It is believed that this series of reactions, taken together, accounts for the kinetic behavior in the oxidation of nitric oxide by oxygen. The effect of nitrogen dioxide and the greater than second-order dependence of the nitric oxide concentration show that the reaction is complicated and that the classical, simple termolecular mechanism giving a true third-order reaction is an oversimplification—but a surprisingly good one at the higher pressures.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Mechanism of the Permanganate–Oxalate Reaction

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RECEIVED NOVEMBER 19, 1954

Ultraviolet absorption spectra of the di- and trioxalate complexes of manganese(III) have been measured for the first time. Studies of the decomposition of these complexes confirm the observations of Taube in a different medium that a monoöxalate complex is kinetically important at low oxalate concentrations. Spectrophotometric and titrimetric studies of solutions containing both permanganate and manganese(III) demonstrate that there are no significant concentrations of the oxidation states +4, +5 and +6. These experiments also show that oxalate can replace manganous ion in providing three of the four electrons involved in reducing permanganate to manganese(III), but manganous ion is much preferred if it is available. Studies at low oxalate concentration support a previous proposal that permanganate itself usually reacts only with an oxalate complex of manganese(II), but the monoöxalate complex of manganese(III) may also be reactive. These observations permit the most detailed mechanism that has yet been proposed for the reduction of permanganate to manganese(III).

Introduction

The reaction between permanganate and oxalate ions has been a subject of kinetic study for almost ninety years, and two recent publications[2,3] have provided independent bibliographies of the extensive literature on the reaction. It has become clear that when manganous and oxalate ions are initially present in excess the reaction involves two processes

$$MnO_4^- + 4Mn^{++} + 5nC_2O_4^= + 8H^+ \longrightarrow 5Mn(C_2O_4)_n^{3-2n} + 4H_2O \quad (A)$$

$$2Mn(C_2O_4)_n^{3-2n} \longrightarrow 2Mn^{++} + (2n - 1)C_2O_4^= + 2CO_2 \quad (B)$$

where n may be 1, 2 or 3. These processes each take place in several steps, and detailed mechanisms are not clear. Also, these two processes are not sufficient to describe the reaction under all conditions. The results presented here supplement previous studies of this system and contribute to the elucidation of the detailed mechanism of the reaction. The data tend to support a partial mechanism proposed earlier,[4] and they permit even more detailed postulates about the nature of some of the individual steps.

Experimental

Reagents.—Solutions of potassium permanganate were prepared by customary procedures and standardized against sodium oxalate. Solutions of sodium oxalate were prepared fresh every two weeks; attempts to stabilize them by addition of acid led to formation of peroxide. Solutions of manganous perchlorate were standardized by precipitation as the ammonium phosphate and ignition to the pyrophosphate. The sodium perchlorate, used to maintain constant ionic strength of 1.00 M, was prepared from sodium carbonate and perchloric acid and was analyzed by evaporation. The reagents and analytical procedures are discussed with references in the original dissertation.[1]

General Procedure.—The reactions were started in glass-stoppered Erlenmeyer flasks fitted with a center well into which the permanganate was pipetted. The remaining solutions were pipetted into the outer portion of the flask, and the flask was swept with tank nitrogen while thermostated at 25.00 ± 0.01°. The reaction volume was always 100 ml.

The reaction was started by inverting and shaking the stoppered flask. At specified times, some reaction mixtures were compared with a Beckman Model DU spectrophotometer against blanks containing all the constituents except permanganate. A few supplementary observations were made with a Cary Recording Spectrophotometer, Model 11. The other solutions were titrated for oxidizing power by quenching with sodium iodide at appropriate times.

Titration Procedures.—The titrations were complicated because some solutions formed hydrogen peroxide in spite of efforts to flush out atmospheric oxygen. Two procedures were developed for including and excluding the oxidizing power of this peroxide.

Procedure α was designed to measure total oxidizing power of manganese and peroxide. The reaction mixture was quenched with a solution containing 25 ml. of 2.5 M sulfuric acid, 0.5 ml. of 3% ammonium molybdate (to catalyze reduction of peroxide), and 10 ml. of 10% sodium iodide. The quenched solution was allowed to stand for 10 minutes in the thermostat before it was diluted with 200 ml. of water and titrated with thiosulfate with starch as indicator. The procedure gave identical results against the original permanganate whether or not oxalate and manganous ion were present. Negligible blanks were obtained in solutions swept out with nitrogen but containing no added permanganate.

Procedure β was designed to measure oxidizing power due to manganese in states above +2 but not to measure hydrogen peroxide. The contents of the reaction flask were poured rapidly into 100 ml. of water containing 1 g. of sodium iodide and the liberated iodine was rapidly titrated with thiosulfate, the entire operation requiring less than a minute. In experiments containing a large excess of oxalate ion, it was necessary to add some acid to the quench in order to get sufficiently rapid reduction of the higher oxidation states of manganese. The initial titer of a sample of permanganate was a little lower by procedure β than by procedure α, but the difference was usually within 3%.

Results

Equilibria Involving Oxalate Complexes of Manganese(III).—Manganese(III) forms a yellow dioxalate complex,[5] $Mn(C_2O_4)_2^-$, and a red trioxalate

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[1] Based on a Dissertation submitted by Seymour J. Adler to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry. Persons desiring to consult the more complete report or to obtain a microfilm thereof may address the Library, Columbia University, New York 27, New York.

