of the periodic table. Systematic correlation of the results was obtained by comparing compounds of similar structure. However, these comparisons need to be tempered by the realization of the importance that the crystal potential plays with the compounds.

Registry No. Al, 7429-90-5; Al(acac)$_3$, 13963-57-0; Al_2O_3, 1344-28-1; AlN, 24304-00-5; Al_2S_3, 1302-81-4; AlI_3, 7784-23-8; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; $LiAlH_4$, 16853-85-3; AlF_3, 7784-18-1; K_3AlF_6, 13775-52-5; Ga_2O_3, 12024-21-4; Ga_2S_2, 39356-33-7; Ga(acac)$_3$, 14405-43-7; Ga_2S_3, 12024-22-5; GaI_3, 13450-91-4; $GaBr_3$, 13450-88-9; GaF_3, 7783-51-9; In, 7440-74-6; InCl, 13465-10-6; In_2S_3, 12030-24-9; In_2O_3, 1312-43-2; In(acac)$_3$, 14405-45-9; InI_3, 13510-35-5; InF_3, 7783-52-0; $InBr_3$, 13465-09-3; $InCl_3$, 10025-82-8; Tl_2O_3, 1314-32-5; TlI, 7790-30-9; Tl_2S_3, 12039-17-7; Tl_2S, 1314-97-2; TlCl, 7791-12-0; TlBr, 7789-40-4; TlF, 7789-27-7; Nb, 7440-03-1; NbS_2, 12136-97-9; NbN, 24621-21-4; $NbBr_5$, 13478-45-0; $NbCl_5$, 10026-12-7; $KNbO_3$, 12030-85-2; Nb_2O_5, 1313-96-8; K_2NbF_7, 16924-03-1; NbF_5, 7783-68-8; Ta, 7440-25-7; $KTaO_3$, 12030-91-0; TaS, 41203-00-3; Ta_2O_5, 1314-61-0; TaS_2, 12143-72-5; Ta_5Si_3, 12067-56-0; $TaBr_5$, 13451-11-1; $TaSi_2$, 12039-79-1; $TaCl_5$, 7721-01-9; TaF_5, 7783-71-3; K_2TaF_7, 16924-00-8; W, 7440-33-7; WC, 12070-12-1; WBr_6, 13701-86-5; Li_2WO_4, 13568-45-1; WBr_5, 13470-11-6; WO_3, 1314-35-8; WCl_6, 13283-01-7; $WOCl_4$, 13520-78-0.

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A Kinetic Study of the Permanganate–Manganous Ion Reaction to Form Manganic Ion in Sulfuric Acid Media

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Received March 13, 1973

The reduction of permanganate ion by manganous ion was studied in sulfuric acid media using the stopped-flow technique. All reactions were studied at two wavelengths, $\lambda = 524$ nm (loss of MnO_4^-) and $\lambda = 419$ nm [gain of Mn(III)]. At all experimental conditions it was observed that the rates of reactant loss and product gain agreed with each other to within ±7%. The reaction was found to obey the rate expression $-d[MnO_4^-]/dt = {}^1/_5(d[Mn(III)]/dt) = \{k_0 + k_1[H^+] + k_2[H^+]^2\}[Mn(II)]^2[MnO_4^-]$. The values of k_0, k_1, and k_2 were shown to be 100 M^{-2} sec^{-1}, 19 M^{-3} sec^{-1}, and 63 M^{-4} sec^{-1}, respectively.

Introduction

The reaction between manganous and permanganate ions in acid solution has been the subject of numerous investigations.[1-7] It was observed that the final product was an insoluble form of tetravalent manganese, the net reaction being

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

Polissar[3] noted that the reaction has an induction period, and, in addition, is autocatalyzed by the solid MnO_2 produced. Tompkins[7] observed that several anions, among them SO_4^{2-} ion, combine with the intermediate Mn^{3+} to give an unstable complex. Adamson[5] using radioactive manganese studied the exchange rates between Mn(II) and Mn(VII), Mn(VI) and Mn(VII), and Mn(II) and Mn(III) and concluded that the rate-determining step in perchloric acid solution was the electron-exchange reaction

$$MnO^+ + MnO^{2+} \rightarrow \text{electron exchange}$$

His kinetic analysis gave the expression

$$R = k[H^+]^a[Mn^{2+}]^b[MnO_4^-]^c$$

for the velocity of the rate-determining step in the exchange reaction where the approximate values of a, b, and c are ${}^4/_3$, ${}^4/_3$, and ${}^1/_3$, respectively. In these previous studies, the acidity and the manganous ion concentration were such as to favor the formation of solid manganese dioxide.

