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The Oxidation of Manganese(II) by Chromium(VI) in the Presence of Oxalate Ion

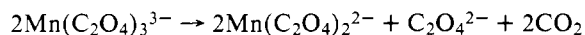
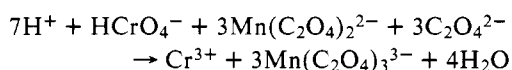
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Abstract: Manganese(II) is oxidized quantitatively to $\text{Mn}(\text{C}_2\text{O}_4)_3^{3-}$ by HCrO_4^- in the presence of oxalate ion. The reaction proceeds according to the rate law: $\text{rate} = -d[\text{Cr(VI)}]/dt = k'[\text{HCrO}_4^-][\text{Mn}(\text{C}_2\text{O}_4)_2^{2-}][\text{C}_2\text{O}_4^{2-}][\text{H}^+]^2$. The first-order dependence on a one-electron reductant is uncommon for chromate oxidations and has been found previously for reducing agents such as $\text{Mo}(\text{CN})_8^{4-}$ and $\text{Fe}(\text{CN})_6^{4-}$ which form a bridge to Cr(VI) by expanding the coordination sphere of chromate. This similarity and the observed rate law suggest an activated complex containing a doubly bridging oxalate ion, I. This reaction provides a rational explanation for reported Mn(II) catalyses of some Cr(VI) oxidations as opposed to the well-known inhibition effect caused by Mn(II) trapping of Cr(IV) intermediates.

Studies of Cr(VI) oxidations of oxalic acid abound in the literature.¹⁻⁵ The catalysis of the reaction by Mn(II) was first observed by Dhar.¹ This runs contrary to the general effect of Mn(II) on chromate oxidations—an inhibition caused by Mn(II) capture of the Cr(IV) intermediate, which has been frequently used as a tool in studying the oxidation of other substrates.⁶ The interesting Mn(II) catalyzed oxidation of oxalic acid has been studied by various workers. Chakravarti and Ghosh² found that the reaction order in oxalate decreased in the presence of Mn(II) toward zero. Bakore and Jain³ obtained similar results with respect to order in oxalate, and found a first-order dependence on Mn(II), with the rate constant varying with $[\text{HCrO}_4^-]^{0.65}$,_{initial}. Both these studies followed the reaction by iodometric titration of the remaining oxidant, and under conditions of excess Cr(VI) over Mn(II).

Recently, Rocek and co-workers elucidated the uncatalyzed reaction of Cr(VI) as well as the reaction of the intermediates Cr(V) and Cr(IV) with oxalic acid.⁵ They observed later that in the presence of Mn(II) the decrease in absorbance at the Cr(VI) 350 nm peak appeared to proceed in two stages (Figure 1).⁷ The rate of decay in the second step corresponds to that observed by Taube⁸ for the decomposition of $\text{Mn}(\text{C}_2\text{O}_4)_3^{3-}$. Significantly, we have observed that solutions of this complex are capable of oxidizing iodide to I_2 . Since the earlier studies of Mn(II) catalysis measured Cr(VI) iodometrically without realizing that Mn(III) was present in significant concentrations, it is apparent that their data were wrongly considered and the reaction should be restudied spectrophotometrically. We report here the mechanism of the first step in the two-step process observed by Rocek.



Experimental Section

Reagent grade chemicals were used without further purification. The concentration of the $\text{Mn}(\text{ClO}_4)_2$ stock solution was checked spectrophotometrically, following oxidation to MnO_4^- using the method of Willard and Greathouse.⁹

Measurements. All kinetic and stoichiometric measurements were made by observing changes in absorbance due to the formation of $\text{Mn}(\text{C}_2\text{O}_4)_3^{3-}$ at 525 nm, where interference by Cr(VI) is negligible, using a Cary 14 spectrophotometer equipped with a water-circulating cell holder connected to a temperature bath.

