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A KINETIC STUDY OF THE PERMANGANATE—OXALATE REACTION AND KINETIC DETERMINATION OF MANGANESE(II) AND OXALIC ACID BY THE STOPPED-FLOW TECHNIQUE

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SUMMARY

The reduction of permanganate by oxalate in the presence of manganese(II) ion in acidic media is described. All reactions were run at 525 nm and constant ionic strength 1.0 M. The reaction was found to obey the rate expression $-d[MnO_4^-]/dt = k [Mn^{2+}] [C_2O_4^{2-}]^2 [MnO_4^-] [H^+]^{-2} = k' [MnC_2O_4] [MnO_4^-]$. The values of k and k' were shown to be 5.4×10^4 M^{-1} s^{-1} and 8.2×10^4 M^{-1} s^{-1}, respectively. Reaction rate methods for the determination of manganese(II) and oxalic acid are reported. The rate of disappearance of permanganate was monitored automatically and related directly to manganese-(II) and oxalic acid concentrations. Manganese(II) in the ranges $1—10 \times 10^{-4}$ M and $1—10 \times 10^{-3}$ M and oxalic acid in the range 0—20 μg ml^{-1} can be determined very rapidly with a precision of 1—2%.

The reaction between permanganate and oxalate ions has been investigated frequently for over a century [1—6]. The reaction in acidic solutions is comparatively slow, the net reaction being

$$2 MnO_4^- + 5 C_2O_4^{2-} + 16 H^+ \longrightarrow 2 Mn^{2+} + 10 CO_2 + 8 H_2O \qquad (1)$$
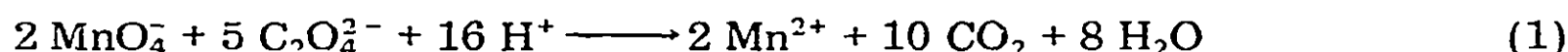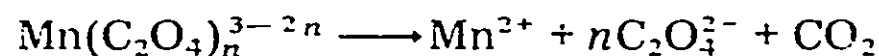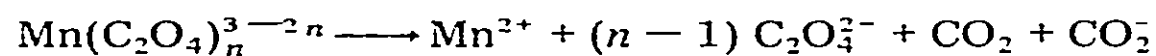
This is the basis for the widely used standardization of permanganate solutions. Manganese(II) ions, one of the products of the reaction, has a very profound accelerating effect on the initial stages of the reaction. It has been suggested that, when manganese(II) ions are present from the start, the reaction proceeds in two main stages. First, the reacting mixture changes color, becoming yellow or cherry red for low and high free oxalate concentrations, respectively. The main reaction during this first stage is a rapid oxidation—reduction reaction between permanganate and manganese(II) which leads to oxalate complexes of manganese(III) and perhaps of other oxidation states of manganese. Adler and Noyes [6] proposed a general scheme for the first stage: the reaction starts with the step

$$MnO_4^- + MnC_2O_4 \longrightarrow MnO_4^{2-} + MnC_2O_4^+ \qquad (1A)$$

If manganese(II) ions are at high concentration (condition A), then Mn(VI) + Mn(II) $\longrightarrow$ 2 Mn(IV) and Mn(IV) + Mn(II) $\longrightarrow$ 2 Mn(III). If manganese-(II) ions are at low concentration, then Mn(VI) + $C_2O_4^{2-}$ $\longrightarrow$ Mn(IV) + 2 CO_2 and 2 Mn(IV) + $C_2O_4^{2-}$ $\longrightarrow$ 2 Mn(III) + 2 CO_2. In this scheme, Mn(II) may be present as Mn^{2+}, MnC_2O_4 or $Mn(C_2O_4)_2^{2-}$, and Mn(III) as Mn^{3+}, $MnC_2O_4^+$ $Mn(C_2O_4)_2^-$ or $Mn(C_2O_4)_3^{3-}$.

This postulated scheme was based on the following facts: (a) permanganate reacts slowly or not at all with oxalate [7]; (b) the reaction of permanganate and Mn^{2+} is very slow in acidic solutions which do not contain complexing agents; (c) complex formation occurs in a mixture of Mn^{2+} and oxalate; and (d) coulombic repulsion occurs between permanganate and higher oxalate complexes with manganese.