Kalra and Gosh[8] observed that when the acidity is high, and the Mn(II)/Mn(III) ratio is about 25 or greater in a sulfate medium, the reaction between permanganate ion and manganous ion occurs stoichiometrically to yield Mn(III) according to the net reaction

$$8H^+ + MnO_4^- + 4Mn^{2+} \rightarrow 5Mn^{3+} + 4H_2O$$

The stability of the Mn(III) produced is also dependent upon the acidity and the [Mn(II)]/[Mn(III)] ratio. When the latter ratio is at least 25 and the sulfuric acid concentration is about 4.5 M, the Mn(III) produced is stable for several months.

The procedure described by Kalra and Gosh for the preparation of Mn(III) has been used by them[8] and others[9] in kinetic studies involving Mn(III) as either a reactant or a catalyst. The present work was initiated in order to elucidate the mechanism by which Mn(III) (rather than MnO_2) is formed at conditions similar to those described by Kalra and Gosh.

Experimental Section

Reagents. Triply distilled water was used in the preparation of all solutions.

Baker Analyzed reagent grade potassium permanganate was used in the preparation of all permanganate in sulfuric acid solutions. These solutions were prepared just prior to use to avoid permanganate decomposition.

Manganous, Mn(II), solutions were prepared using Fisher, reagent grade $MnSO_4 \cdot H_2O$ in sulfuric acid. In all kinetic runs the sulfuric acid concentration in the Mn(II) and the MnO_4^- solutions was the same.

The total ionic strength was maintained constant at $\mu = 3.96$ M using sodium bisulfate.

Manganic ion, Mn(III), was prepared by the method of Kalra and Gosh, discussed earlier.

Spectra. All spectra were taken using a Cary 14 recording spectrophotometer.

Kinetic Measurements. Rates of reaction were followed by measuring both the decrease in absorbance of MnO_4^- at 524 nm and the increase in absorbance of Mn(III) at 419 nm. The reaction was

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(1) Gorgeau, *Ann. Chim. Phys.*, **66**, [3], 153 (1862).
(2) Guyard, *Bull. Soc. Chim. Fr.*, [2] 1, 89 (1864).
(3) M. J. Polissar, *J. Phys. Chem.*, 39, 1957 (1935).
(4) M. J. Polissar, *J. Amer. Chem. Soc.*, 58, 1372 (1936).
(5) A. W. Adamson, *J. Phys. Colloid Chem.*, 55, 293 (1951).
(6) F. C. Tompkins, *Trans. Faraday Soc.*, 38, 28 (1942).
(7) F. C. Tompkins, *Trans. Faraday Soc.*, 38, 131 (1942).
(8) H. L. Kalra and S. Ghosh, *Z. Phys. Chem.* (*Leipzig*), 231, 21 (1966).
(9) J. I. Morrow and L. Silver, *Inorg. Chem.*, 11, 231 (1972).

followed using an Aminco minimonochromator with the Aminco-Morrow stopped-flow apparatus[10] attached. The detector used was an R-136 photomultiplier tube (PMT) powered by a Harrison 6515A dc power supply. The PMT output was fed into an Aminco linear-log kinetic photometer and the logarithmic (absorbance) signal was then displayed using the Tektronix 564B storage oscilloscope.

Where increased accuracy and sensitivity was required, the Aminco DASAR (Data Acquisition Storage and Retrieval) system was used. This system performs a 12-bit A to D conversion at various sample rates permitting small optical changes to be measured with higher accuracy. The digital information is stored in a solid-state memory and can be retrieved through various output modes. A reconstructed analog signal can be displayed on the built-in display monitor and a permanent record obtained using a teletype which also generates a computer compatible tape.

All kinetic measurements were performed at 25.0 ± 0.1°.