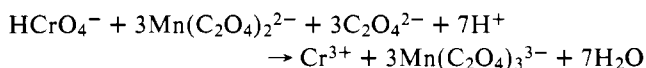
All runs contained a large excess of an oxalate-acid oxalate buffer, to ensure that MnC_2O_4 would not reprecipitate. LiClO_4 was added to maintain ionic strength at ~ 0.6 M. However, it is very difficult to maintain ionic strength in such concentrated solutions of divalent ions, and there is some doubt as to how much meaning the concept has in

such situations. A radiometer pH meter was used to measure hydrogen ion concentration. Its calibration was checked against standard solutions of HClO_4 in a 0.6 M solution of LiClO_4 .

Half-lives obtained from the absorbance vs. time curves were used to obtain pseudo-first-order rate constants, k_{obsd} . The reaction generally obeyed good first-order kinetics for disappearance of Cr(VI). However, as pH increased, the relative rate of decay of Mn(III) became high enough to interfere with observation of the production of Mn(III). Above \sim pH 4.5, the interference became too great to obtain any value of half-lives. No measurement was done at pH below 3 because preliminary measurements indicated that the reaction would become too fast to measure accurately. Actually it was discovered in treating the data of Hasan and Rocek that the rate leveled off and then decreased at pH < 3, so that our study might well have been extended to higher acidities.

Results

Stoichiometry. Observation at 525 nm with excess Mn(II) revealed formation of 3 mol of $\text{Mn}(\text{C}_2\text{O}_4)_3^{3-}$ for each mole of Cr(VI) consumed. It is known that $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ will not reduce Cr(VI). Therefore a Mn(II)-oxalate complex must be the only reducing agent for chromium in this pH range.



Kinetics. Table II summarizes kinetic data based on k_{obsd} for first-order decay in [Cr(VI)]. Most data were obtained after the first or second half time.

Mn(II) Dependence. Two runs, not listed, contained an excess of Cr(VI) over Mn(II). They showed a pseudo-first-order reaction indicating first-order dependence on Mn(II). A series of runs with varying concentrations of excess Mn(II) indicates that $k_{\text{obsd}} \propto [\text{Mn(II)}]$ (Figure 2).

Hydrogen Ion and Oxalate Dependence. Figure 3 shows k_{obsd} vs. $[\text{H}^+]$ for a series of runs with total oxalate concentration held constant. It shows a dependence which varies from second to first order as $[\text{H}^+]$ increases. Runs in which $[\text{Ox}]_T$ varied indicated a dependence ranging from second to first order in oxalate. Since the predominant Mn(II) species present in these studies are MnC_2O_4 and $\text{Mn}(\text{C}_2\text{O}_4)_2^{2-}$, this suggests an activated state formed by reactions of HCrO_4^- , $\text{Mn}(\text{C}_2\text{O}_4)_2^{2-}$, $\text{C}_2\text{O}_4^{2-}$, and two H^+ . Assuming this, the following equation is obtained:

$$k_{\text{obsd}} = k'[\text{Mn}(\text{C}_2\text{O}_4)_2^{2-}][\text{C}_2\text{O}_4^{2-}][\text{H}^+]^2 \quad (1)$$

A simple derivation gives k_{obsd} in terms of k' and known quantities:

$$k_{\text{obsd}} = k'K_2K_a^2[\text{Mn(II)}]_T[\text{Ox}]_T^2[\text{H}^+]^2/(K_a + [\text{H}^+] + K_2K_a[\text{Ox}]_T)(K_a + [\text{H}^+]) \quad (2)$$

