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Kinetics of the Disproportionation of Manganate in Acid Solution

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The kinetics of the disproportionation of manganate have been studied in acid solution using stopped-flow techniques. The disappearance of manganate at 610 nm is governed by a pseudo-first-order rate law, while the appearance of permanganate at 520 nm is governed by a second-order rate law. Both rate constants show a first-order dependence on hydrogen ion concentration. The results are interpreted in terms of the formation of a MnO_3 intermediate. Activation parameters have been measured.

Introduction

During the course of studying the kinetics of permanganate redox reactions, manganate has been proposed as an intermediate in several cases.^{1,2} In order to study the reduction of manganate by reducing agents it became necessary to study the behavior of manganate toward disproportionation in acid solution. Lister and Yoshino³ presented a one-step disproportionation scheme as part of their study of the manganate-periodate reaction in basic solution, but no kinetic study in acid has as yet been undertaken.

Experimental Section

Manganate solutions were prepared as follows. Weighed amounts of recrystallized Baker Analyzed potassium permanganate were placed in a 25-ml beaker with a small weighed (50–100 mg) pellet of Baker Analyzed sodium hydroxide. Three or four milliliters of distilled water was added and the resultant solution was warmed gently on a hot plate. As the solution approached dryness, the manganate formed spontaneously and quantitatively. The manganate was transferred quantitatively to a 100-ml volumetric flask using a predetermined volume of standard 0.4 *N* NaOH. This solution was carefully diluted to mark with distilled water. Handled this way, by taking the weight of the NaOH pellet into account, and thus varying the amount of 0.4 *N* NaOH solution used, a final solution could be made that was quite reproducibly 0.20 *N* in NaOH and was of the desired concentration of manganate. This solution was placed in one of the drive syringes of a stopped-flow apparatus. In the other drive syringe was placed a standard solution of perchloric acid. The concentration of the acid was, for example, 0.22 *N*, and thus after mixing at time $t = 0$ the manganate found itself in a sodium perchlorate solution 0.01 *N* in hydrogen ion. The excess of hydrogen ion was varied in this fashion from 0.01 to about 0.1 *M*. The excess hydrogen ion was determined precisely by titrating with standard base.

When using a more conventional method of detection, for example, single-shot oscilloscope recording, no mixing artifacts could be observed on mixing pure acid with base in the stopped-flow apparatus. In these tests the signal was amplified to a greater extent than it was during the kinetic runs hopefully to ensure detection of such artifacts.

On mixing with base there was, of course, a small temperature jump. Using literature values⁴ for the heats of formation of dilute NaOH and HClO_4 , a value of 0.8° was calculated for this temperature rise under our conditions. Although the single-shot method of detection showed no acid-base mixing artifacts, the signal averager used in the kinetic runs did show a display whose appearance was "kinetic." The kinetics were followed by taking the signal from the photomultiplier of the stopped-flow apparatus, passing it through a current to voltage transducer, and then splitting the resultant voltage signal with a BNC "T" connector. The signal was then passed into a 564 Tektronix storage scope and into a Nicolet 1072 signal averager. As many as 16 repetitive runs were signal averaged (although six to eight were sufficient for most kinetic conditions) at 8 bits vertical resolution and, typically, 100–200 $\mu\text{sec}/\text{address}$ time

resolution. If a "bad" run appeared during the collection, the entire series was wiped out. (For this purpose, the 564 scope gain was set higher than that of the signal averager and its viewing scope.) Care was taken to wait between runs to allow for the observation cuvette to readjust thermally. The stop syringe was adjusted so that a maximum convenient volume of solution was delivered from the drive syringes. This ensured that all the fresh solution to be mixed came from the drive syringes which are in best contact with the thermostating liquid.

Using these precautions, no problems were incurred in the collection of precise, signal-averaged kinetic data at either of the two wavelengths followed provided that the hydrogen ion concentration was kept below a certain minimum value. That is, the kinetics of manganate disappearance at 610 nm is pseudo first order, depending on hydrogen ion concentration. Thus on increasing the hydrogen ion concentration the reaction will go faster and faster until at last no change in absorbance would be observed. Using signal averaging, however, this observation proved not to be the case. Here the decrease in the change in absorbance due to the kinetics was at last overshadowed by the change in absorbance due to the acid-base mixing so that at "high" hydrogen ion concentration a final limiting rate constant was obtained. Needless to say, in determining the hydrogen ion dependence of the manganate disappearance, only runs obtained at low hydrogen ion concentration were used. At the higher concentration, where possible interference by the mixing artifacts would become important, runs were not used. This point was determined simply by looking at a single-shot kinetic trace and observing the presence or absence of a change in absorbance at the appropriate gain.

