809. *The Mechanism of Decomposition of Potassium Permanganate in Alkaline Solution and its Bearing on Oxidation by this Reagent.*

By M. C. R. Symons.

The rates of change in colour of permanganate and of oxygen evolution have been measured for the reaction $4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^{2-} + 2H_2O + O_2$. The results obtained for the first 65% and for the last 35% of the decomposition are in agreement, respectively, with the equations

$$K_5 = \frac{b}{a}\left(\frac{2b^3}{a^2S_3} - K_4\right) \text{ and } K_7 = \frac{b}{a}\left(\frac{b^3}{aS_2} - K_3\right)$$

where K_3, K_4, K_5, and K_7 are constants, a is the initial concentration of permanganate, b the concentration of alkali, and S_2 and S_3 are respectively the slopes of the lines obtained by plotting time against (i) the reciprocal of the concentration of permanganate for the last 35%, and (ii) that of the square of the concentration of permanganate for the first 65% of the decomposition.

A mechanism involving the intermediate formation of the radicals and ions $\cdot OH$, $\cdot O^-$, HO_2^-, and $\cdot O_2^-$ is proposed, and the contribution made by these particles to oxidations by permanganate is discussed.

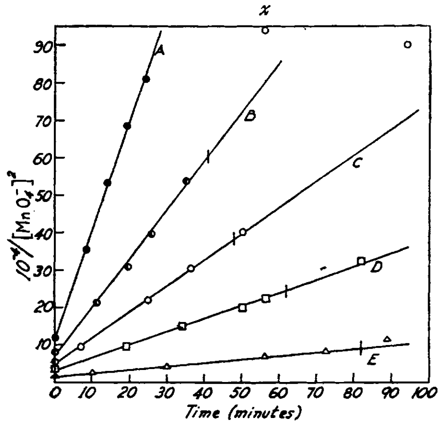
The rate of the reaction $4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^{2-} + 2H_2O + O_2$ was measured at various temperatures and concentrations of alkali by Ferguson, Lerch, and Day (*J. Amer. Chem. Soc.*, 1931, **53**, 126), who, however, reached no conclusions as to the mechanism of the reaction. Working at concentrations of alkali below 0·72M, Duke (*ibid.*, 1948, **70**, 3975) found that the reaction rate is greatly increased by addition of barium ion to precipitate manganate; the reaction then follows a zero-order law. Since under these conditions the reaction was heterogeneous, Duke postulated that the rapid equilibrium reaction $MnO_4^- + H_2O \longrightarrow MnO_4^{2-} + H^+ + \cdot OH$ is followed by a slow adsorption of hydroxyl radicals on the glass surface, where they combine to form hydrogen peroxide, which is then rapidly oxidized to give oxygen.

The theory that the free hydroxyl radical is the active oxidizing agent in many reactions of alkaline permanganate, first postulated by Stamm ("Newer Methods of Volumetric Analysis," trans. by Oesper, Van Nostrand Co. Inc., New York, 1938), has recently been criticized by Drummond and Waters (*J.*, 1953, 435). It has, however, been invoked to explain certain observations concerning the oxidation of optically active branched-chain carboxylic acids by means of potassium permanganate in concentrated alkaline solution (Kenyon and Symons, *J.*, 1953, 3580).

In an attempt to throw more light on the problem, the rate of decomposition of permanganate has been measured photometrically at 25° for alkali concentrations between 2·76 and 7·73M. The reactants were mixed in glass-stoppered Pyrex test-tubes, and portions removed and diluted for measurement, the dilution effectively quenching the reaction. Absorption by the green manganate ion was minimized by fitting green filters (No. 5) to the " Spekker " photometer, and the small residual absorption by this ion was readily estimated since the absorptions caused by manganate and permanganate were additive. The validity of this method was checked by comparing the results with those obtained by measuring the rate of evolution of oxygen. The rates of decomposition were sensibly the same, whether the reaction mixture was kept in darkness or exposed to bright light, maintained at reduced pressure, or kept in contact with fine glass helices. Consistent results were only obtained by either procedure when the water was twice distilled from permanganate in concentrated alkaline solution and all glassware was repeatedly washed with a similar solution.