The second stage of the reaction of permanganate and oxalate in the presence of manganese(II) ions involves slow decomposition of the various manganese-(III)—oxalate complexes formed in the rapid first stage [6]

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

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

where $n = 1$, 2 or 3 and the former reaction is rate-determining. At very low oxalate concentrations, the following step can take place

$$MnO_4^- + MnC_2O_4^+ \longrightarrow MnO_4^{2-} + Mn(IV)$$
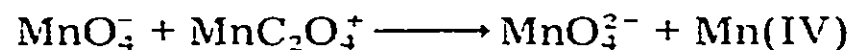
Using titrimetric methods, Taube [3] showed that the second stage of the reaction can be represented by

$$-d\,[Mn(III)]\,/dt = 2k_1\,[Mn(C_2O_4)^+] + 2k_2\,[Mn(C_2O_4)_2^-] +$$

$$2k_3\,[Mn(C_2O_4)_3^{3-}] \tag{2}$$

Values of $k_1 = 11.8$ min^{-1}, $k_2 = 0.046$ min^{-1} and $k_3 = 0.00205$ min^{-1} at 25°C were reported. The small values of k_2 and k_3 explain the unusual delay of the overall reaction at high excess of oxalate.

The first step of the disappearance of permanganate is very fast and quantitative experimental data are not available. In the present work, it was possible to calculate kinetic parameters for the first stage 1A by following directly the destruction of the permanganate color at 525 nm using the stopped-flow technique. The accelerating effect of Mn^{2+} on the reaction is also used in kinetic procedures for the determination of Mn^{2+} and oxalic acid in the range 1×10^{-3}—1×10^{-2}, and 5—20 μg ml^{-1}, respectively.

EXPERIMENTAL

Apparatus

A Durrum-Gibson stopped-flow spectrophotometer (Model D-110) was used with 2-cm path-length cells for the kinetic investigation of the reaction and the determination of manganese. The signal from the photomultiplier

was fed to a log amplifier (Durrum photometric log amplifier, Model D-131) and then to the differential amplifier of a Textronix storage oscilloscope. The reaction was followed on the scope and photographed with a Polaroid camera.

For the automatic measurement of reaction rate in the determination of manganese, an automatic curve slope meter [8] was used. This system is suitable for slope measurements in any region of the reaction curve by integration at two different times. An automated stopped-flow spectrophotometer constructed as described by O'Keefe and Malmstadt [9] was used in the oxalic acid determination. The system interfaced to a PDP 8/f minicomputer provides for automatic aliquotting and mixing of sample and reagent (100 μl) as well as data acquisition.

Reagents and working solutions

Potassium permanganate stock solution (0.0100 M) was prepared by the classical method and standardized against primary standard sodium oxalate. The sodium oxalate stock solution (0.1000 M) was prepared by dissolving 13.40 g of reagent in 1 l of water; it was renewed every two weeks. Manganese-(II) standard stock solution (5.00 $\times$ 10^{-2} M) was prepared by dissolving 18.1 g of $Mn(ClO_4)_2 \cdot 6H_2O$ in 1 l of water and standardized against standard EDTA solution. Perchloric acid, sulphuric acid and sodium perchlorate were of analytical grade.

Working solutions. Solution A (oxidizing) contained $KMnO_4$, $HClO_4$ and $NaClO_4$ in the appropriate proportions. Solution B (reducing) contained $Mn(ClO_4)_2$, $Na_2C_2O_4$, $HClO_4$ and $NaClO_4$ in the appropriate proportions. The concentrations of perchloric acid and sodium perchlorate in solutions A and B were the same in order to maintain the same acidity and ionic strength in the reaction mixtures. All concentrations given in the tables and figures are the actual concentrations in the reacting mixture (half of the initial) at zero time after mixing.

The ionic strength was held constant in all experiments at I = 1.00 M and the temperature in all runs was 25 $\pm$ 0.2° C.

Procedures

Kinetic investigation of the reaction. The instrument was calibrated for 0 and 100% transmittance, and the two 20-ml reservoir syringes and 2-ml drive syringes were filled with working solutions A and B. The reproducibility of the traces was checked by several runs and then the picture was taken with the Polaroid camera and evaluated as described below.