[2] R. M. Noyes, *Trans. N. Y. Acad. Sci.*, **13**, 314 (1951).

[3] E. Abel, *Monatsh.*, **83**, 695 (1952).

[4] J. M. Malcolm and R. M. Noyes, THIS JOURNAL, **74**, 2769 (1952).

[5] The formulas do not include water that may also be bound in these complexes. Our data furnish no information on extent of hydration.

complex, $Mn(C_2O_4)_3^{=}$. The visual absorption spectra were studied at 0° by Cartledge and Ericks,[6] and the equilibrium constant for the interconversion was evaluated. Spectra at higher temperatures are harder to evaluate because the solutions are unstable. We have formed solutions with sufficient excess of manganous ion that process (A) above is almost instantaneous and have scanned them with the Cary spectrophotometer. The Beckman spectrophotometer was used to follow the change of absorption with time at selected wave lengths, and the concentrations of Mn(III) in identical solutions were measured titrimetrically at comparable times by procedure β. Molar extinction coefficients, E, at different wave lengths were calculated from the relation

$$D \equiv \log (I_0/I) = Ecl \qquad (1)$$

where D is optical density, c is concentration in mole/liter, and l is cell length in cm. Figure 1 shows the spectra for the two oxalate complexes and for the red pyrophosphate complex of manganese(III).[7]

Since our studies were carried out at 25° in 1.00 M sodium perchlorate solution, the equilibrium constant (involving concentrations rather than activities) for interconversion of the complexes was determined spectrophotometrically under the same conditions. Since the (concentration) ionization constants of oxalic acid have not been measured in this medium, they were also estimated by a procedure of successive approximations that led to the best internal consistency of the data. The equilibrium constants obtained were

$$Mn(C_2O_4)_3^{=} \rightleftarrows Mn(C_2O_4)_2^- + C_2O_4^{=} \qquad K_M = 8.75 \times 10^{-4} \qquad (2)$$

$$H_2C_2O_4 \rightleftarrows H^+ + HC_2O_4^- \qquad K_1 = 1.05 \times 10^{-1} \qquad (3)$$

$$HC_2O_4^- \rightleftarrows H^+ + C_2O_4^{=} \qquad K_2 = 2.00 \times 10^{-4} \qquad (4)$$

Previously reported values of K_M are 38 × 10^{-4} in dilute solution at 0°[6] and 14 × 10^{-4} in 2.00 M potassium chloride at 25°.[8] Values of 0.79 × 10^{-1} and 1.91 × 10^{-4} have been reported for K_1 and K_2, respectively, in 1.04 M potassium chloride.[9]

Rate of Decomposition of Manganese(III) Complexes.—Taube[8] has made the definitive kinetic study of the decomposition of oxalate complexes of manganese(III) (process B above). He found contributions from three different oxalate complexes but feared that chloride ion, which he used to maintain ionic strength, might be entering some of the complexes with little oxalate. We therefore carried out a less extensive study in perchlorate medium at 25°. The solutions contained enough initial manganous and oxalate ions that process (A) took place almost instantaneously, and the subsequent process (B) was followed both spectrophotometrically and titrimetrically by procedure β. If k_{ex} is the experimental first-order rate constant and if three different oxalate complexes contribute to the decomposition

$$-\frac{d[Mn(III)]}{dt} = k_{ex}[Mn(III)] = k_1[MnC_2O_4^+] + k_2[Mn(C_2O_4)_2^-] + k_3[Mn(C_2O_4)_3^{=}] \qquad (5)$$

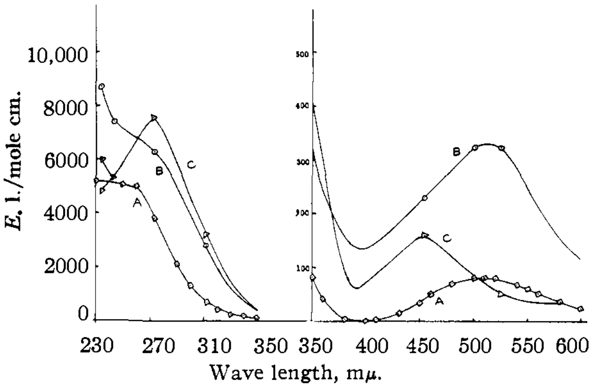

Fig. 1.—Molar extinction coefficients of manganese(III) complexes: A, $Mn(H_2P_2O_7)_3^{=}$; B, $Mn(C_2O_4)_3^{=}$ (cherry red); C, $Mn(C_2O_4)_2^-$ (yellow).