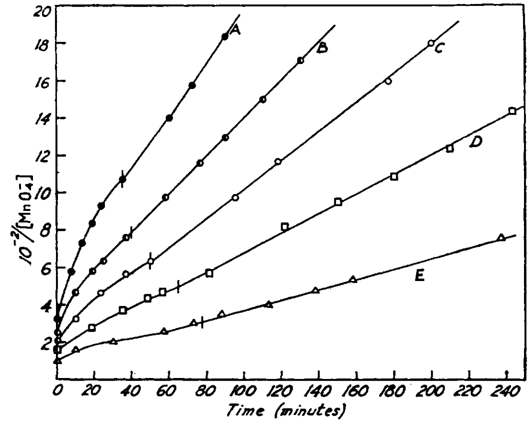
Up to 65% decomposition, a plot of the square of the reciprocal of the permanganate concentration against time is linear. For a fixed concentration of alkali, the slopes obtained are proportional to the initial concentration (*a*) of permanganate raised to a power between —2 and —3; for a fixed initial concentration of permanganate, the slopes are proportional to the concentration (*b*) of alkali raised to a power between 3 and 4. For the remainder of the decomposition, the reaction changes and a plot of the reciprocal of the concentration of permanganate against time is linear. Again, the slopes are proportional to between the third and the fourth power of alkali, but now to the initial concentration of permanganate raised to a power between —1 and —2. The results of a series of experiments for which the concentration of alkali was 7·73M are shown as a third-order plot covering 65% decomposition in Fig. 1 and as a second-order plot covering 90% of the reaction in Fig. 2.

FIG. 1. *Series I.*



The point *x* relates to Graph *B*.

FIG. 2. *Series I.*



For *A*—*E* see Table 1 (p. 3958)

Only one formulation has been found which gives rise to a kinetic expression compatible with these results. In arriving at this formulation, it has been assumed that only simple electron- and proton-transfer reactions take place, that no reaction occurs between unstable intermediates, that permanganate is not even transiently reduced beyond the manganate stage, and finally, that the hydroxyl ion, being present in large excess, will undergo reaction at all possible stages.

(1) $\mathrm{MnO_4^- + OH^- \rightleftharpoons MnO_4^{2-} + \cdot OH}$
(2) $\mathrm{\cdot OH + OH^- \rightleftharpoons \cdot O^- + H_2O}$
(3) $\mathrm{MnO_4^- + OH^- + \cdot O^- \rightleftharpoons MnO_4^{2-} + HO_2^-}$
(4) $\mathrm{MnO_4^- + HO_2^- \rightleftharpoons MnO_4^{2-} + HO_2}$
(5) $\mathrm{HO_2 + OH^- \rightleftharpoons O_2^- + H_2O}$
(6) $\mathrm{MnO_4^- + O_2^- \longrightarrow MnO_4^{2-} + O_2}$

Since the rate of the total reaction is unaffected by variation in oxygen pressure, reaction (6) must be irreversible, and hence application of Christiansen's formulation (*Z. physikal. Chem.*, 1936, **33**, *B*, 145; 1937, **37**, *B*, 374) leads to the expression

$$\frac{dt}{dx} = \frac{K_1}{(a-x)b} + \frac{K_2x}{(a-x)b^2} + \frac{K_3x}{(a-x)^2b^3} + \frac{K_4x^2}{(a-x)^3b^3} + \frac{K_5x^3}{(a-x)^3b^4} + \frac{K_6x^3}{(a-x)^4b^4}$$

where $K_1 = \frac{1}{k_1},\ K_2 = \frac{k_{-1}}{k_1k_2},\ K_3 = \frac{k_{-1}k_{-2}}{k_1k_2k_3},$ etc.

