrer; the optical density changes were recorded on a Zeiss PM.11 recording spectrophotometer.

## RESULTS AND DISCUSSION

### STOICHIOMETRY AND RATE EQUATION

The number of moles of  $\text{Mn}^{\text{III}}$  produced per mole of  $\text{Mn}^{\text{VII}}$  consumed was found to be on average 4.76 (table 1), by absorbance measurements on these species using the relevant extinction coefficients. The 5 % discrepancy is probably due to a limited reaction of the higher oxidation states with water, but is too small to vitiate our

interpretation. Satisfactory first-order plots (fig. 1) for  $[\text{Mn}^{\text{VII}}]$  were obtained with an excess [manganese(II)], and variation of the latter led to the kinetic equation,  $-d[\text{Mn}^{\text{VII}}]/dt = k[\text{Mn}^{\text{II}}]^2[\text{Mn}^{\text{VII}}]$ . The equation was found (table 2) to hold over a four-fold range of  $[\text{Mn}^{\text{II}}]$  and a ten-fold range of  $[\text{Mn}^{\text{VII}}]$ , and remained unaltered when  $\text{Mn}^{\text{III}}$  was added initially to the reaction solution.

TABLE 1.—STOICHIOMETRY  
temp.  $24.4^\circ$ ; ionic strength made 3.31 with  $\text{LiClO}_4$ ;  $0.104 \text{ M Mn}^{\text{II}}$

$[\text{H}^+]$	$10^4 [\text{Mn}^{\text{VII}}]_0$	$10^4 [\text{Mn}^{\text{III}}]_\infty$	$[\text{Mn}^{\text{III}}]_\infty/[\text{Mn}^{\text{VII}}]_0$
3.00	1.25	5.95	4.77
3.00	0.60	2.76	4.60
1.20	1.23	5.97	4.86
1.20	0.68	3.28	4.82

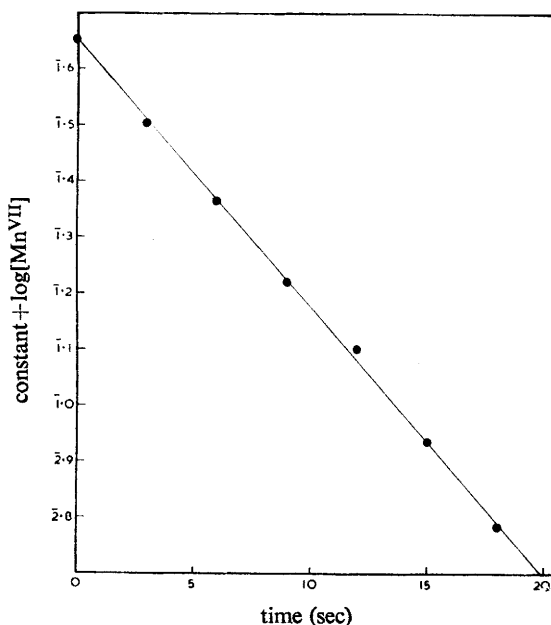


FIG. 1.—Typical first-order rate plot for  $3.0 \text{ M HClO}_4$  at  $11.4^\circ$ , with  $0.104 \text{ M Mn}^{\text{II}}$  and  $10^{-4} \text{ M Mn}^{\text{VII}}$  initially.

TABLE 2.—RATE CONSTANTS IN  $3.0 \text{ M PERCHLORIC ACID}$

temp. $^\circ\text{C}$	$[\text{Mn}^{\text{II}}]$	$10^{-2} k \text{ (l}^2 \text{ mole}^{-2} \text{ min}^{-1}\text{)}$
10.2	0.091	6.4
	0.070	6.2
	0.048	6.4
	0.024	6.1
24.4	0.104	6.8
	0.104	6.8 <sup>a</sup>
	0.104	6.9 <sup>b</sup>
11.1	0.104	6.3
	0.104	6.3 <sup>c</sup>
	0.104	6.4 <sup>d</sup>
	0.104	6.4 <sup>d</sup>

Initially  $10^{-4} \text{ M Mn}^{\text{VII}}$ , except <sup>a</sup>  $7 \times 10^{-5} \text{ M}$ , <sup>b</sup>  $5 \times 10^{-5} \text{ M}$ ; <sup>c</sup>  $1.8 \times 10^{-3} \text{ M Mn}^{\text{III}}$ , <sup>d</sup>  $2.3 \times 10^{-3} \text{ M Mn}^{\text{III}}$  added initially.