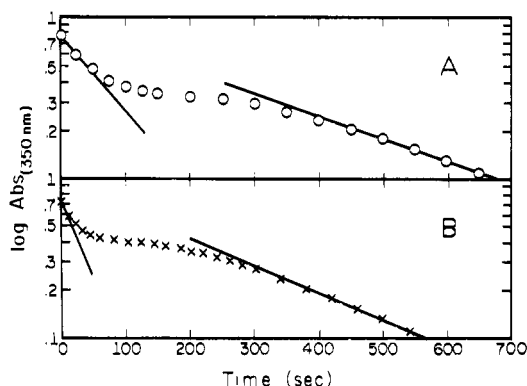


Figure 1. Logarithmic plot of absorbance at 350 nm vs. time. In both runs, $[\text{H}_2\text{C}_2\text{O}_4] = 0.106 \text{ M}$, $[\text{HClO}_4] = 0.097 \text{ M}$, and $[\text{Cr(VI)}] = 4.24 \times 10^{-4} \text{ M}$: (O) $[\text{Mn(II)}] = 0.0127 \text{ M}$; (X) $[\text{Mn(II)}] = 0.0254 \text{ M}$. Data furnished by F. Hasan and J. Rocek to the authors.

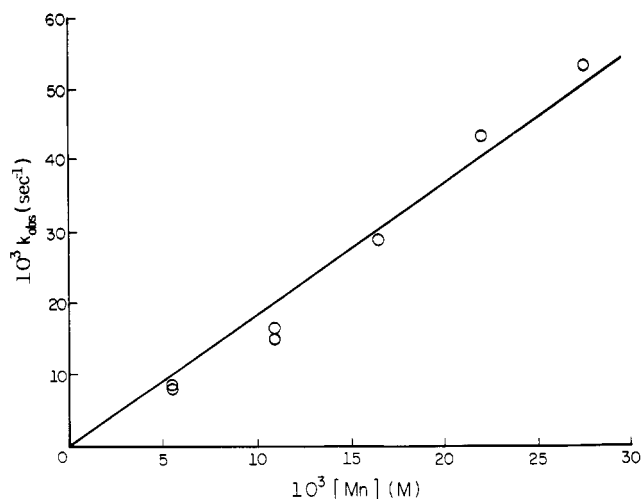


Figure 2. Dependence of k_{obsd} on $[\text{Mn(II)}]_{\text{T}}$: $[\text{Ox}]_{\text{T}} = 0.40 \text{ M}$, and $\text{pH} \approx 3.9$. Some deviations from the line are due to variations in pH which were not compensated for.

where $[\text{Mn(II)}]_{\text{T}} = [\text{MnC}_2\text{O}_4] + [\text{Mn}(\text{C}_2\text{O}_4)_2^{2-}]$ and $[\text{Ox}]_{\text{T}} = [\text{HC}_2\text{O}_4^-] + [\text{C}_2\text{O}_4^{2-}]$ which are valid approximations in the ranges of concentrations studied. (See Table I for values of constants.)

Figure 4 shows a plot of $[\text{H}^+]^2[\text{Ox}]_{\text{T}}^2/k_{\text{obsd}}$ vs. the combined denominator terms in eq 2 for a series of runs with constant $[\text{Mn(II)}]_{\text{T}}$. The slope of the graph is $(k'K_2K_a^2/[\text{Mn(II)}]_{\text{T}})^{-1}$. Using values of K_2 and K_a from Table I and $[\text{Mn(II)}] = 1.06 \times 10^{-2} \text{ M}$, one may calculate $k' = (1.2 \pm 0.1) \times 10^9 \text{ M}^{-4} \text{ s}^{-1}$.

Temperature Dependence. Reaction rates were measured over the temperature range 25–50 °C for systems containing primarily $\text{Mn}(\text{Ox})_2^{2-}$, HCrO_4^- , and a fixed $\text{HC}_2\text{O}_4^-/\text{C}_2\text{O}_4^{2-}$ buffer. Figure 5 shows an Eyring plot¹⁰ of $-\ln(hk_{\text{obsd}}/kT)$ vs. $1/T$ from which values of +10.85 kcal/mol for ΔH^\ddagger and $-32 \text{ cal mol}^{-1} \text{ K}^{-1}$ for ΔS^\ddagger were obtained. ΔH for ionization of carboxylic acids and formation of $\text{Mn}(\text{Ox})_2^{2-}$ are both small compared to the overall ΔH^\ddagger .