(k and k_- being the rate constants of the forward and the reverse reactions), and $(a - x)$ and x representing the concentrations of permanganate and manganate at time t.

The term involving $(a - x)^{-4}$ would give rise, on integration, to an expression containing $(a - x)^{-3}$. In order to be compatible with the experimental results, it must be assumed that K_6 is small and that the sixth term in this expression may be neglected for the first part of the reaction. After integration, this expression becomes

$$t = -x\left(\frac{K_2a}{b^2} + \frac{K_5}{b^4}\right) - \left[\ln\left(\frac{a}{a-x}\right)\right]\left(\frac{K_1}{b} + \frac{K_2}{b^2} - \frac{K_3 - K_4}{b^3} + \frac{3K_5a}{b^4}\right) + \left(\frac{a}{a-x} - 1\right)\left(\frac{K_3 - 2K_4}{b^3} - \frac{3K_5}{b^4}\right) + \left[\frac{a^2}{(a-x)^2} - 1\right]\left(\frac{K_4}{2b^3} + \frac{K_5a}{2b^4}\right)$$

This equation may be solved for K_1, K_2, K_3, K_4, and K_5. However, since the experimental results give a linear plot of t against $1/(a - x)^2$, it may be deduced at once, if this formulation is correct, that t is governed largely by the terms involving $1/(a - x)^2$, and hence that K_1, K_2, and K_3 are not appreciably greater than K_4 or K_5. The present results cannot be used to give further information regarding the values of K_1, K_2, and K_3, though more precise measurements during the initial stages of reaction might prove useful in this respect. At a first approximation, therefore, all terms other than those involving $1/(a - x)^2$ may be considered constant, and the following relation should hold:

$$1/S_3 = a^2K_4/2b^3 + a^3K_5/2b^4 \quad . \; . \; . \; . \; . \; . \; . \; . \quad \text{(i)}$$

where S_3 is the slope of the graph of t against $1/(a - x)^2$.

In order to compare this equation with the results obtained during the first 65% of decomposition, a representative number of experimental values were substituted and the resulting equations solved in pairs for K_4. The values of K_5 given in col. 7 of Table 1 were then calculated for each experiment, an average value of 920 for K_4 being used.

TABLE 1.

Series	10^3a(M)	b(M)	S_2	$10^{-3}S_3$	$10^{-5}K_7$	$10^{-5}K_5$	Series	10^3a(M)	b(M)	S_2	$10^{-3}S_3$	$10^{-5}K_7$	$10^{-5}K_5$
IA	2·9	7·73	15·5	29·8	80·1	74·0	IIA	2·325	2·76	—	1·2	—	66·1
IB	3·86	,,	10·8	13·3	77·2	74·8	IIB	5·8	,,	0·135	0·085	92·8	66·0
IC	4·83	,,	7·94	7·1	77·0	74·6	IIIA	1·45	3·58	3	12	81·5	67·2
ID	6·15	,,	5·40	3·55	83·1	75·0	IIIB	2·9	,,	—	1·7	—	67·8
IE	9·67	,,	2·80	0·97	78·5	74·2	IVA	47·5	7·73	0·175	0·011	78·5	59·3

As $x \rightarrow a$, the reaction would be expected to become of fourth order, whereas, in fact, it becomes of second order in permanganate. It must, therefore, be assumed that there is an alternative route for the formation of oxygen when the concentration of permanganate is small. It is known that hydrogen peroxide decomposes rapidly in concentrated alkaline solution though the rate of decomposition is reduced if the alkali used has been specially purified (Shanley and Greenspan, *Ind. Eng. Chem.*, 1947, **39**, 1536). The rate of decomposition is greatly increased by addition of traces of heavy-metal ions, such as are present in "AnalaR" grade sodium hydroxide. One possible mode of decomposition is:

$$\text{(7)} \qquad HO_2^- + X + OH^- \xrightarrow{k_7} X^{2-} + H_2O + O_2$$

(where X and X^{2-} are respectively the oxidized and the reduced form of the catalyst), followed by re-oxidation of X^{2-} to X.