If all the manganese(III) is present in oxalate complexes and if we define the additional equilibrium constant

$$K_0 = \frac{[MnC_2O_4^+][C_2O_4^{=}]}{[Mn(C_2O_4)_2^-]} \qquad (6)$$

then we can write

$$k_{ex} = \frac{k_1 + \frac{k_2}{K_0}[C_2O_4^{=}] + \frac{k_3}{K_0K_M}[C_2O_4^{=}]^2}{1 + \frac{1}{K_0}[C_2O_4^{=}] + \frac{1}{K_0K_M}[C_2O_4^{=}]^2} \qquad (7)$$

Our spectrophotometric studies did not furnish any evidence for a monoöxalate complex, so unity in the denominator was negligible in all our experiments. Then equation 7 can be rearranged to

$$k_{ex}(K_M + [C_2O_4^{=}]) = \frac{k_1K_0K_M}{[C_2O_4^{=}]} + k_2K_M + k_3[C_2O_4^{=}] \qquad (8)$$

The plot in Fig. 2 at high oxalate concentrations (where the first term on the right of equation 8 is negligible) shows how k_2 and k_3 may be evaluated, and the plot in Fig. 3 at lower concentrations shows that the monoöxalate complex does indeed contribute kinetically to the decomposition in perchlorate medium. We did not attempt to evaluate K_0 either kinetically or spectrophotometrically, but the data in Table I show our good agreement with the prior results of Taube.[8] The differences in values of k_3 and K_M seem to be outside the estimated errors in both series of experiments; they probably represent medium effects.

TABLE I

KINETIC AND EQUILIBRIUM DATA ON MANGANESE(III) COMPLEXES

Medium	This investigation 1.00 M $NaClO_4$	Taube[8] 2.00 M KCl
k_3, min.$^{-1}$	2.93 × 10^{-2}	4.1 × 10^{-2}
k_2, min.$^{-1}$	9.23 × 10^{-2}	9.2 × 10^{-2}
k_1, min.$^{-1}$	....	23.6
K_M	8.8 × 10^{-4}	14 × 10^{-4}
K_0	....	2.49 × 10^{-7}
k_1K_0	3.8 × 10^{-6}	5.9 × 10^{-6}

Solutions Containing Manganese(III) and Permanganate.—Permanganate was added to several solutions containing too little initial manganous ion for process (A) to go to completion. During the fast initial formation of manganese(III), the oxidizing

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[6] G. H. Cartledge and N. P. Ericks, THIS JOURNAL, **58**, 2065 (1936).

[7] J. J. Lingane and R. Karplus, *Ind. Eng. Chem., Anal. Ed.*, **18**, 191 (1946).

[8] H. Taube, THIS JOURNAL, **70**, 1216 (1948).

[9] H. M. Dawson and J. E. Smith, *J. Chem. Soc.*, 2534 (1929).

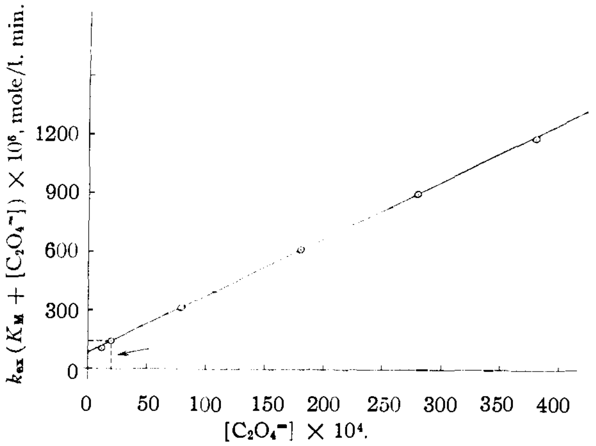

Fig. 2.—Rate data used to evaluate k_2 and k_3. Inset shows region of Fig. 3.

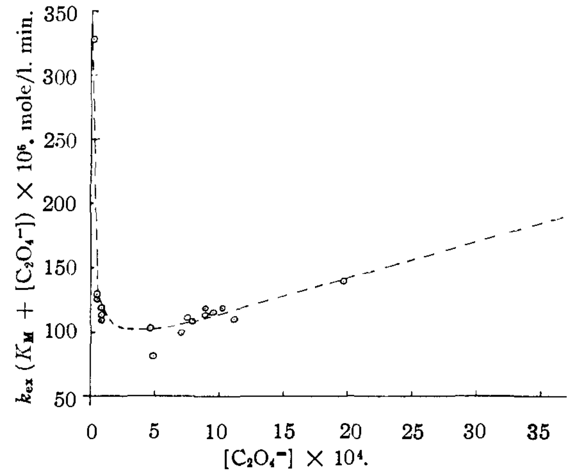

Fig. 3.—Rate data at low oxalate concentration. Curve is calculated from eq. 8 with constants from Table I.

titer dropped slightly but usually less than 10%. Since process (A) does not change the oxidizing titer against iodide, this drop in titer (which has been reported previously[8,10]) indicates that oxalate can be oxidized by some process other than (B) provided permanganate is present in the solution.

Solutions resulting from the fast initial reaction contained both permanganate and manganese(III); their subsequent history was followed both titrimetrically and spectrophotometrically. The concentration of permanganate decreased steadily, and the concentration of manganese(III) rose to a maximum at the time the permanganate disappeared and then decreased as predicted by rate data for process (B). The oxidizing titer against iodide by procedure β was never more than a few per cent. greater than the value calculated from the quantities of permanganate and manganese(III) estimated spectrophotometrically. These more definite observations confirm the conclusion reached by indirect evidence[4] that these solutions never contain significant concentrations of manganese between oxidation states +3 and +7. At the instant permanganate disappeared, all of the manganese in the solution could usually be accounted for as Mn(III) within the probable error of a few per cent.

Figures 4 and 5 show spectrophotometric studies of typical solutions containing predominantly the di- and trioxalate complexes. Since manganese(III) is the only other manganese species present in significant concentration with permanganate, the net process in the build-up of complex can be written as $MnO_4^- \rightarrow Mn(III)$. The rate of this process appears to be independent of the concentration of permanganate, so the reduction of permanganate is probably initiated by the occurrence of process (B).