Discussion

The first-order dependence of this reaction on Mn(II) is interesting. Many simple one-electron reductants such as Fe^{2+} and VO^{2+} give rise to second-order dependence on the reductant in Cr(VI) oxidations. Species which show first-order dependence include $\text{Mo}(\text{CN})_8^{4-}$,¹¹ $\text{Fe}(\text{CN})_6^{4-}$,¹² $\text{Fe}(\text{phen})_3^{2+}$,¹³ and $\text{Fe}(\text{bpy})_3^{2+}$.¹² In the case of $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$, it has been suggested that they follow a first-order dependence

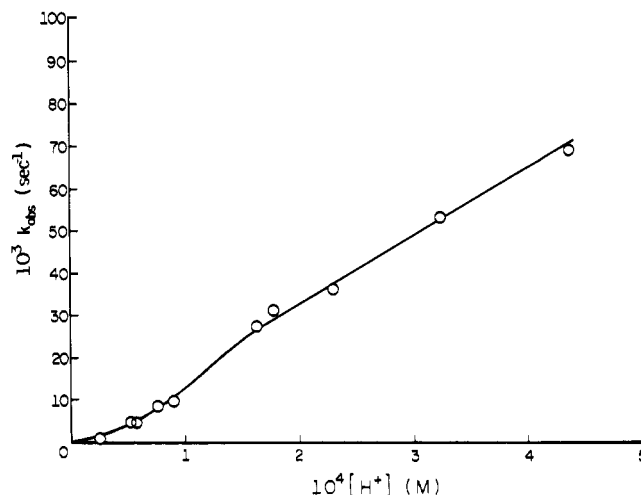


Figure 3. Dependence of k_{obsd} on $[\text{H}^+]$: $[\text{Mn(II)}]_{\text{T}} = 0.01055 \text{ M}$, and $[\text{Ox}]_{\text{T}} = 0.40 \text{ M}$.

Table I. Formation Constants of Oxalate Complexes^{a,d}

<i>n</i>	Mn(II)	Log $K_{f(n)}$	Mn(III)	E^0
	$\mu = 0$	$\mu = 1.0$	$\mu = 2.0$	$\text{Mn}(\text{Ox})_n^{3-2n}/\text{Mn}(\text{Ox})_n^{2-2n}$
0	—	—	—	1.51
1	3.9	3.0	9.98	1.16 ^b
2	1.43 ^c	2.1	6.59	0.85 ^b
3	<(0.1) ^c	0.7	2.85	0.63 ^b

^a "Stability Constants", The Chemical Society, London, 1964, pp 365–366. ^b Calculated using E^0 for aquo complexes and the formation constants listed above. ^c No experimental values listed. Value in parentheses estimated as upper limit. ^d $K_a = [\text{H}^+][\text{C}_2\text{O}_4^{2-}]/[\text{HC}_2\text{O}_4^-] = 6.3 \times 10^{-5} \text{ M}$. ^e K_2 probably is not sensitive to changes in μ , since neutral (MnC_2O_4) is involved.