Not all of the artifact is due to the acid-base mixing, for on prolonged signal averaging (≥ 10) at modest gain, a "kinetic" trace can be observed on mixing pure water with water, taking the usual precaution of thermostating. This effect is similar to that reported by Gibson⁵ when injecting warm solution into a cold observation tube. This effect should become more important as the use of 12-bit (and higher) A/D converters becomes more prevalent in chemical kinetics. (Recently, using the Aminco DASAR (a 12-bit collector) and the Aminco stopped-flow apparatus we found it extremely difficult to mix water with water at this resolution, it being almost impossible not to observe a small but not entirely negligible "kinetic" looking trace.)

The disappearance of manganate and the formation of permanganate were followed kinetically at 610 and 520 nm, respectively. At these wavelengths the extinction coefficients of manganate were determined to be 970 and 340,³ while those of permanganate are 212 and 2227 $\text{M}^{-1} \text{cm}^{-1}$. It was observed that at 520 nm the total amount of permanganate formed was half the amount of manganate initially present, determined at 610 nm, thus in part verifying the stoichiometry $2\text{Mn(VI)} \rightarrow \text{Mn(VII)} + \text{Mn(V)}$. The fate or the nature of the Mn(V) species formed in the disproportionation is not known, however, MnO_2 is not formed.

Results and Discussion

The kinetic results show the disappearance of manganate observed at 610 nm and the formation of permanganate followed at 520 nm were governed by different rate laws. At 610 nm plots of $\log(D - D_\infty)$ vs. time were linear over

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(5) Q. H. Gibson, "Rapid Mixing and Sampling Techniques in Biochemistry," B. Chance, R. H. Eisenhardt, Q. H. Gibson, and K. K. Lonberg-Holm, Ed., Academic Press, New York, N. Y., 1964, p 116.

Table I. Experimental Rate Constants and Their Hydrogen Ion and Temperature Dependence^a

25°			17.8°			10.0°		
[H ⁺], M	k'_{610}, sec ⁻¹	10 ⁻⁵ k'_{520}, M ⁻¹ sec ⁻¹	[H ⁺], M	k'_{610}, sec ⁻¹	10 ⁻⁵ k'_{520}, M ⁻¹ sec ⁻¹	[H ⁺], M	k'_{610}, sec ⁻¹	10 ⁻⁵ k'_{520}, M ⁻¹ sec ⁻¹
0.0041	37.0 ± 4	4.56 ± 0.04	0.00364	20.0 ± 2	2.42 ± 0.09	0.0153	45.9 ± 4	6.12 ± 0.09
0.0081	83.7 ± 8	8.01 ± 0.09	0.00778	43.5 ± 2	4.96 ± 0.18	0.0179	55.4 ± 4	7.08 ± 0.07
0.010	117 ± 22	14.9 ± 0.26	0.0145	78.6 ± 4	10.0 ± 0.16	0.0249	72.2 ± 7	9.42 ± 0.26
0.0153	164 ± 30	17.5 ± 0.24	0.0243	133 ± 3	16.2 ± 0.09	0.0520	166 ± 7	22.0 ± 0.35
0.020	211 ± 29	28.5 ± 0.66	0.0437		27.2 ± 0.55	0.0577		23.1 ± 0.18
0.039	233	45.8 ± 0.60	0.0576		41.0 ± 1.3			
0.083	220	112 ± 1.0						
0.101	240	123 ± 1.0						

^a Initial MnO₄²⁻ concentrations ranged from 2 × 10⁻⁵ to 5 × 10⁻⁴ M.

several half-lives showing a first-order dependence on the green color of manganate. At 520 nm, plots of 1/(D_∞ - D) vs. time were linear showing a second-order rate law for the formation of the purple color of permanganate.

The rate constants obtained at 610 and 520 nm as a function of hydrogen ion concentration and temperature are presented in Table I. The temperatures shown are the thermostating bath temperatures and are approximately 0.8° lower than the reaction temperature. The hydrogen ion concentrations are the excess hydrogen ion concentrations after mixing as determined by titration. All reactions were run under pseudokinetic conditions, the hydrogen ion being flooded.

The last three entries for k'_{610} at 25° are seen to be the same. Here we have reached the limit as stated above of measuring first-order rate constants with our apparatus and these hydrogen ion concentrations. The second-order constants at 520 nm are still measurable, showing the concentration effect on the rate constants and that the behavior is indeed different at the two wavelengths.