Replacement of equations (4), (5), and (6) in the previous formulation by (7), treatment of (7) as irreversible, and application of Christiansen's formulation results in the expression

$$\frac{dt}{dx} = \frac{K_1}{(a-x)b} + \frac{K_2x}{(a-x)b^2} + \frac{K_3x}{(a-x)^2b^3} + \frac{K_7x^2}{(a-x)^2b^4[X]}$$

where [X] is constant and $K_7 = k_{-1}k_{-2}k_{-3}/k_1k_2k_3k_7$. By using a procedure similar to that previously described, the terms, obtained by integration, having $(a - x)$ in the denominator, may be rearranged to give

$$1/S_2 = aK_3/b^3 + a^2K_7/b^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

where S_2 is the slope of the graph of t against $1/(a - x)$.

Col. 6 of Table 1 contains values of K_7 obtained for each experiment by assuming an average value of $7{\cdot}24 \times 10^3$ for K_3 obtained from equation (ii) by substituting a representative number of experimental figures and solving for K_3 in pairs.

The values for K_5 and K_7 are reasonably constant for a fixed concentration of alkali, and the small variation with a large change in the concentration of alkali may well be due to a change in the activity coefficient of the hydroxyl ion, for which no allowance is made. It is considered that the results obtained from measurements of the rate of oxygen evolution (Series IV) show that the photometric method is satisfactory. At the same time, the similarity of the results obtained by the two methods serves to show that there is no accumulation of any of the intermediates involved, and justifies the application of stationary-state kinetics.

TABLE 2.

Stage	$G°$ (kcal./mole)	K'	k_+/k_{-3}	k_-/k_{-3}	Stage	$G°$ (kcal./mole)	K'	k_+/k_{-3}	k_-/k_{-3}
(1)	+33	10^{-24}	—	—	(5)	− 9·1	10^7	10	10^{-6}
(2)	0	1	—	—	(6)	−26	10^{19}	—	—
(3)	−18·6	10^{13}	10^{13}	1	(7)	—	—	10^{-3}	—
(4)	+ 5·6	10^{-4}	8	8×10^4					

Accordingly, it is postulated that this alternative route for the formation of oxygen, namely, the catalysed decomposition of hydrogen peroxide, although of no importance during the major part of the reaction, predominates when the concentration of permanganate is low. It is hoped that further light may be thrown on this aspect of the problem by the use of more highly purified sodium hydroxide.

DISCUSSION

Duke (*loc. cit.*) formulates the first stage in the decomposition as a reaction between permanganate ions and water rather than hydroxide ion, since he maintains that reactions between ions of like charge are improbable. However, the reverse step constitutes a reaction between three particles, all of which are present in minute concentration. This difficulty is partially overcome by the sequence

$$MnO_4^- + H_2O \longrightarrow MnO_4^{2-} + OH + H^+$$
$$MnO_4^{2-} + OH \longrightarrow MnO_4^- + OH^-$$

but the reaction would then become independent of the concentration of alkali, which is contrary to observation. The theory that hydroxyl radicals are intermediates in fast reactions between permanganate and other negative ions is unlikely if stage (1) is accepted. As an alternative, it is postulated that direct electron-exchange reactions between negative oxy-ions may be facilitated by their size and ease of polarization.

The formation of the radical ion $\cdot O^-$ would, *a priori*, seem probable in strongly alkaline solution, and there is some evidence for its formation in alkaline solution (Gordon, Hart, and Hutchison, *J. Amer. Chem. Soc.*, 1952, **74**, 5548). If it be assumed that the acid strengths of hydroxyl radicals and water are comparable, then the free-energy change for stage (2) is zero (Weiss, *J. Chim. phys.*, 1952, **48**, cl, concludes that K_{OH} should be at least as great as that of H_2O_2). The third stage, which is unlikely to be a single reaction between three negative ions, probably comprises the three reactions $MnO_4^- + O^- \longrightarrow MnO_4^{2-} + O$; $O + OH^- \longrightarrow HO_2^-$; and $MnO_4^{2-} + HO_2^- \longrightarrow MnO_4^- + OH^- + {\cdot}O^-$.