because they are outersphere reductants. However, the reactions of $\text{Mo}(\text{CN})_8^{4-}$ and $\text{Fe}(\text{CN})_6^{4-}$ are far faster than those of the former two and are clearly innersphere reactions as indicated by their products, among which are polynuclear complexes with Cr(III).^{11,12} To explain these reactions it has been suggested that the rate-limiting step for most Cr(VI) reductions involves the expansion of the coordination number from four for the tetrahedral configurations of HCrO_4^- and H_3CrO_4 to six for the octahedral configuration most common for Cr(IV) and Cr(III).¹¹ Ferrocyanide and octacyanomolybdate(IV) are capable of nucleophilic attack on Cr(VI), expanding the coordination in the VI \rightarrow V reduction step. With reductants such as Fe^{2+} and VO^{2+} the reorganization does not take place until the V \rightarrow IV reduction. If the rate law determined for the Mn(II)-oxalate reduction is formulated as rate = $k''[\text{Mn}(\text{C}_2\text{O}_4)_3^{4-}][\text{HCrO}_4^-][\text{H}^+]^2$, then it is of the same form as the rate law for $\text{Mo}(\text{CN})_8^{4-}$ which is also second-order in hydrogen ion. Using a value of $K_3 = 0.1$ (see Table I) we obtain a value for k'' of $(1.2 \pm 0.1) \times 10^{10} \text{ M}^{-3} \text{ s}^{-1}$. This rate constant is far greater than those observed for ferrocyanide and octacyanomolybdate(IV) (An error in k reported for $\text{Mo}(\text{CN})_8^{4-}$ has been found. It is $8.8 \times 10^4 \text{ s}^{-1} \text{ M}^{-3}$ rather than 8.8×10^{-4} .) indicating that it, too, must be an innersphere reaction. By analogy, therefore, this suggests the activated complex I. It is then postulated that this activated complex rapidly breaks down to $\text{Mn}(\text{C}_2\text{O}_4)_3^{3-}$ and H_3CrO_4 . Rocek^{5b} has found that Cr(V) is stabilized in oxalate solution, and is only reduced comparatively slowly by oxalate. Similarly the H_3CrO_4 produced in our system can rapidly form an octahedral $\text{OCr}(\text{OH})_3(\text{C}_2\text{O}_4)^{2-}$ which is rapidly reduced by the

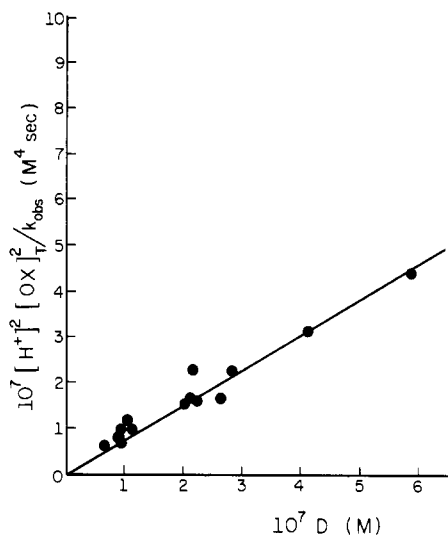


Figure 4. $[H^+]^2[Ox]_T^2/k_{obs}$ vs. D , where $D = (K_a + [H^+] + K_a K_2 [Ox]_T)(K_a + [H^+])$; $[Mn(II)]_T = 0.01055$ M. Slope of line equals $(k' K_2 K_3 K_a^2 [Mn(II)]_T)^{-1}$. Points near the origin tend to deviate above the line as a result of interference by the decay of Mn(III) with the measurement of k_{obs} .

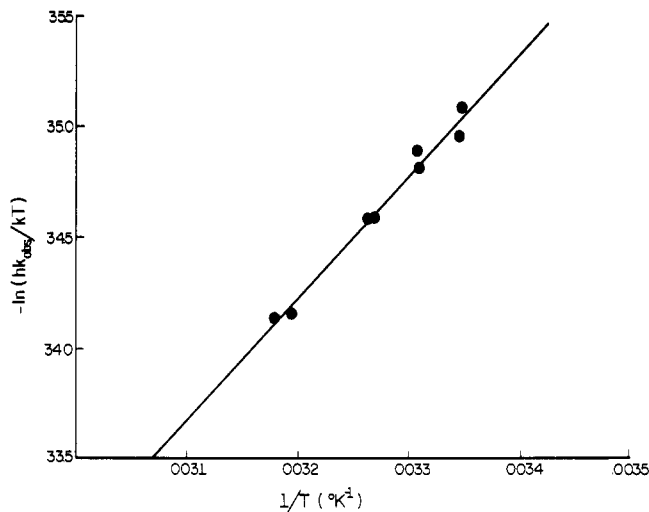
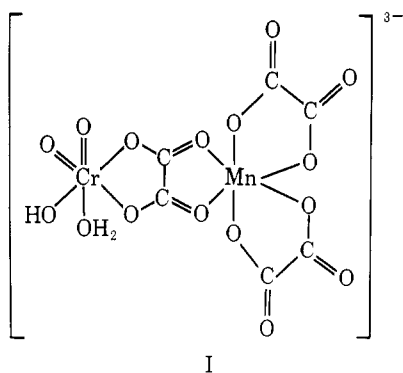