Results and Discussion

At the experimental conditions, the reaction did not exhibit an induction period nor was it autocatalytic.

The reaction rates were found to be very strongly ionic strength dependent. At ionic strength, $\mu = 3.96\ M$, the reaction was first order in permanganate ion (Table I), second order in manganous ion (Table II), and zero order in manganic ion (Table III).

In all kinetic runs at a given set of experimental conditions, the observed rate constants, k_{obsd}, for both the loss of MnO_4^- (measured at 524 nm) and the gain of Mn(III) (measured at 419 nm) agreed with each other to within ±7%.

The first-order rate constant, k_{obsd}, is defined by eq I

$$-\frac{d[MnO_4^-]}{dt} = {}^1\!/_5\frac{d[Mn(III)]}{dt} = k_{\text{obsd}}[MnO_4^-] \qquad (I)$$

where at constant acidity

$$k_{\text{obsd}} = k_H\,[Mn(II)]^2$$

The third-order rate constant, k_H, was found to be acid dependent.

Hydrogen Ion Dependency and Discussion. Table IV gives the effect of acidity upon k_H. The value of k_H was found to be related to the acidity by eq II in the range from $[H_2SO_4]_0 = 0.72\ M$ to $[H_2SO_4]_0 = 3.96\ M$.

$$k_H = \frac{k_{\text{obsd}}}{[Mn(II)]^2} = k_0 + k_1[H^+] + k_2[H^+]^2 \qquad (II)$$

The plot of $(k_H - k_0)/[H^+]$ *vs.* $[H^+]$ is linear with a slope of k_2 and an intercept of k_1. This is shown in Figure 1. The values of k_0, k_1, and k_2 are 100 M^{-2} sec^{-1}, 19 M^{-3} sec^{-1}, and 63 M^{-4} sec^{-1}, respectively.

The observed results may be interpreted by several mechanisms, all but one of which postulate the presence of intermediate species for which there is no supportative evidence. The remaining, and more reasonable, mechanism is

$$MnO_4^- + 2Mn^{2+} \xrightarrow{k_1} 2MnO_2 + Mn^{3+} \qquad (1)$$

$$4H^+ + MnO_2 + Mn^{2+} \xrightarrow{k_2} 2Mn^{3+} + 2H_2O \qquad (2)$$

Reaction 1 is rate determining. In this mechanism, the acid dependency can be explained if the permanganate ion behaves like a weak Bronsted base

$$MnO_4^- + H^+ \overset{K_3}{\rightleftharpoons} HMnO_4 \qquad (3)$$

and

$$2H^+ + MnO_4^- \overset{K_4}{\rightleftharpoons} MnO_3^+ + H_2O \qquad (4)$$

both additional species also reacting with Mn^{2+}. The exis-

Table I. Variation of k_H with $[MnO_4^-]_0$[a]

$10^4[MnO_4^-]_0$	k_{obsd}, sec^{-1}	k_H, M^{-2} sec^{-1}
1.0	0.28	448
2.5	0.28	448
5.0	0.27	432

[a] In all runs $[H_2SO_4]_0 = 1.98\ M$ and $[MnSO_4]_0 = 0.025\ M$.

Table II. Variation of k_H with $[MnSO_4]_0$[a]

$[MnSO_4]_0$	k_{obsd}, sec^{-1}	k_{calcd},[b] sec^{-1}	k_H,[c] M^{-2} sec^{-1}
0.025	0.27	0.23	432
0.050	0.93	0.93	384
0.075	2.0	2.1	352
0.10	3.4	3.5	340
0.15	7.4	7.7	320

[a] In all runs $[KMnO_4]_0 = 5.0 \times 10^{-4}\ M$ and $[H_2SO_4]_0 = 1.98\ M$. [b] This column contains values of k_{obsd} calculated using eq II, $k_{\text{obsd}} = \{k_0 + k_1[H^+] + k_2[H^+]^2\}[Mn(II)]^2$, with $k_0 = 100\ M^{-2}$ sec^{-1}, $k_1 = 19\ M^{-3}$ sec^{-1}, and $k_2 = 63\ M^{-4}$ sec^{-1}. It was provided to more readily show the second-order manganous ion dependency. [c] The downward drift of k_H values with increasing $[MnSO_4]_0$ is due to protonation of the SO_4^{2-} to form HSO_4^-, thereby lowering the actual acidity of the solution which in turn causes the reaction to progress more slowly.