The approximate standard free-energy changes ($\Delta G°$) and hence the equilibrium constants (K') for the individual steps in the postulated mechanism have been calculated from the values given by Latimer ("Oxidation Potentials," Prentice-Hall Inc., New York, 1952) and are given in Table 2, together with values for the velocity constants k_3, k_{-3}, k_4, k_{-4}, k_5, k_{-5}, and k_7 expressed as multiples of k_{-3}, which have been derived from the equilibrium constants and the observed values for K_3, K_4, K_5, and K_7.

In arriving at these values, no allowance has been made for the extra energy required to overcome the repulsive forces between the negative ions involved in stages (1), (3), (4), and (6). The tabulated free-energy values may therefore require considerable modification, but, since the permanganate ion is large, a quantitative estimation would be difficult and has not been attempted. A consideration of these figures suggests that, provided K_6 is large, which is probable, k_{-5}/k_6 is very small, which is in agreement with the main part of the reaction being of third, rather than fourth, order. It is possible that the radical ion ${\cdot}O^-$ has a high mobility as a result of exchange reactions such as ${\cdot}O^- + OH^- \rightleftharpoons OH^- + {\cdot}O^-$ or ${\cdot}O^- + H_2O \rightleftharpoons OH^- + {\cdot}OH \rightleftharpoons H_2O + {\cdot}O^-$ which would, in part, explain the very large value derived for k_3.

The experiments described above show that when the concentration of alkali is greater than 2·76N, the reaction is affected neither by light nor by the area of solid surface. However, Duke's results indicate that at relatively low concentrations of alkali, the reaction does become heterogeneous.

The assumption that permanganate is not transiently reduced beyond the manganate stage seems justified, since no formulation has been found involving, say, MnO_4^{3-}, which fits the kinetic results. It is noteworthy, however, that when manganate solutions are heated with a large excess of alkali, more oxygen is evolved and a bright blue compound is formed. This is presumably a compound of quinquevalent manganese (MnO_4^{3-}) (Lux, *Z. Naturforsch.*, 1946, **1**, 281) and may well be formed by a similar mechanism. It is, therefore, considered that these results support the theory that potassium permanganate may act as a source of free hydroxyl radicals (or ${\cdot}O^-$ radical ions) when in concentrated alkaline solution, although there seems no reason to suppose that its usual mode of reaction is *via* attack by these radicals. In fact, it would seem unreasonable to suppose that hydroxyl ions should yield electrons to permanganate more readily than a substance with a smaller electron affinity, unless the hydroxyl ions are in very great excess.

Drummond and Waters (*loc. cit.*) have given evidence that, under mild conditions, the permanganate ion only acts as an electron abstractor. The conditions used, however, were such that, in the absence of organic material, oxygen evolution would be negligible and it is therefore possible that they would have failed to detect oxidation due to attack by the hydroxyl radical or the ${\cdot}O^-$ radical ion. That may account, in part, for the differences found by these authors between the mode of reaction of alkaline permanganate and of Fenton's reagent. [However, it is not certain that all oxidations by Fenton's reagent are brought about by free hydroxyl radicals (Cahill and Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 2312), and many are known to be reactions with hydrogen peroxide catalysed by free hydroxyl radicals—a mode of reaction clearly impossible with alkaline permanganate.]