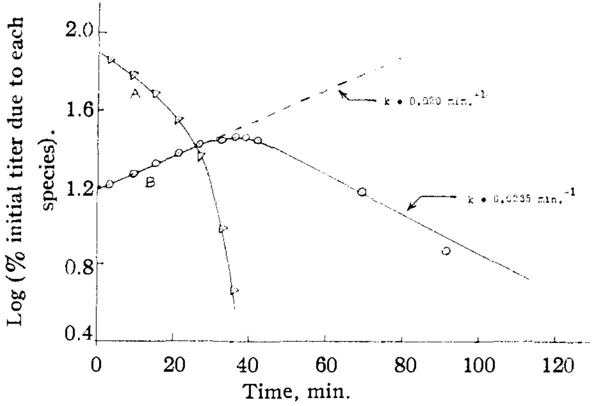

Fig. 4.—Change with time of concentration of MnO_4^- (A) and $Mn(C_2O_4)_3^{\equiv}$ (B). Solution was mixed to contain 1.000 × 10^{-4} *M* $KMnO_4$, 0.50 × 10^{-4} *M* $Mn(ClO_4)_2$, 200 × 10^{-4} *M* $Na_2C_2O_4$, 20 × 10^{-4} *M* $HClO_4$ and 1.00 *M* $NaClO_4$.

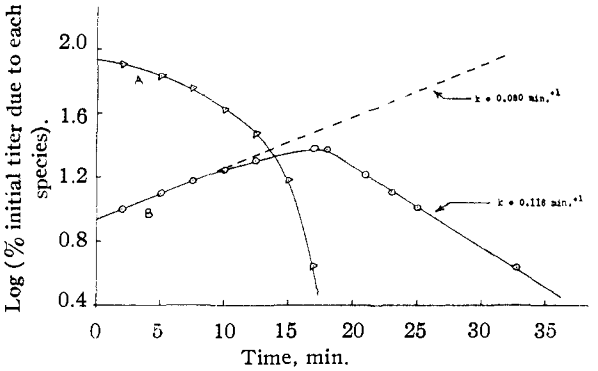

Fig. 5.—Change with time of concentrations of MnO_4^- (A) and $Mn(C_2O_4)_2^-$ (B). Solution was mixed to contain 2.000 × 10^{-4} *M* $KMnO_4$, 0.50 × 10^{-4} *M* $Mn(ClO_4)_2$, 50 × 10^{-4} *M* $Na_2C_2O_4$, 200 × 10^{-4} *M* $HClO_4$ and 1.00 *M* $NaClO_4$.

In the solution containing the cherry-red trioxalate complex, Fig. 4 shows that, at a given concentration of manganese(III), the net rate of the process $MnO_4^- \rightarrow Mn(III)$ is equal to the net rate of process B ($Mn(III) \rightarrow Mn(II)$) that would be observed if the solution contained no permanganate. This result would be obtained if one permanganate is reduced to manganese(III) during the reoxidation of one manganese(II) produced by process (B).

In the solution containing the yellow dioxalate complex, the reactions are more rapid, and Fig. 5 shows that the rate of the process $MnO_4^- \rightarrow Mn(III)$ is less than the rate of process (B) would be in the absence of permanganate. The mechanistic

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(10) M. J. Polissar, This Journal, 58, 1372 (1936).

implications of these observations will be discussed in detail later.

Studies at Low Oxalate Concentration.—When manganous and oxalate ions are both present at moderate concentrations, process (A) is almost instantaneous. That it is not completely so is suggested by the observation in Fig. 5 that the concentration of manganese(III) reaches its maximum slightly before the complete disappearance of permanganate. In order to examine this effect, some early titrimetric studies by procedure α were made on solutions containing manganous and oxalate ions at very low concentrations but stoichiometrically in excess of permanganate. Some of these runs are plotted in Fig. 6. These runs confirm our previous observation[4] that the color of permanganate may persist for almost a minute even when manganous and oxalate are both present in stoichiometric excess of the requirements for process (A). The runs also confirm that increasing concentration of manganous ion increases the rate of attack on permanganate.

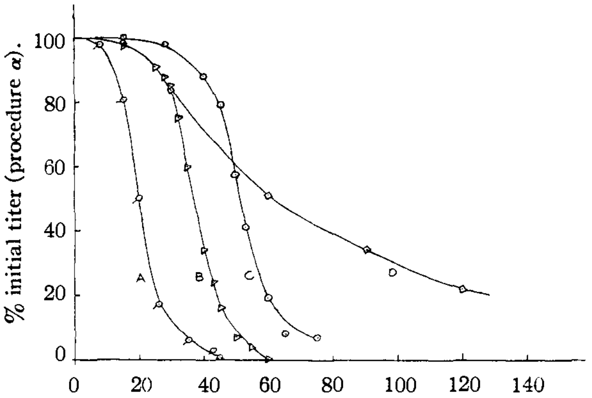

Fig. 6.—Change of titer with time for runs at low oxalate concentration. All solutions were mixed to contain 1.000 × 10^{-4} *M* $KMnO_4$, 200 × 10^{-4} *M* $HClO_4$ and 1.00 *M* $NaClO_4$.