VARIATION OF MEDIUM- AND HYDROGEN-ION CONCENTRATIONS,  
 TEMPERATURE AND IONIC STRENGTH

In several systems,<sup>9</sup> appreciable medium effects on rates and equilibria have been observed when  $H^+$  is replaced, at constant ionic strength, by medium ions other than  $Li^+$ . In conformity, we found the closest approximation to linearity for observed  $k$  values against  $[H^+]$  with  $Li^+$  solution, while  $Al^{3+}$ ,  $Zn^{2+}$  and  $Na^+$  solutions gave curves attributable to medium effects (fig. 2). Further attention is thus directed

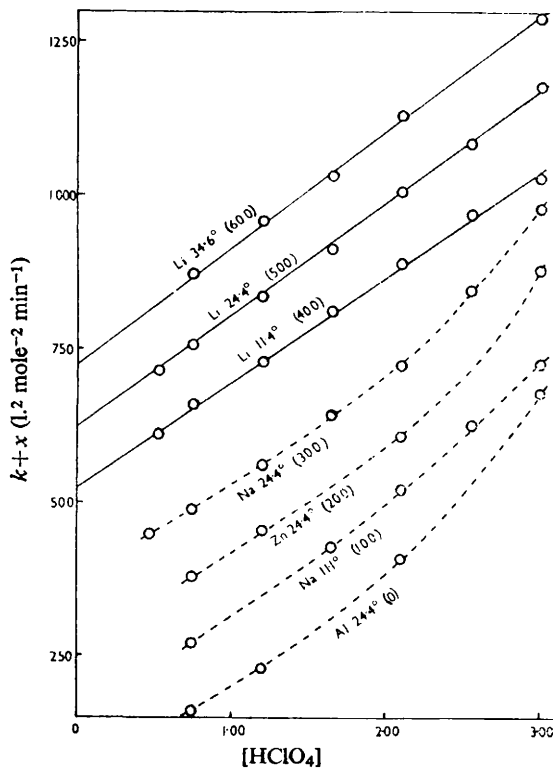
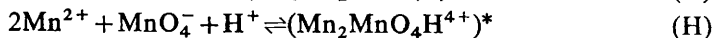
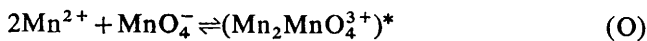


FIG. 2.—Dependence of observed rate constants  $k$  on  $[H^+]$  at constant ionic strength 3.31, with different medium cations at the given temperatures. The  $Li$  lines were fitted by computer in the derivation of  $\Delta E^*$  and  $\Delta S^*$  values; the curves were drawn arbitrarily. ( $x$  is an arbitrary term introduced to separate the curves vertically: values in parentheses.)

only to the  $Li^+$  solution results, and the possibility of  $[H^+]^2$  kinetic terms neglected.

The activated complexes inferred (tri-ionic in  $Mn$ ; cf. an earlier prediction<sup>10</sup>) are thus



where an  $Mn^{2+}MnO_4^-$  ion pair is a possible precursor to the activated complex in (O). Both activated complexes necessarily have oxidation numbers (ON) totalling 11.