By comparing the optical density at the first point of observation with the value predicted for this reading at zero time from a knowledge of the concentration in the storage syringe, one may estimate the extent of the reaction at this point at either wavelength. Thus, at 17.8°, for example, we estimate that at 610 nm and a hydrogen ion excess of 0.0145 M we are following the last 30% of the reaction, the first 2 half-lives being lost in dead time. At 520 nm under the same conditions, we are able to follow the kinetics after only about 12% of the reaction has proceeded. (This particular example was found to be in slight error due to a faulty stop mechanism, although the relative amount of reaction seen at each wavelength and the kinetic rate constant are correct. The result was included here to show how signal averaging allows for obtaining good kinetic data from a small amount of reaction.)

The green color of manganate disappears rapidly in acid solution to form a new species by a pseudo-first-order process. It is this species that participates in the disproportionation to form permanganate and a Mn(V) species by a pseudo-second-order process.

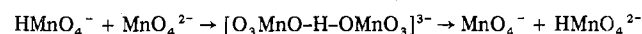
The k'_{520} values listed in Table I are obtained from the slopes of 1/(D_∞ - D) vs. time plots. The true second-order rate constant, k'_{520}, is obtained by multiplying these slopes by the extinction coefficient of MnO₄⁻ at 520 nm

$$k'_{520} (M^{-1} \text{ sec}^{-1}) = [\epsilon_{\text{Mn(VII)}}] [\text{slope}]$$

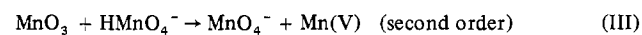
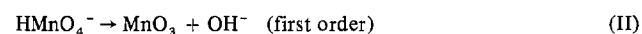
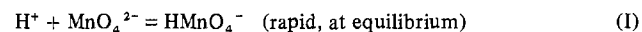
To this end, the absorbance of the other species, such as Mn(V), were taken to be zero, although this might not be the case. At 520 nm $\epsilon_{\text{MnO}_4^-}$ is 2227 M⁻¹ cm⁻¹, and, using a 2-cm path length reaction vessel, the true second-order rate constants, based on permanganate formation, were calculated.

At all three temperatures, the rate constants at both wavelengths varied linearly with hydrogen ion concentration, passing, within experimental error, through the origin. Table II shows the final concentration-independent rate constants. Activation parameters were calculated using the temperature dependence of these rate constants. At 610 nm $\Delta H^\ddagger = 12.7 \pm 1.6$ kcal and $\Delta S^\ddagger = 2.5 \pm 0.6$ eu while at 520 nm $\Delta H^\ddagger = 11.8 \pm 1.2$ kcal and $\Delta S^\ddagger = 18.1 \pm 4.2$ eu.

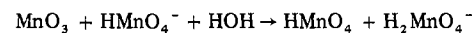
If the disappearance of manganate, first order each in hydrogen ion and in manganate, is indeed just a simple protonation reaction, then the question arises as to why it is not diffusion controlled.⁶ Further, the first-order hydrogen ion dependence occurring in the bimolecular formation of permanganate would seem to rule out a step involving two HMnO₄⁻ species reacting in the disproportionation step, while a reaction between HMnO₄⁻ and MnO₄²⁻ to form a proton bridge, would still leave unanswered the question of why the protonation of manganate is measurable.



A mechanism consistent with the kinetic findings is



In keeping with the findings concerning Mn(V) chemistry,⁷ step III may be



reestablishing the tetrahedral Mn species and anticipating a highly protonated Mn(V) species.

The ionization constant for HMnO₄⁻ has been estimated by Lister³ to be 7 × 10⁻¹¹. A constant this small would be consistent with the suggestion that manganate itself is probably not a reactant.

Whether MnO₃ is actually formed as an intermediate in step II cannot be established conclusively from kinetic data alone, but a Mn(VI) species of this sort would be consistent with the Symons⁸ observations that manganate readily exchanges oxygen with solvent, whereas permanganate does not. It might be expected that step II be reversible, but in acid solution apparently the reverse step presents no complication to the observed kinetics.

The second-order rate constant, k_{520}, appears to be independent of ionic strength. At 25° and ionic strengths of 0.05 and 0.2 M, adjusted with NaClO₄, the rate constants are 19.3 × 10⁵ and 18.6 × 10⁵ M⁻¹ sec⁻¹, respectively, at hydro-

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(8) M. C. R. Symons, *J. Chem. Soc.*, 3676 (1954).