Curve and run no.	A(12)	B(11)	C(13)	D(16)
$Na_2C_2O_4 \times 10^4$	2.60	2.60	2.60	10.0
$Mn(ClO_4)_2 \times 10^4$	50.0	10.00	5.00	10.0

Figure 6 does not clearly demonstrate the importance of oxalate for the initial attack on permanganate, for the titrimetric procedure measures both permanganate and manganese(III), and the reduction of the latter is slowed by increasing oxalate concentration. Some rough visual experiments showed unequivocally that decreasing oxalate concentration slowed the disappearance of permanganate color until the concentration range of Fig. 6 was reached. In duplicates of runs 11 and 16, the permanganate color in run 11 (lowest oxalate) decreased less rapidly than the other at first but then accelerated rapidly and disappeared somewhat sooner. This experiment indicates that the autocatalytic behavior shown in Fig. 6 is most important at very low oxalate concentrations. This autocatalytic behavior requires that attack on permanganate itself is facilitated by some species produced in the reaction. Induction periods have previously been observed only in solutions containing insufficient manganous ion for process (A). Since the concentration of manganous ion does not change much during the initial stages of our runs, some intermediate must be still more efficient in promoting attack on permanganate itself, and this intermediate appears to be more important as the oxalate concentration is lowered.

In a few additional experiments at very low acid concentration, precipitates of manganese dioxide appeared during the run. The rate of loss of titer seemed to decrease after the formation of such a precipitate.

Effect of Oxygen.—Titrimetric studies were made on a few solutions that had been flushed with oxygen, and the results were compared with similar solutions flushed with nitrogen by the usual procedure. Data for solutions containing the tri- and dioxalate complexes are presented in Figs. 7 and 8, respectively. The data indicate that the formation of peroxide is much more rapid in solutions containing the yellow dioxalate complex and that the total oxidizing titer in such a solution actually goes through a minimum as the concentration of manganese(III) decreases. We performed another experiment in which the concentration of free oxalate

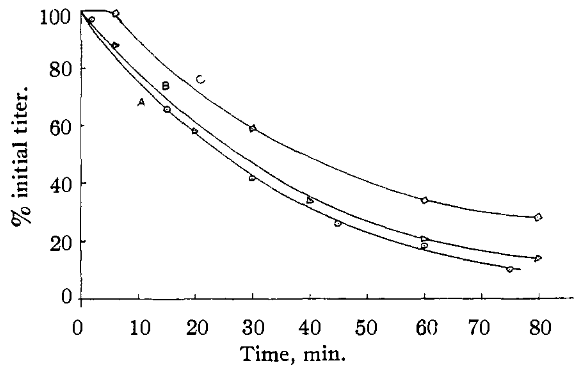

Fig. 7.—Effect of oxygen on titer of solutions containing $Mn(C_2O_4)_3^{=}$: A, Procedure β flushed with nitrogen; B, procedure β flushed with oxygen; C, procedure α flushed with oxygen. Solutions were mixed to contain 1.000 × 10^{-4} *M* $KMnO_4$, 10.0 × 10^{-4} *M* $Mn(ClO_4)_2$, 300 × 10^{-4} *M* $Na_2C_2O_4$, 20 × 10^{-4} *M* $HClO_4$ and 1.00 *M* $NaClO_4$.

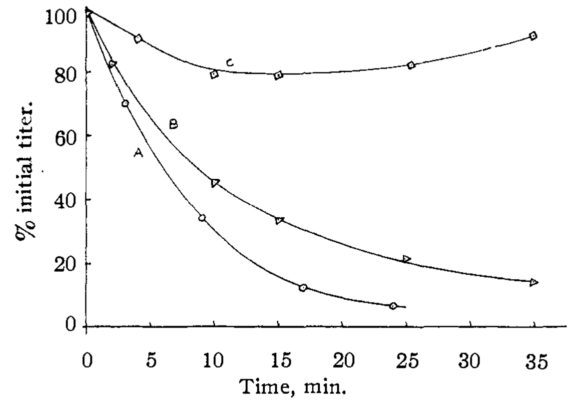

Fig. 8.—Effect of oxygen on titer of solutions containing $Mn(C_2O_4)_2^-$: A, procedure β flushed with nitrogen; B, procedure β flushed with oxygen; C, procedure α flushed with oxygen. Solutions were mixed to contain 1.000 × 10^{-4} *M* $KMnO_4$, 5.00 × 10^{-4} *M* $Mn(ClO_4)_2$, 200 × 10^{-4} *M* $Na_2C_2O_4$, 600 × 10^{-4} *M* $HClO_4$ and 1.00 *M* $NaClO_4$.

ion was about the same as in Fig. 8 so that the rate of decomposition of manganese(III) complexes was about the same, but the concentration of hydrogen ion was about a quarter as great. The results were virtually identical with Fig. 8; therefore, hydrogen ion does not affect the reaction with oxygen in this range of acidity.

Detailed Discussion of Mechanism

Decomposition of Manganese(III) Complexes (Process B).—Since process (B) is the simpler one, we shall consider it first. The kinetics demonstrate that the transition state for the rate-determining step contains one atom of manganese(III) and one, two or three oxalate ions. Kinetics cannot distinguish between unimolecular decomposition of a complex like $Mn(C_2O_4)_3^{\equiv}$ and bimolecular reaction like $Mn(C_2O_4)_2^- + C_2O_4^=$, but Taube[11] has presented an argument that $MnC_2O_4^+$ reacts by unimolecular decomposition.