Kinetic determination of manganese(II). A solution containing 2.00 $\times$ 10^{-4} M $KMnO_4$, 0.100 M $HClO_4$ and 0.900 M $NaClO_4$ was used as oxidizing solution A. Standard solutions containing 1.00 $\times$ 10^{-4}—1.00 $\times$ 10^{-3} M and 1.00 $\times$ 10^{-3}—1.00 $\times$ 10^{-2} Mn(II), 3.00 $\times$ 10^{-2} M $Na_2C_2O_4$, 0.100 M $HClO_4$ and 0.900 M $NaClO_4$ were used to draw the calibration curves. Unknown solutions of manganese(II) contained the same concentrations of the reagents.

For each series of runs, the appropriate delay time and integration time were selected on the automatic curve slope meter, and the output voltage values related to the slope of the reaction curves were reported.

Kinetic determination of oxalic acid. The oxidizing solution A was the same as in the manganese(II) determination. Standard and unknown solutions containing 0—20 μg ml^{-1} oxalic acid and 1.00×10^{-4} M Mn(ClO$_4$)$_2$, 0.300 M HClO$_4$ and 0.700 M NaClO$_4$ were used. The two 100-μl syringes of the automated stopped-flow system were automatically filled and the solutions were transferred and mixed rapidly. The change in absorbance was monitored at 525 nm during the selected measurement time and used to obtain the reaction rate in mA s^{-1} by the least-squares method, the calibration curve and the values of the unknowns being printed out.

RESULTS AND DISCUSSION

Kinetic investigation of the reaction

The molar absorptivity of permanganate at 525 nm is $\epsilon = 2020$ l mol^{-1} cm^{-1} (confirmed literature value). Few of the other reacting species absorb significantly at this wavelength. The dioxalate and trioxalate complexes of manganese(II) have comparatively small molar absorptivities at 525 nm (70 and 350 l mol^{-1} cm^{-1}, respectively). However, the pK_{inst} values for the three complexes are 9.98, 6.59 and 2.85 for the mono-, di-, and tri-oxalate, respectively [10], thus the concentrations of these complexes during the first stage of the reaction are low, and their contribution to the absorption of the reacting mixture is almost negligible.

The rate law for the studied reaction can be given by the equation

$$-d\,[MnO_4^-]/dt = k\,[Mn^{2+}]^x\,[C_2O_4^{2-}]^y\,[H^+]^z\,[MnO_4^-]^w \tag{3}$$

For constant concentrations of Mn^{2+}, C$_2$O$_4^{2-}$ and H$^+$, the rate of the reaction can be made dependent only on the permanganate concentration. If the concentration of permanganate is very low compared to the concentration of the other reactants, then

$$-d\,[MnO_4^-]/dt = k_{obs}\,[MnO_4^-]^w \tag{4}$$

with $k_{obs} = k\,[Mn^{2+}]_o^x\,[C_2O_4^{2-}]_o^y\,[H^+]_o^z$ $\tag{5}$

where subscript o refers to initial concentrations. Under the above-mentioned conditions, k_{obs} can be determined by applying different techniques; the Guggenheim method for first-order reactions [11] was used here.

Absorbance values were read from the oscilloscope photographs (by calibration 10.00 V on the scope was equivalent to unit absorbance A) and the quantity $\ln(A_{t+\tau} - A_t)$ for different times t after mixing was calculated; τ is an arbitrary time interval, chosen to equal about one half-life of the reaction. A plot of $\ln(A_{t+\tau} - A_t)$ versus t gave a straight line, which means that the reaction is first order in respect to permanganate. The slope of this plot is the observed reaction rate constant, k_{obs}. Table 1

TABLE 1

Variation of k_{obs} with $[MnO_4^-]_o$
(In all runs $[C_2O_4^{2-}]_o = 1.5 \times 10^{-2}$ M, $[Mn^{2+}]_o = 1.0 \times 10^{-2}$ M and $[H^+]_o = 0.1$)

$[MnO_4^-]_o$ $(10^{-5}$ M)	1.0	2.0	4.0	8.0	10.0
k_{obs} (s^{-1})	20.7	20.5	20.4	19.4	19.2

shows the values of k_{obs} measured at various permanganate concentrations. It can be seen that k_{obs} is independent of the permanganate concentration (RSD = 4% over the range), thus the assumption of first-order kinetics was correct.