Table II. Concentration-Independent Rate Constants and Their Temperature Dependence

	25°	17.8°	10°
$k_{610}, M^{-1} \text{ sec}^{-1}$	$(1.08 \pm 0.06) \times 10^4$	$(5.44 \pm 0.06) \times 10^3$	$(3.28 \pm 0.01) \times 10^3$
$k_{520}, M^{-2} \text{ sec}^{-1}$	$(1.27 \pm 0.04) \times 10^8$	$(6.89 \pm 0.03) \times 10^7$	$(4.18 \pm 0.02) \times 10^7$

gen ion concentrations of 0.015 and 0.0143 *M*. For comparison from Table I at ionic strength 0.1, the rate constant calculated from the equation of this line at 0.0145 *M* H^+ is $17.9 \times 10^5 M^{-1} \text{ sec}^{-1}$. The lack of any ionic strength dependence would support the suggestion of the neutral reactant, MnO_3 , although at ionic strengths this high, other explanations are possible.

The manganate disproportionation reaction may be further complicated by still another slow reaction (or reactions) occurring after the two reported here. At both wavelengths studied, long after the D_∞ values have been well established, the optical density begins to increase. The duration of this reaction is 10–20 sec (compared to a few milliseconds for the manganate reaction) before a new final D_∞ value is reached. This new reaction appears to be first order in color appearance and would seem to be the decomposition of the Mn(V) species produced in the first reaction to form a final Mn(IV) species, although it seems unlikely that the Mn(V) reaction can be this slow. At first it was suspected

that colloidal MnO_2 was forming at a slow rate. However, no precipitate of MnO_2 is seen in a reasonable length of time. The visible spectrum of the reacted solution shows the pronounced spectrum of permanganate and in addition features that may be attributed to the unknown final product. On prolonged standing, of course, MnO_2 appears, but then the permanganate has also decomposed. The kinetics of this reaction will be investigated when more information on the nature of the reactants and products is known, but at least it is clear that it does not interfere with the kinetics presented here.

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Registry No. Manganate, 14333-14-3; permanganate, 14333-13-2.

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X-Ray Photoelectron Spectra of Inorganic Molecules. IX.^{1,2} Distinction between Bridging and Terminal Metal-Chlorine Bonds in Metal Halide Clusters of Rhenium(III) and Molybdenum(II)

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The X-ray photoelectron spectra of chloride clusters of rhenium(III) and molybdenum(II) containing strong metal-metal bonds are reported. Measurements of the chlorine 2p binding energy spectra of the parent chlorides and their derivatives with a variety of donor molecules have shown that for the rhenium and molybdenum compounds the binding energy order is $Cl_b > Cl_t$ and $Cl_b > Cl_{b'} > Cl_t$, respectively; Cl_b , $Cl_{b'}$, and Cl_t denote chlorine atoms in intracuster metal-chlorine bridges, intercluster metal-chlorine bridges, and terminal metal-chlorine bonds, respectively. These assignments have been confirmed by recording the binding energy spectra of complexes in which the terminal metal-chlorine bonds have been progressively replaced. The magnitude of the separation between the binding energies associated with Cl_b and Cl_t , ~1.4 eV for rhenium(III) and ~2.3 eV for molybdenum(II), allows this technique to provide definitive structural information on metal chloride clusters. In the present study this is applied to the complexes of molybdenum(II) chloride $[Mo_6Cl_8]Cl_4$ with 1,2-bis(diphenylphosphino)ethane, 2,2'-bipyridyl, 1,10-phenanthroline, and 2,2',2''-terpyridyl. The X-ray photoelectron spectrum of the phase known as β -molybdenum(II) chloride has also been examined and it is shown that this compound does not have a metal-metal bonded cluster structure related to that of $[Mo_6Cl_8]Cl_4$.

Introduction

In our recent studies on the redox behavior of rhenium(III) chloride toward monodentate heterocyclic tertiary amines,^{3,4} we isolated a new class of polymeric rhenium(II) derivatives of the type $[Re_3Cl_6L_3]_n$, where L = pyridine, β - or γ -picoline, isoquinoline, quinaldine, or benzimidazole, together with the acridinium salt $\{[AcrH]_2Re_3Cl_8\}_n$. Since these products were amorphous to X-rays and a structure solution was not feasible by a single-crystal X-ray structure analysis, we re-

sorted to X-ray photoelectron spectroscopy (ESCA)⁵ as a possible means of providing definitive structural information on these derivatives. From a preliminary study of the chlorine 2p binding energies of these complexes, together with related measurements on several adducts of rhenium(III) chloride of the type $Re_3Cl_9L_3$, L = pyrazine, triphenylphosphine, or dimethylformamide, and the complex anions $Re_3Cl_{11}^{2-}$ and $Re_3Cl_{12}^{3-}$,^{3,4} we were able to establish that the rhenium(II) derivatives possessed two types of rhenium-chlorine bonds, terminal (or intercluster bridges) and intracuster bridges. The separation between the binding energies

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