With the observed dependence,  $k = k_0 + k_H[H^+]$ , written in terms of the transition-state theory for both kinetic paths (H) and (O),<sup>11</sup>

$$k = \frac{kT}{h} \exp\left(\frac{\Delta S_0^*}{R} - \frac{\Delta E_0^*}{RT}\right) + [H^+] \frac{kT}{h} \exp\left(\frac{\Delta S_H^*}{R} - \frac{\Delta E_H^*}{RT}\right),$$

an iterative least-squares programme<sup>12</sup> could be used to fit the four activation parameters to the 19 observed  $k$  values, for the least-square % deviation between  $k(\text{calc.})$  and  $k(\text{obs.})$ . The values so obtained were  $\Delta E_0^*$ ,  $-0.6$  kcal,  $\Delta S_0^*$ ,  $-59$  cal/mole deg.;  $\Delta E_H^*$ ,  $0.2$  kcal,  $\Delta S_H^*$ ,  $-56$  cal/mole deg.,  $k(\text{calc.})$  fitting  $k(\text{obs.})$  with a r.m.s. deviation of only 1.47 % (maximum deviation, 3 %). Rate constants  $k_0$  and  $k_H$  calculated from these  $\Delta E^*$  and  $\Delta S^*$  are given in table 3. Trial fittings of three activation parameters with arbitrary variations in the fourth showed  $\pm 0.3$  kcal in  $\Delta E_H^*$ ,  $\pm 0.1$  kcal in  $\Delta E_0^*$  and  $\pm 1$  cal/mole deg. in the  $\Delta S^*$  values to be the approximate limits beyond which the r.m.s. deviations increased sharply. While the actual errors may be somewhat larger, a negative  $\Delta E^*$  (as  $\Delta E_0^*$ ) is not impossible in a multi-step multi-ionic reaction.

TABLE 3.—RATE CONSTANTS  $k_0$  AND  $k_H$   
(ionic strength 3.31 with  $\text{LiClO}_4$ )

temp.	$k_0$ , l. <sup>2</sup> mole <sup>-2</sup> min <sup>-1</sup>	$k_H$ , l. <sup>3</sup> mole <sup>-3</sup> min <sup>-1</sup>
11.4°	122.8	172.3
24.4°	122.8	183.6
34.6°	122.7	190.7

TABLE 4.—RATE CONSTANT  $k$  WITH IONIC STRENGTH  $I(\text{LiClO}_4)$   
temp. 24.4°; 1.20 M  $\text{HClO}_4$

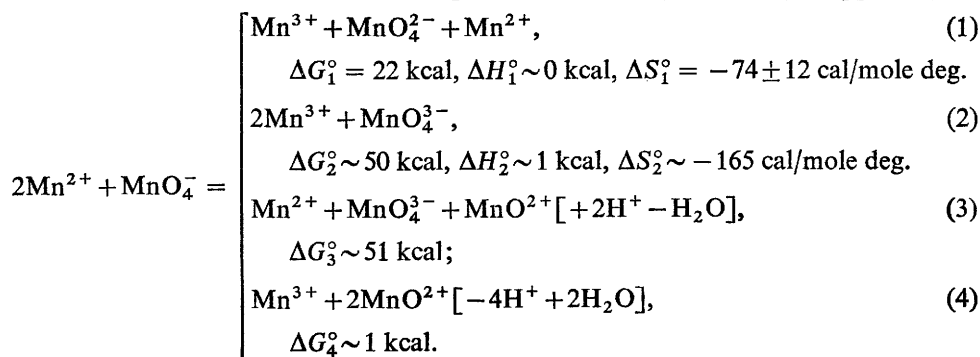
$I$	$k$ (l. <sup>2</sup> mole <sup>-2</sup> min <sup>-1</sup> )
3.31	337
2.41	206
1.51	128

(These values fit the arbitrary function  $\log k = 1.846 - 0.1253\sqrt{I} + 0.2756I$ .)

An increase of  $k$  with ionic strength  $I$ , at constant  $[\text{H}^+]$ , was noted (table 4). A Bjerrum-Brønsted expression for multimolecular ionic reactions predicts an increase of  $k_H$  with  $I$ , but zero effect on  $k_0$ .