Table III. Variation of k_H with $[Mn(III)]_0$[a]

$10^3[Mn(III)]_0$	k_{obsd}, sec^{-1}	k_H, M^{-2} sec^{-1}
0	7.1	316
1.25	7.3	324
2.50	7.2	320
5.00	7.4	328
10.0	7.3	312

[a] In these runs $[H_2SO_4]_0 = 1.98\ M$, $[MnSO_4]_0 = 0.15\ M$, and $[KMnO_4]_0 = 5.0 \times 10^{-4}\ M$.

Table IV. Variation of Rate Constant with Acidity[a]

$[H_2SO_4]_0$	$[H_2SO_4]_0$[b]	k_{obsd}, sec^{-1}	k_H, M^{-2} sec^{-1}
0.720	0.670	0.35	140
1.26	1.21	0.53	212
1.62	1.57	0.74	296
1.98	1.93	0.94	376
2.52	2.47	1.36	544
3.06	3.01	1.78	712
3.24	3.19	2.04	816
3.96	3.91	2.90	1160

[a] In all runs $[KMnO_4]_0 = 5.0 \times 10^{-4}\ M$ and $[MnSO_4]_0 = 0.050\ M$. [b] Due to protonation of the SO_4^{2-} ion (from $MnSO_4$), the actual $[H_2SO_4]_0$ is less than that indicated in column one. The corrected values are listed in column two.

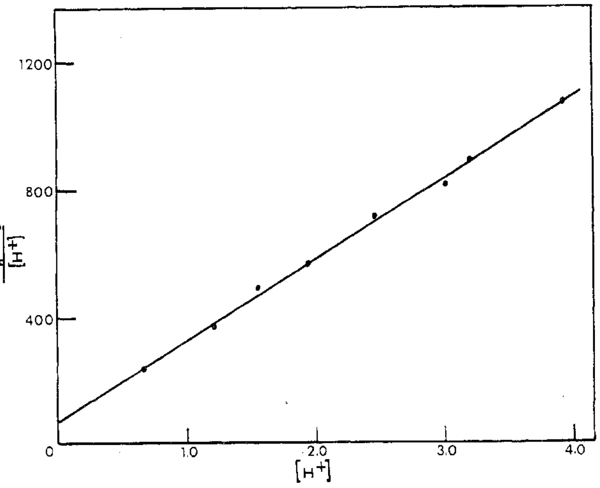

Figure 1. Linear plot of eq II, $k_H = k_0 + k_1[H^+] + k_2[H^+]^2$. The slope of the plot is k_2, and the intercept, k_1.

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[10] J. I. Morrow, *Chem. Instrum.*, 2, 375 (1970).

tence of MnO_3^+ in concentrated solutions of sulfuric acid had been speculated on by Thorpe and Hambly.[11] It is assumed in this mechanism that all protolytic steps are rapid.

That Mn(III) does not participate in any reversible step is shown by its zero-order kinetic dependency, Table III. Reaction 2 may be written as the sum of two rapid steps, the first being an equilibrium step

$$4H^+ + MnO_2 \overset{K_5}{\rightleftarrows} Mn^{4+} + 2H_2O \qquad (5)$$

and

$$Mn^{4+} + Mn^{2+} \xrightarrow{k_6} 2Mn^{3+} \qquad (6)$$

where $k_2 = K_5k_6$. Reaction 6 has been shown by Bradley and Van Preagh[12] to be rapid and reversible. At our experimental conditions, the product Mn^{3+} is highly favored. This is due to our higher acid concentrations, higher manganous ion concentrations, and the complexation of Mn(III) by SO_4^{2-} ion. This proposed mechanism is in agreement with the observations that there is no induction period and that the observed rate of disappearance of MnO_4^- is equal to the rate of appearance of the product, manganic ion.