The intermediate from the first step may either be manganese(I) or a radical-ion from a one-electron oxidation of oxalate. We favor the radical-ion but can add nothing to the arguments of Taube[8,11] and others.

Kinetic measurements cannot distinguish between $C_2O_4^-$ and CO_2^-, but we favor CO_2^- because it is easier to see how this species could react with atmospheric oxygen to form a peroxy compound.[12] Duke[13] also favored this structure because of analogies between this reaction and cleavage during oxidation of 1,2-glycols.

The CO_2^- intermediate may react either with a manganese(III) species or with another CO_2^-. Since CO_2^- is present in very low concentration and is a strong reductant for other oxidizing agents, we favor reaction with Mn(III). Taube[8,11] has demonstrated that $MnC_2O_4^+$ is very effective at reacting with this intermediate but that $Mn(C_2O_4)_2^-$ is less reactive.

The above considerations suggest the following sequence for process (B)

$$Mn(C_2O_4)_n^{3-2n} \longrightarrow Mn^{++} + (n-1)C_2O_4^= + CO_2 + CO_2^- \quad (B1)$$

$$Mn(C_2O_4)_n^{3-2n} + CO_2^- \longrightarrow Mn^{++} + nC_2O_4^= + CO_2 \quad (B2)$$

We have not attempted to indicate whether the radical intermediate exists in neutral or ionized form. If the acidity is comparable to that of formic acid, our intermediate was HCO_2 in solutions containing the yellow dioxalate complex and was chiefly CO_2^- in solutions containing the cherry red trioxalate complex. Figure 8 and a similar run gave identical results for hydrogen ion concentrations of 3.5×10^{-2} and 9.7×10^{-3}. Either the neutral and ionic forms of the intermediate have the same relative reactivity between oxygen and manganese(III), or the intermediate was predominantly in the same (presumably un-ionized) form in both solutions. The smaller amount of oxygen absorption in Fig. 7 indicates either that molecular oxygen reacts less easily with CO_2^- than with HCO_2 or that the trioxalate complex is more efficient than the dioxalate at oxidizing the intermediate; the data of Taube[11] suggest the former explanation.

Reduction of Permanganate with Oxidation of Manganese(II) (Process A).—Permanganate does not react directly with oxalate. Launer and Yost[14] showed that the two species could coexist for over a week if the solution contained a large excess of fluoride to complex traces of lower oxidation states of manganese. The Guyard reaction of permanganate and manganous ions to form manganese dioxide is also slow in acid solutions that do not contain complexing agents. Figure 6 and experiments discussed above demonstrate that the rate of attack on permanganate is increased by increasing the concentration of either manganous or oxalate ions. This observation is especially significant because increasing oxalate concentration slows the subsequent decomposition of manganese(III). Figure 6 seems entirely consistent with our previous proposal[4] that permanganate reacts initially with an oxalate complex of manganese(II). Complex formation has been demonstrated by solubility[15] and spectrophotometric[4] measurements; we postulate that the reactive species is the neutral monooxalate complex because of coulombic repulsion between permanganate and higher complexes.

The initial step may involve transfer of one or more electrons. We favor the single electron process because manganate is a well known species and because of evidence discussed below for other reactions in which permanganate undergoes a one electron change in the first step.

These arguments lead to the initial step

$$MnO_4^- + MnC_2O_4 \longrightarrow MnO_4^= + MnC_2O_4^+ \quad (A1)$$

In a rough visual experiment, the time of fading of the permanganate color was combined with the reported[15] dissociation constant of MnC_2O_4 to indicate that the bimolecular rate constant for step (A1) is of the order of 10^3 liter/mole sec. if the proposed mechanism is correct.

The manganate is unstable in acid solution and would disproportionate in the absence of reducing agents. However, excess manganous ion will preferentially reduce it to manganese(III). From analogy with reduction by oxalate ion discussed below, we propose the steps

$$Mn(VI) + Mn(II) \longrightarrow 2Mn(IV) \quad (A2)$$

$$Mn(IV) + Mn(II) \longrightarrow 2Mn(III) \quad (A3)$$

The manganate may undergo partial hydrolysis without change in oxidation state before it reacts with manganous ion, and we make no attempt to propose exact formulas for any of the species above manganese(III). Presumably these formulas depend on *p*H and oxalate concentration.

Reduction of Permanganate with Oxidation of Oxalate (Process C).—Processes (A) and (B) are not sufficient to describe the reaction under all conditions. We have already mentioned that there may be a rapid initial loss of oxidizing titer that is not consistent with either process. In Fig. 4, the

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[11] H. Taube, THIS JOURNAL, **69**, 1418 (1947).

[12] The authors are indebted to Professor Cheves Walling for this argument.

[13] F. R. Duke, THIS JOURNAL, **69**, 2885 (1947).

[14] H. F. Launer and D. M. Yost, *ibid.*, **56**, 2571 (1934).