Figure 5. Eyring plot of $-\ln(hk_{obs}/kT)$ vs. $1/T$: $[Mn(II)]_T \approx 6.7 \times 10^{-3}$ M, $[Ox]_T = 0.40$ M, pH 4.02. Slope of the line equals $\Delta H^\ddagger/R$.



abundant $Mn(C_2O_4)_2^{2-}$ via a transition state like the one above for the Cr(VI). The labile Cr(IV) produced can acquire oxalate ligands from solution before being reduced to produce the observed distribution of Cr(III) products among hexaquo- and mono-, bis-, and trisoxalato species.^{14,15} In Roček's mechanism for the uncatalyzed oxidation of oxalic acid by Cr(VI) none of the chromium passes through a Cr(IV) inter-

Table II. Observed and Calculated Rate Constants, $a, b T = 25^\circ$

$[Mn(II)]_T^c$ ($M \times 10^{-3}$)	$[Ox]_T$ (M)	$[H^+]$ ($M \times 10^{-4}$)	$k_{obsd}(exptl)$ ($s^{-1} \times 10^{-3}$)	$k_{obsd}(calcd)$
5.53	0.40	0.98	8.35	6.44
5.53	0.40	1.18	8.00	8.11
11.05	0.40	1.15	15.1	17.3
11.05	0.40	1.32	16.5	20.8
16.58	0.40	1.44	29.0	35.3
22.10	0.40	1.32	43.3	43.6
27.63	0.40	1.32	52.0	54.8
11.05	0.40	4.47	69.0	67.3
11.05	0.40	0.676	9.50	8.80
11.05	0.40	2.04	38.5	33.6
11.05	0.40	0.646	7.30	8.27
10.55	0.40	3.24	53.3	50.8
10.55	0.40	0.240	1.44	1.68
10.55	0.40	4.36	69.3	62.3
10.55	0.40	2.29	36.5	35.3
10.55	0.40	0.89	10.05	12.1
10.55	0.40	0.750	9.00	9.67
10.55	0.40	0.562	5.09	6.43
10.55	0.40	0.513	5.25	5.62
10.55	0.40	1.78	31.5	27.7
10.55	0.40	1.62	27.7	25.0
10.55	0.30	2.08	23.9	22.3
10.55	0.30	0.813	8.77	7.66
10.55	0.20	1.32	5.87	8.10
10.55	0.10	3.71	8.15	6.40

^a All runs were made with $[Cr(VI)]_{initial} = 5 \times 10^{-4}$ M. ^b Experimental rate constants tend to be smaller than the true values for the reaction as a result of interference by the decay of $Mn(Ox)_3^{3-}$. The effect becomes more pronounced the slower the reaction is. ^c $[Mn(II)] = [Mn(II)]_t - 1.125 \times 10^{-3}$. Initial data were obtained between first and second $t_{1/2}$.

mediate, so only a small fraction of Cr(III) product contains more than one oxalate ligand. In our mechanism for the Mn(II)-catalyzed reaction all the chromium passes through the Cr(IV) state, giving rise to a high proportion of bis- and trisoxalatochromium(III).