Summary

At experimental conditions where Mn(III) is formed as the product rather than MnO_2, the rate expression for the reduction of MnO_4^- by Mn(II) is

$$-\frac{d[MnO_4^-]}{dt} = {}^1/_5\frac{d[Mn(III)]}{dt} =$$

$$\{k_0 + k_1[H^+] + k_2[H^+]^2\}[MnO_4^-][Mn(II)]^2$$

Due to the higher acidity, the higher manganous ion concentrations, and the ability of SO_4^{2-} to complex with manganic ion, the reaction path (mechanism) is necessarily different when Mn(III) rather than MnO_2 is the favored product. Undoubtedly, the electron-exchange reaction between MnO^{2+} and MnO^+ is no longer rate determining as observed by Adamson[5] in perchlorate media. In a few runs made in perchlorate media rather than sulfate media MnO_2 was observed to slowly precipitate out of solution thereby emphasizing the importance of complexation of Mn(III) by SO_4^{2-} to stabilize Mn(III) as the reaction product.

Acknowledgment. The authors acknowledge the National Science Foundation Undergraduate Research Participation Program for partial support of this research.

Registry No. Mn^{2+}, 16397-91-4; MnO_4^-, 14333-13-2.

[11] T. E. Thorpe and F. J. Hambly, *J. Chem. Soc.*, 13, 175, (1888).

[12] J. Bradley and G. Van Preagh, *J. Chem. Soc.*, 1624 (1938).

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Kinetics and Mechanism of the Decomposition of the Uranium(V)-Chromium(III) Complex and of its Reaction with Excess Chromium(II)

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Received March 16, 1973

The kinetics of the decomposition of the $U^V \cdot Cr^{III}$ binuclear complex and of its reaction with excess Cr(II) have been studied. The decomposition of the complex was found to be a first-order process under the experimental conditions used, the values of ΔH^* and ΔS^* being 12.8 ± 0.1 kcal mol^{-1} and −21.2 ± 0.4 eu, respectively. The rate was found to be virtually independent of acid concentration and ionic strength. The rate of reaction between $U^V \cdot Cr^{III}$ and excess Cr(II) was also found to be independent of acid concentration but was strongly influenced by ionic strength, this effect being found consistent with the Debye–Huckel equation. For this reaction $\Delta H^* = 3.16 \pm 0.30$ kcal mol^{-1} and $\Delta S^* = -35.2 \pm 1.0$ eu. Reaction mechanisms consistent with the results are discussed.

Introduction

Excess Cr(II) will reduce U(VI) to U(IV) according to the equation

$$U(VI) + 2Cr(II) + 4H^+ \rightarrow U(IV) + 2Cr(III) + 2H_2O \qquad (1)$$

However, as shown previously,[1,2] the mechanism of this reaction is rather complex, the first step being the formation of a U^V-Cr^{III} binuclear complex (reaction 2).

$$U(VI) + Cr(II) \rightarrow U^V \cdot Cr^{III} \qquad (2)$$

The kinetics of the formation of the $U^V \cdot Cr^{III}$ complex have recently been examined,[3] and in this paper we describe the results obtained from a study of the kinetics of (a) the decomposition of the intermediate and (b) the reaction of the intermediate with excess Cr(II) according to reaction 3.

$$Cr(II) + U^V \cdot Cr^{III} + 4H^+ \rightarrow U(IV) + 2Cr(III) + 2H_2O \qquad (3)$$

The work was undertaken to provide the data necessary for comparing the mechanism and kinetics of the reactions of the $U^V \cdot Cr^{III}$ species with those of analogous systems which have been studied previously.

Experimental Section

Reagents. The procedures used for the preparation of $UO_2(ClO_4)_2$, $NaClO_4$, $HClO_4$, and $DClO_4$ stock solutions and for the preparation and handling of the Cr(II) solutions are described elsewhere.[3]

Measurement of Reaction Rates. An Aminco-Morrow stopped-flow apparatus[3] was used to follow the reactions, but for this work the output of the instrument was recorded by an on-line PDP-8L computer rather than by the more usual storage oscilloscope. In this arrangement (Figure 1), the output of photomultiplier is passed, *via* an amplifier and analog-digital converter, to the core of the computer for storage. The computer is activated *via* the strobe circuit by the closing of the trigger on the stopped-flow apparatus. The system then samples the photomultiplier output at preset time intervals, stores data until the completion of a run, and displays the results *via* a teletype or punched tape. The output consists of a series of numbers

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