In accord with this is the deduction drawn from a study of the behaviour of optically active compounds (Kenyon and Symons, *loc. cit.*), *viz.*, that the conversion of branched-chain carboxylic acids $RR'CH{\cdot}[CH_2]_n{\cdot}CO_2H$ into the corresponding hydroxy-acids $RR'C(OH){\cdot}[CH_2]_n{\cdot}CO_2H$ by the use of potassium permanganate in concentrated alkaline solution ($MnO_4^- \longrightarrow MnO_4^{2-}$) proceeds *via* the formation of the radical-ions $RR'\dot{C}{\cdot}[CH_2]_n{\cdot}CO_2^-$. These reactions take place rapidly under conditions such that in dilute alkaline solution the acids are unaffected. Accordingly, it is postulated that the hydrogen abstraction is brought about by the hydroxyl radical or the ${\cdot}O^-$ radical-ion rather than the permanganate ion.

These two modes of oxidation of organic compounds

$$RH + OH^- \rightleftharpoons R^- + H_2O; \quad R^- + MnO_4^- \longrightarrow R\cdot + MnO_4^{2-}$$

and

$$MnO_4^- + OH^- \rightleftharpoons MnO_4^{2-} + \cdot OH; \quad RH + \cdot OH \longrightarrow R\cdot + H_2O$$

both result in the formation of the radical R• as an unstable intermediate. An alternative mode of reaction involves the formation of a stable organic molecule by a two-electron change, together with a compound of quinquevalent manganese. Since, in strongly alkaline solution, compounds of quinquevalent manganese are relatively stable and the reaction $MnO_4^- + MnO_4^{3-} \longrightarrow 2MnO_4^{2-}$ is fast, this mechanism seems to be compatible with the observed formation of manganate as an end-product. (Even if a compound of quadrivalent manganese were formed by disproportionation before oxidation occurred, this would still be oxidized to manganate by permanganate in concentrated alkaline solution.)

Such a mechanism could account for the oxidation of pinacol and for the initial formation of a *cis*-glycol when compounds containing an olefinic bond are oxidized by this reagent (Boeseken, *Rec. Trav. chim.*, 1922, **41**, 199). The alternative mechanism proposed by Drummond and Waters (involving the transient formation of an organic radical-ion) does not explain *cis*-addition, nor is it compatible with the observed reactions between potassium permanganate and acrylonitrile (Symons, *Research*, 1953, **6**, 5S). Thus, it has been found that, when a few drops of neutral permanganate are added to a large excess of a saturated aqueous solution of acrylonitrile, manganese dioxide is rapidly formed, but no polymer separates. If a transient radical-ion were formed, this would either be capable of initiating polymerization itself, or would react with water to give a radical identical with that produced by reaction with hydroxyl radicals. (The observation that polymerization is initiated when concentrated alkali is present can hardly be due to a change in the properties of the permanganate ion but may well be the result of attack by radicals formed as a side reaction between permanganate and hydroxide ions.)

EXPERIMENTAL

Materials.—All reagents used were of "AnalaR" grade. Water for preparing solutions and for final washing of apparatus was twice distilled from permanganate in concentrated alkaline solution. Glassware was repeatedly washed with a similar solution of permanganate. The permanganate and hydroxide solutions were boiled and filtered before being standardized.

Procedure.—The desired quantities of sodium hydroxide solution and water were placed in a glass-stoppered Pyrex tube in a thermostat at 25° ± 0·02°. Potassium permanganate solution was then added, and the mixture shaken until homogeneous. At known times, 2- or 4-ml. samples were removed by pipette and placed in a 25-ml. flask. After dilution to the mark, the extinction of the solution was measured with a "Spekker" photometer fitted with green filters (No. 5). The extinctions for solutions of permanganate and manganate of known concentration were measured separately, and hence the small absorption due to the presence of manganate was estimated by the use of a plot showing the combined reading due to manganate and permanganate against $[MnO_4^-]$.

For the second method, a modified hydrogenation apparatus was used, in which the reaction vessel could be vigorously shaken (at such a rate that the results were independent of the rate of shaking), and the volume of oxygen evolved was measured to within ±0·01 ml. at constant pressure. The reaction was carried out in a constant-temperature room at 25° ± 0·1°.

Thanks are expressed to Dr. J. W. Smith for his interest in this work, and to Imperial Chemical Industries Limited for a grant.

BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, June 24th*, 1953.]