The *cis*-dioxochromium(VI) depicted in our transition complex is kinetically indistinguishable from one with one oxo group and three hydroxo groups attached. However, Wold and Wold¹⁶ observed that ¹⁷O NMR data on $HMoO_4^-$ exchange with water was consistent with the formulation of $HMoO_4^-$ as a *cis* dioxo octahedral species $[MoO_2(OH)_3(OH_2)]^-$. *Cis* dioxomolybdenum(VI) monomers abound in the aqueous chemistry of that element.¹⁷ By analogy we therefore formulate activated states involving oxalate catalyzed Cr(VI) oxidations as *cis* dioxo octahedral complexes.

One piece of evidence in support of our proposed transition state is our qualitative observation that using malonate instead of oxalate in our system gives a far slower reaction despite the fact that malonate forms a series of complexes with Mn(II) and Mn(III) which are very similar to the oxalate complexes. If the oxalate reaction were proceeding via an outersphere mechanism one would expect the malonate reaction to proceed at a similar rate. In our mechanism the difference is clearly explained since the geometry of malonate's chelate ring prevents it from chelating both the manganese and the chromium at the same time.

The basic rate law is also supported by an analysis of Roček and Hasan's data at pH 1 (Figure 1). For the initial decay step, graph A yields $k_{obsd} = 17.3 \times 10^{-3} s^{-1}$ and graph B gives $k_{obsd} = 34.6 \times 10^{-3} s^{-1}$. Using the k'' we obtained from our data applied to their reaction conditions, we calculate $k_{obsd} = 10.5 \times 10^{-3} s^{-1}$ for the experiment in graph A, and $k_{obsd} = 21.0 \times 10^{-3} s^{-1}$ for the experiment in graph B. While this is hardly

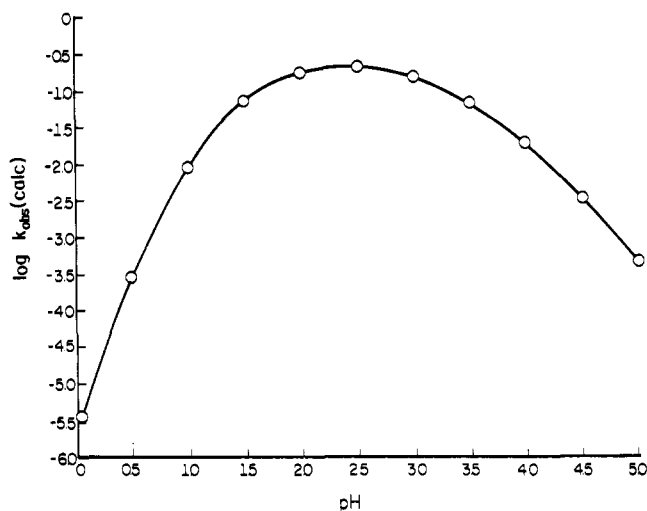


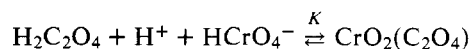
Figure 6. Sample plot of $\log k_{obsd}$ (calcd) vs. pH from 0 to 5: $[Mn(II)]_T = 0.01$ M, $[Ox]_T = 0.50$ M.

perfect agreement with the experimental values, it is within a factor of 2, and considering the wide range of acidities and other variables in reaction conditions, it supports a mechanism of this type and establishes the validity of our assumptions about the nature of the activated complex. Figure 6 shows a plot of calculated $\log(k_{obsd})$ vs. pH for a system of constant $[Mn(II)]_T$ and constant $[Ox]_T$ using our experimental value of k'' .

Though a mechanism involving $HCrO_4^-$, $Mn(C_2O_4)_3^{4-}$, and two H^+ was suggested by the analogy to $Mo(CN)_8^{4-}$, they are not the only possible precursors that could be constructed from the observed rate law to yield the same activated complex. We considered these possibilities in the light of our data at pH 3–4.5 and Rocek and Hasan's data at pH 1.