For determination of the reaction order with respect to manganese(II) ions, the concentration of permanganate was kept 10—100 times less than that of Mn^{2+} ions. Table 2 shows the calculated k_{obs}. From Eqn. (5), taking logarithms and substituting Q for the first term yields

$$\log k_{obs} = Q + x \log [Mn^{2+}]_o \qquad (6)$$

A plot of the results of Table 2 according to Eqn. (5) gives a straight line with slope $x = 1.01$ $(r = 0.999)$. This proves first-order kinetics with respect to Mn^{2+} ion. The same method was applied to determine the exponents y and z in Eqn. (3). Table 2 shows the experimental data and the initial concentrations of all the reactants. The values of y and z were found to be 2.04 $(r = 0.998)$ and -1.95 $(r = 0.998)$, respectively.

These results show that the reaction is first order with respect to permanganate and manganese(II) ions, second order with respect to oxalate and minus second order with respect to hydrogen ion. Thus Eqn. (3) should be

TABLE 2

Variation of k_{obs} with $[Mn^{2+}]_o$, $[C_2O_4^{2-}]_o$ and $[H^+]_o$

Variation with $[Mn^{2+}]_o$ [a]		Variation with $[C_2O_4^{2-}]_o$ [b]		Variation with $[H^+]_o$ [c]	
$[Mn^{2+}]_o$ $(10^{-3}$ M)	k_{obs} (s^{-1})	$[C_2O_4^{2-}]_o$ $(10^{-3}$ M)	k_{obs} (s^{-1})	$[H^+]_o$ (M)	k_{obs} (s^{-1})
1.0	1.68	—	—	0.10	2.16
2.0	3.08	2.5	0.11	0.30	0.28
4.0	6.51	3.5	0.19	0.50	0.11
6.0	9.90	5.0	0.40	0.90	0.028
8.0	13.3	7.5	0.94	—	- -
10.0	16.7	10.0	1.82	—	—

[a] In all runs $[MnO_4^-]_o = 1.0 \times 10^{-4}$ M, $[C_2O_4^{2-}]_o = 1.5 \times 10^{-2}$ M and $[H^+]_o = 0.1$. [b] In all runs $[MnO_4^-]_o = 3.97 \times 10^{-5}$ M, $[Mn^{2+}]_o = 4.9 \times 10^{-3}$ M and $[H^+]_o = 0.10$ M. [c] In all runs $[MnO_4^-]_o = 1.98 \times 10^{-4}$ M, $[Mn^{2+}]_o = 5.0 \times 10^{-3}$ M and $[C_2O_4^{2-}]_o = 1.0 \times 10^{-2}$ M. Ionic strength was kept constant at $I = 1.0$ with $NaClO_4$.

$$-d\,[MnO_4^-]/dt = k\,[Mn^{2+}]\,[C_2O_4^{2-}]^2\,[MnO_4^-]\,[H^+]^{-2} \tag{7}$$

From Eqn. (5) and the known initial concentrations of Mn^{2+}, $C_2O_4^{2-}$ and H^+, the values of k were calculated for each experiment. The mean value, k, was found to be $5.4 \times 10^4\ M^{-1}\ s^{-1}$ (RSD = 11%).

If the reaction in this stage proceeds through the manganese(II)—oxalate complex as in reaction 1A, then the kinetic equation should be

$$-d\,[MnO_4^-]/dt = k'\,[MnC_2O_4]\,[MnO_4^-] \tag{8}$$

Oxalate and hydrogen ions do not appear in this equation because they are included in the equilibrium of the MnC_2O_4 complex. When known values of the dissociation constants of oxalic acid and the stability constant of manganese monoxalate are used, the mean value of k' is $8.2 \times 10^3\ M^{-1}\ s^{-1}$ (RSD = 11%). This value is of the same order of magnitude as the k' value suggested by Adler and Noyes [6].

Kinetic determination of manganese(II)