#### MECHANISM

The overall reaction (i) provides no guide to the mechanism, which clearly proceeds via the formation of intermediate Mn oxidation states. The rate-controlling feature of the reaction is the entropy loss on formation of the activated complexes, the unusual  $\Delta E^*$  and  $\Delta S^*$  values being consistent with enhancement, on transfer of charge, of the ion-water interactions involving the three Mn ions. Since they arise largely from just such changes in hydration,<sup>13</sup> thermodynamic quantities for formation from reactants, of intermediate Mn ions having  $\Sigma\text{ON} = 11$ , are compared below with  $\Delta G_0^*$ , etc., for path (O); they impose further restrictions on the possible composition of the corresponding activated complex. Though the data are limited to relatively stable structures amenable to electrode potential estimates, in general such structures should be, *a priori*, the most probable kinetically. Thus (see appendix):



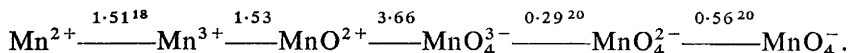
Apart from (1) and (4), the  $\Delta G^\circ$  values (cf.  $\Delta G_0^* = 17$  kcal) at first sight preclude participation of the remaining combinations in the activated complex. Notably,  $\Delta E_0^*$  and  $\Delta S_0^*$  are reflected in  $\Delta H_1^\circ$  and  $\Delta S_1^\circ$ . However, the oxidation states in (2) and (3) are not necessarily ruled out since resonance, on juxtaposition in the transition state, is to be expected<sup>14</sup> (simple ion-triplet formation being unlikely to offer appreciable stabilization). These oxidation states are further favoured if the  $\text{Mn}^{\text{V}}$  structure, with  $\text{H}^+$  present, is the oft-invoked<sup>15</sup> diprotonated form  $\text{MnO}_3^-$ , or, more probably,  $\text{H}_2\text{MnO}_4^-$ .<sup>15</sup> Decreases (probably large) would then be expected in  $\Delta G_2^\circ$  and  $\Delta G_3^\circ$ , which refer above to  $\text{MnO}_4^{3-}$  specifically.<sup>20</sup> Consequently, a symmetrical activated complex  $(\text{HOMn})^{2+}\text{H}_2\text{MnO}_4^-(\text{MnOH})^{2+}$  (cf. (2)), following two H-atom transfers from the  $\text{Mn}^{\text{II}}$  ions to  $\text{Mn}^{\text{V}}$ , is then allowed,  $\Delta G^\circ$  for  $\text{Mn}_{\text{aq}}^{3+} \rightarrow \text{MnOH}^{2+} + \text{H}^+$  being only 0.1 kcal.<sup>8</sup>

Reaction (4), consuming *four* protons (cf. (O) and (H)), can thus only represent a post-transition-state combination unless the given oxidation states, but now constituted with fewer protons, can form with a  $\Delta G^\circ \leq \Delta G_0^*$ . In either case, or with  $\text{Mn}^{\text{IV}}$  otherwise generated, the reaction  $\text{Mn}^{\text{II}} + \text{Mn}^{\text{IV}} \rightarrow 2\text{Mn}^{\text{III}}$  (fast in  $\text{H}_2\text{SO}_4$  solution<sup>16</sup> and probably so in perchlorate<sup>17</sup>) provides a feasible final step.

The conformity of both the  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{MnO}_4^-$ ,  $\text{MnO}_4^{2-}$  exchanges with the outer-sphere model<sup>18, 19</sup> provides support for the assumption implicit above of an outer-sphere mechanism. The alternative is an oxygen-bridged ion-contact mechanism, where the  $\Delta G^\circ$  criteria would be relaxed to the problematical extent of the Mn—O—Mn bonding interactions concomitantly invoked.