(A) $H_3CrO_4^+$ and $Mn(C_2O_4)_3^{4-}$. This formulation reduces our original mechanism to a simple bimolecular reaction. In this form rate = $k^{(a)}[H_3CrO_4^+][Mn(C_2O_4)_3^{4-}]$. Therefore $k^{(a)}[H_3CrO_4^+] = k''[HCrO_4^-][H^+]^2$. So $k^{(a)}$ would have to equal k'' times the dissociation constants for $H_3CrO_4^+$ and H_2CrO_4 . The dissociation constant for H_2CrO_4 is 5; thus by Pauling's rule the dissociation constant for $H_3CrO_4^+$ should be approximately 10^6 . Therefore $k^{(a)} = (5 M)(10^6 M)(1.2 \times 10^{10} M^{-3} s^{-1}) = 6 \times 10^{16} M^{-1} s^{-1}$ which is far greater than the limit for a diffusion controlled process.

(B) $CrO_2(C_2O_4)$ and $Mn(C_2O_4)_2^{2-}$. Recently Rocek and co-workers have demonstrated oxalic acid catalysis of the chromic acid oxidations of $Fe(phen)_3^{2+}$ ¹⁸ and I^- ¹⁹ which they attribute to the formation of oxalyl chromate according to the equation



where K has been determined as $7.5 M^{-2}$. Formation of this species requires one more hydrogen ion than we have observed in our rate law, and if this mechanism were used to evaluate our data, it would result in a k_{obsd} two to four orders of magnitude larger than the experimental values at pH 1.

(C) $[CrO_2(OH)(OH_2)(C_2O_4)]$ and $Mn(C_2O_4)_2^{2-}$. This mechanism involves the reaction of $C_2O_4^{2-}$ with $HCrO_4^-$ followed by protonation of the resulting octahedral chromium(VI) species followed by attachment of $Mn(C_2O_4)_2^{2-}$ to Cr(VI) through the oxalate forming the activated complex. This mechanism is kinetically indistinguishable from the first mechanism in the absence of independently determined formation constants for trisoxalatomanganese(II) or the postu-

lated octahedral oxalatochromate species. We have been unable to detect any difference in the visible spectrum of chromate(VI) in water at pH 4 and in 0.5 M oxalate at pH 4, and therefore originally assumed that no such complex was formed. However, Mason²⁰ has observed catalysis of the oxidation of arsenite by oxalate, and by nitrilotriacetic acid, EDTA, and other carboxylic acid chelates. It is unlikely that these chelates coordinate to H_3AsO_3 and suggests that they may be acting by expanding the coordination sphere of chromium(VI) to the octahedral state preferred by product chromium(IV). Clearly it is possible for such a complex to form in the present system as well. The lack of evidence for any detectable amount of the complex in solution requires that postulated oxalatochromate be a kinetic intermediate with $K_f < 0.1$. This postulate is attractive in that it allows comparison with other oxalate catalyses and offers a reason for the addition of protons to the acid chromate. Octahedral oxyacids are much weaker than tetrahedral oxyacids; e.g., $K_a(H_2SO_4) \gg K_a(Te(OH)_6)$. We have shown a reaction between $H_3CrO_4^+ + Mn(C_2O_4)_3^{4-}$ to be untenable.

Despite the small concentrations of oxalatochromate(VI) complex present, it is evident from the rate of our reaction compared to that for $Mo(CN)_8^{4-}$ or $Fe(CN)_6^{4-}$ that oxalate has a powerful catalytic effect. This can be attributed to several factors. First as a chelate oxalate can cause the expansion of the chromate coordination sphere far more effectively than monodentate $-C \equiv N:$. The extensively delocalized π -bonding in the oxalate bridge serves as an effective route for electron transfer from one metal center to the other. Also, as indicated by Rocek's studies oxalate stabilizes Cr(V) relative to Cr(VI) increasing the Cr(VI) \rightarrow (V) oxidation potential.

It is clear from the work of Rocek, Mason, and this study that oxalate can catalyze many different chromate oxidations. Further study will be required to determine if a single basic role for oxalate in catalysis of chromate oxidations can be found.

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