The first-order kinetics of the reaction in manganese(II) ion enables a kinetic method to be evolved for determination of manganese(II). The rate of disappearance of permanganate at 525 nm is measured and compared with the concentration of manganese(II) ions in the reacting mixture. A 1.0×10^{-4} M permanganate concentration was selected for first-order conditions; oxalate must be in excess over permanganate and manganese(II), and a final concentration of 1.5×10^{-2} M proved to be optimal. The acidity chosen prevented formation of manganese(IV) oxide and kept the reaction time in the range 100—500 ms. Figure 1 shows typical oscilloscope traces for the
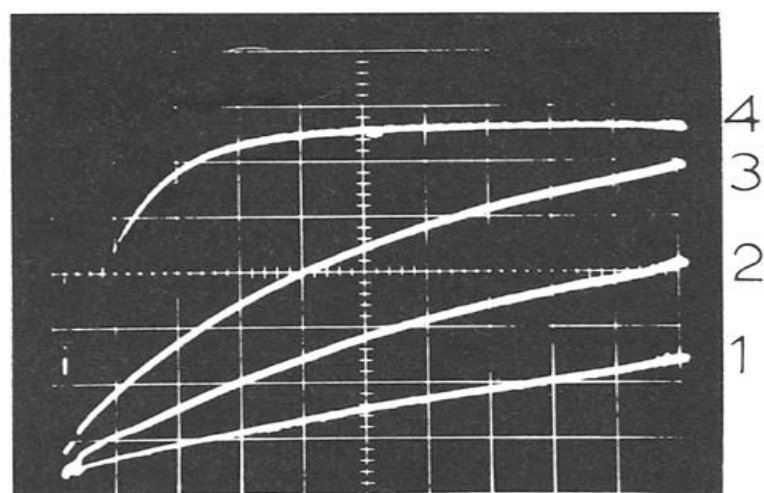

Fig. 1. Oscilloscope photograph of the reaction of permanganate and oxalate in the presence of various concentrations of manganese(II). Conditions: 1.0×10^{-4} M $KMnO_4$ in 0.1 M $HClO_4$ and 0.9 M $NaClO_4$ with 3.0×10^{-2} M $Na_2C_2O_4$. Mn^{2+}: (1) 2.0×10^{-4} M; (2) 5.0×10^{-4} M; (3) 10.0×10^{-4} M; (4) 50.0×10^{-4} M in 0.1 M $HClO_4$ and 0.9 M $NaClO_4$. Base line is 6.0 V. Ordinate scale 500 mV/division; abscissa scale 500 ms/division (10 V = 1 absorbance unit).

TABLE 3

Results for the automatic slope measurements for the determination of manganese(II)

Mn(II) conc. (10⁻⁴ M)		Slope (mV s⁻¹)	Relative error (%)	Mn(II) conc. (10⁻⁴ M)		Slope (mV s⁻¹)	Relative error (%)
Taken	Found[a]			Taken	Found[a]		
2.00	1.90	386	−5.0	20.0	18.6	3863	−7.0
4.00	4.15	800	+3.8	40.0	38.9	7906	−2.8
6.00	5.92	1124[b]	−1.3	60.0	60.2	12143[c]	+0.3
8.00	8.03	1511	+0.4	80.0	80.5	16190	+0.6
9.00	8.94	1679	−0.7	90.0	89.1	17895	−1.0
			Av 2.2				Av.2.3

[a]Working curves: for 1—10 × 10⁻⁴ M, slope = 183.6, intercept = 38.0, r = 0.99996; and for 1—10 × 10⁻³ M, slope = 198.9, intercept = 172.9, r = 0.99998. [b]RSD = 1.1% (n = 10). [c]RSD = 1.0% (n = 10).

reaction of the permanganate with oxalate in the presence of various concentrations of manganese(II). Table 3 shows the results obtained for the determination of manganese(II) in aqueous solutions in two concentration ranges. The average error is 2% and the RSD is about 1%.

The sensitivity of this kinetic method cannot be compared with other methods but it is very rapid and selective and should be useful for the determination of manganese in various samples.

Kinetic determination of oxalic acid

In the automatic kinetic determination of oxalic acid, a more acidic medium was used in order to decrease the reaction rate because the automated stopped-flow instrument used was not suitable for very fast reactions. Table 4 shows typical results for the determination of oxalic acid aqueous solutions in the range 0—20 μg ml⁻¹ with the automated stopped-flow. The precision is about 2%.

TABLE 4

Reaction-rate results for standard oxalic acid solutions

Oxalic acid (μg ml⁻¹)	5.00	10.0	15.0	20.0
Rate (10⁻³ A s⁻¹)[a]	5.03	9.56	14.14	18.22
RSD (% n = 5)	2.8	2.3	2.0	2.1

[a]Working curve: slope = 0.883, intercept = 0.700, r = 0.993. Delay time 10 s, measurement time 8 s. Rate is expressed in milli-absorbance units per second.

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