[15] R. W. Money and C. W. Davies, *Trans. Faraday Soc.*, **28**, 609 (1932); *J. Chem. Soc.*, 400 (1934).

rate at which permanganate is reduced to manganese(III) in a solution containing a large excess of oxalate is exactly the rate at which the manganese(III) present would form manganese(II) if there were no permanganate. We can explain these observations if we postulate the additional process.

$$MnO_4^- + Mn^{++} + (2n + 3/2)C_2O_4^{=} + 8H^+ \longrightarrow 2Mn(C_2O_4)_n^{3-2n} + 3CO_2 + 4H_2O \quad (C)$$

Presumably process (C) starts with the same step as process (A), but the manganese(VI) is reduced by oxalate instead of by manganous ion. However, the reaction cannot produce the radical intermediate formed in process (B). If CO_2^- were produced during any stage of process (C), it would react with manganese(III) or directly with permanganate, the reduction of the products of reaction would produce more CO_2^-, and the kinetics of consumption of permanganate would resemble those in a branched chain explosion.

We can see only two proposals that avoid this mechanistic catastrophe. One possibility is to reject step (B2) and assume that the radical intermediates are inert to the oxidizing species MnO_4^- and Mn(III) and react only by the process

$$CO_2^- + CO_2^- \longrightarrow C_2O_4^{=} \qquad (B2')$$

We are loath to propose this behavior for a species known to reduce mercuric chloride very rapidly.

The other possibility is that oxalate is oxidized only by two-electron transfers so that CO_2^- is never produced as an intermediate in process (C). Two previous studies support this possibility. Kenyon and Symons[16] studied the alkaline oxidation of optically active carboxylic acids containing a tertiary carbon. They found racemization during oxidation with permanganate and postulated a one-electron transfer forming a racemic radical. Oxidation with manganate led to retention of optical activity and was interpreted as involving intermediate lactone formation during a two electron transfer. Merz, Stafford and Waters[17] showed that oxidation of alcohols could be induced during the reduction of permanganate with ferrous ion or hydrogen peroxide. Since potential radical reactions did not take place, the authors decided that the alcohol was oxidized in a two electron step. They favored the valence change Mn(IV) → Mn(II), but there seems no reason to rule out Mn(VI) → Mn(IV). They found some evidence for two competing but mutually exclusive paths, and the other could be Mn(V) → Mn(III) where Mn(V) could be formed during the oxidation of ferrous ion even if it did not form during oxidation of manganous ion.

We conclude that oxalate is oxidized in a two-electron step and propose

$$Mn(VI) + C_2O_4^{=} \longrightarrow Mn(IV) + 2CO_2 \quad (C2)$$

If manganous ion were present, step (C2) would probably be followed by (A3). The argument from Fig. 4 seems to require that manganese(IV) can oxidize oxalate by a two-electron process with the ultimate formation of manganese(III) and without the intermediate formation of manganese(II). The manganese(IV) probably exists as an oxalate complex,[18] and a possible step is

$$2Mn(IV) + C_2O_4^{=} \longrightarrow 2Mn(III) + 2CO_2 \quad (C3)$$

There would be no simple way to distinguish this step from a rapid series of steps in which Mn(IV) disproportionated to Mn(III) + Mn(V) and the Mn(V) oxidized oxalate in a two-electron step.

Since manganous ion is much more efficient than oxalate at reducing the intermediate oxidation states, steps (C2) and (C3) will occur only at very low concentrations of Mn(II). In Fig. 5 we see a run similar to Fig. 4 but at lower oxalate concentration. Under these conditions, process (B) will be speeded and step (A1) will be slowed; hence the steady-state concentration of manganous ion from the decomposition of manganese(III) complexes will be greater. We see that the rate of attack on permanganate is less than the rate of production of manganous ion when the permanganate is consumed. This effect was predicted previously[4] and would be anticipated if some of the manganous ion produced in process (B) reacts by step (A2) or (A3) and becomes unavailable for step (A1). In the limit, the rate of increase of Mn(III) concentration in the presence of permanganate should be only a quarter of the rate of decrease in the absence of permanganate.

Other Reactions of Permanganate.—Up to now, we have assumed that permanganate itself reacts only with the monoöxalate complex of manganese(II). It may also react with CO_2^-, for our data cannot distinguish between the reaction $MnO_4^- + CO_2^- \rightarrow MnO_4^{=} + CO_2$ and the reaction sequence (B2) + (A1).

In solutions with very low oxalate concentration, we must postulate some other direct reaction of permanganate, for Fig. 6 indicates an autocatalytic reaction even though the concentrations of manganous and oxalate ions are not changing greatly. It is not easy to determine the active intermediate, for Fig. 4 requires that at high oxalate concentrations permanganate is inert to all oxidation states of manganese from +3 to +6 inclusive. The most plausible explanation we can develop is that permanganate reacts with $MnC_2O_4^+$ more easily than with MnC_2O_4, but that it does not react with the negatively charged complexes of manganese(III). The proposed reaction is

$$MnO_4^- + MnC_2O_4^+ \longrightarrow MnO_4^{=} + Mn(IV) \quad (D)$$

This interpretation is supported by the qualitative observation reported above that autocatalytic behavior is more pronounced the lower the concentration of oxalate. The effect is probably not a competition for an intermediate between oxidation by permanganate and reduction by oxalate; for the solution contained a significant concentration of manganous ion, and the data show that it is much more efficient than oxalate at reducing the intermediates formed in the reaction.

Reaction with Oxygen.—Our data add very little to the work of Launer[19] on induced oxidation of oxalate. The results are consistent with the steps that he proposed.