#### APPENDIX

$\Delta G^\circ$  values were calculated from the estimates of standard (1 M acid) electrode potentials which, together with the probable structures<sup>7, 20</sup> of the ions to which the potentials refer, follow immediately:



1.53 V for  $\text{MnO}^{2+} + 2\text{H}^+ + e = \text{Mn}^{3+} + \text{H}_2\text{O}$  was derived from the approximate  $K$  value<sup>18</sup> for  $\text{Mn}^{\text{II}} + \text{Mn}^{\text{IV}} \rightleftharpoons 2\text{Mn}^{\text{III}}$  together with the potential for the  $\text{Mn}^{\text{II}}$ ,  $\text{Mn}^{\text{III}}$  couple.<sup>18</sup> The  $\text{Mn}^{2+}$ ,  $\text{MnO}_4^-$  couple<sup>7</sup> was used to relate the potentials involving the cations with those for the anions. The effect of different possible formulations of the cations (e.g.,  $\text{Mn}^{4+}$  for  $\text{Mn}^{\text{IV}}$ ) has been tested and these, together with the use above of potentials measured in differing media, should little affect the preceding discussion.

$\Delta S_1^\circ$  and  $\Delta S_2^\circ$  were obtained from published<sup>7, 21</sup> and estimated ionic entropies, the standard entropy of  $\text{Mn}^{3+}$  being obtained as approximately  $-59$  cal/mole deg. from the temperature dependence of the  $\text{Mn}^{\text{II}}$ ,  $\text{Mn}^{\text{III}}$  electrode potential.<sup>5</sup> Values for  $\text{MnO}_4^{2-}$  and  $\text{MnO}_4^{3-}$  were summarily equated to those<sup>7</sup> for  $\text{CrO}_4^{2-}$  and  $\text{PO}_4^{3-}$  respectively.

We are grateful to referees for some pertinent comments, and acknowledge a South African C.S.I.R. scholarship (to M.J.N.) and an I.C.I. Fellowship (to D.R.R.).

<sup>1</sup> Guyard, *Bull. Soc. chim. France*, 1864, **1**, 89.

<sup>2</sup> Tompkins, *Trans. Faraday Soc.*, 1942, **38**, 128.

<sup>3</sup> Adamson, *J. Colloid Chem.*, 1951, **55**, 293.

<sup>4</sup> Launer and Yost, *J. Amer. Chem. Soc.*, 1934, **56**, 2571. Laitinen, *Chemical Analysis* (McGraw-Hill Book Co., London, 1960).

<sup>5</sup> Rosseinsky, *J. Chem. Soc.*, 1963, 1181. Lingane and Selim, *Acta Chim. Analyt.*, 1959, **21**, 536. Nicol and Rosseinsky, *Chem. and Ind.*, 1963, 1166.

<sup>6</sup> Ogard and Taube, *J. Physic. Chem.*, 1958, **62**, 357.

<sup>7</sup> Latimer, *Oxidation Potentials* (Prentice-Hall, Englewood Cliffs, 1956).

<sup>8</sup> Wells and Davies, *Nature*, 1965, **205**, 692.

- <sup>9</sup> Zielen and Sullivan, *J. Physic. Chem.*, 1962, **66**, 1065. Newton and Baker, *J. Physic. Chem.*, 1963, **67**, 1425.
- <sup>10</sup> Higginson, *Disc. Faraday Soc.*, 1960, **29**, 49.
- <sup>11</sup> Daugherty and Newton, *J. Physic. Chem.*, 1964, **68**, 612.
- <sup>12</sup> Stone, Exeter University, Dept. of Mathematics.
- <sup>13</sup> Evans, *Disc. Faraday Soc.*, 1947, **2**, 217.
- <sup>14</sup> Rosseinsky, *Chem. Rev.*, 1965, **65**, 467.
- <sup>15</sup> Carrington and Symons, *Chem. Rev.*, 1963, **63**, 454.
- <sup>16</sup> Vetter and Manecke, *Z. physik. Chem.*, 1950, **195**, 337.
- <sup>17</sup> Rosseinsky, ref. (5).
- <sup>18</sup> Diebler and Sutin, *J. Physic. Chem.*, 1964, **68**, 174.
- <sup>19</sup> Marcus, *J. Chem. Physics*, 1957, **26**, 871.
- <sup>20</sup> Carrington and Symons, *J. Chem. Soc.*, 1956, 3373.
- <sup>21</sup> Ko and Hepler, *J. Chem. Eng. Data*, 1963, **8**, 59.