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[16] J. Kenyon and M. C. R. Symons, *J. Chem. Soc.*, 3580 (1953).

[17] J. H. Merz, G. Stafford and W. A. Waters, *ibid.*, 638 (1951).

[18] G. H. Cartledge and N. P. Ericks, THIS JOURNAL, **58**, 2069 (1936).

[19] H. F. Launer, *ibid.*, **55**, 865 (1933).

$$CO_2^- + O_2 \rightleftarrows O_2CO_2^- \qquad (E1)$$

$$O_2CO_2^- + Mn^{++} + 2H^+ \longrightarrow Mn(III) + H_2O_2 + CO_2 \qquad (E2)$$

Our data do not seem to indicate whether it is desirable to add the reaction proposed by Weiss[20]

$$CO_2^- + H_2O_2 \longrightarrow CO_2 + OH + OH^- \qquad (E3)$$

A thorough study of the induced oxidation might provide more definite information about these steps and also about the ionization constant of the radical ion and the nature of step (B2).

Summary

If atmospheric oxygen is absent, the following mechanism appears to be consistent with the voluminous information available on the homogeneous reaction between permanganate and oxalate. The equations as presented do not include the many rapid equilibria in the system that involve hydrogen and oxalate ions.

The reaction is initiated by the step

$$MnO_4^- + MnC_2O_4 \longrightarrow MnO_4^{=} + MnC_2O_4^+ \qquad (A1,C1)$$

If manganous ion is present in significant concentration, the subsequent steps are

$$Mn(VI) + Mn(II) \longrightarrow 2Mn(IV) \qquad (A2)$$

$$Mn(IV) + Mn(II) \longrightarrow 2Mn(III) \qquad (A3)$$

If manganous ion is not available, the less favored steps are

$$Mn(VI) + C_2O_4^{=} \longrightarrow Mn(IV) + 2CO_2 \qquad (C2)$$

$$2Mn(IV) + C_2O_4^{=} \longrightarrow 2Mn(III) + 2CO_2 \qquad (C3)$$

These steps involve oxidation of oxalate in two electron transfers and do not produce Mn(II) as an intermediate in (C3).

The Mn(III) subsequently reacts according to the sequence

$$Mn(C_2O_4)_n^{3-2n} \longrightarrow Mn^{++} + (n-1)C_2O_4^{=} + CO_2 + CO_2^- \qquad (B1)$$

$$Mn(C_2O_4)_n^{3-2n} + CO_2^- \longrightarrow Mn^{++} + nC_2O_4^{=} + CO_2 \qquad (B2)$$

where n may be 1, 2 or 3 and step (B1) is rate determining. The rate and equilibrium constants associated with (B1) have been evaluated by Taube[8] and less completely by us.

At very low concentrations of oxalate, permanganate can also react by the step

$$MnO_4^- + MnC_2O_4^+ \longrightarrow MnO_4^{=} + Mn(IV) \qquad (D)$$

Acknowledgment.—This research was supported in part by the Office of Ordnance Research under Contract DA-30-069-ORD-783.

NEW YORK 27, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Kinetics of Competitive Processes when Reactive Fragments are Produced in Pairs

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RECEIVED DECEMBER 2, 1954

If a molecule is dissociated into two radicals in liquid phase, the radicals may undergo primary recombination in the "cage" in which they are formed, may undergo diffusive secondary recombination, or may combine with radicals from other dissociations. A scavenger that can react with radicals may compete with the combination process even at low concentrations, and conventional kinetic expressions are developed to describe the competition. These expressions depend on whether the product of reaction with scavenger is a reactive radical itself or is inert. Only a very reactive scavenger can compete with the secondary recombination of original partners from a dissociation. If such competition does occur, the amount of additional reaction varies approximately as the square root of the concentration of scavenger. Primary recombination occurs too rapidly for competition except in a medium that consists almost entirely of very reactive scavenger. The term "geminate recombination" is proposed for the total of primary and secondary recombination of original partners; this total is usually lumped together in references to "cage" effects.

Introduction

Vinyl polymerization and many other chemical reactions are initiated by the radical fragments produced in pairs by thermal or photochemical dissociation reactions. When it is possible to measure the absolute rate of dissociation, it is usually found that not all of the fragments initiate the reaction of interest and that it is not possible to eliminate competition from reactions between fragments. The purpose of this paper is to develop the kinetics for the competition between these radical–radical reactions and the desired reaction of a radical with some other species (herein referred to as a scavenger). Even in a system containing only one type of radicals and one other chemical species capable of reacting with them three kinetically distinct radical–radical processes may contribute to reduce the efficiency of initiation.

(1) The fragments from a dissociation may undergo "primary recombination" in the "cage" in which they are formed. If this happens, the fragments never attain a separation of as much as a molecular diameter, and recombination takes place in a period that may be of the order of a vibration (10^{-13} sec.) and is certainly less than the time between diffusive displacements (10^{-11} sec.). It is conceivable that molecules in the wall of the "cage" could compete with primary recombination, but they can only do so when the mole fraction of scavenger is near unity and when the scavenger is extremely efficient. In the rest of this paper, we shall neglect primary recombination and consider only those systems in which the dissociating fragments attain separations of at least a molecular diameter.

(2) If the fragments escape the "cage," they undergo random diffusive displacements of the or-