have been examined in this series, exceptions may be found in polymorphic phase transformations in which topotaxy is established relative to a very limited number of nucleation centers.

Kitaigorodskii's study of the topotactic, reversible polymorphic phase transformation of *p*-dichlorobenzene [10]exemplifies a failure of the "memory effect" of conservative twinning. The low-temperature (α) monoclinic phase ($P2_1/a$) and high-temperature (β) triclinic phase ($P\bar{1}$) reversibly interconvert at temperatures approximately 20 °C below the melting points of the separate phases (53 °C). A single crystal of either phase may be repeatedly cycled topotactically through both phases. Whereas an *initial* transformation $\beta \rightarrow \alpha$ should occur without conservative twinning, the reverse change would be expected to yield two conservative twin orientations of the β phase, if many nucleation centers develop within the pseudomorph. This appears not to be the case, for Laue photographs of the β phase no longer display the mirror symmetry of the prior α phase. It is also of interest that the mutual phase alignment, from cycle to cycle, is variable in both directions of the transformation. Accordingly, the successive reverse transformations do not imply simple inverse topotactic matrix relationships. An intriguing memory effect of a different sort, nevertheless, is manifest in the observed invariant orientation of the monoclinic α phase relative to some external reference coordinate system.

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Catalysis in Oxidation Reactions. 3. The Oxalic Acid Catalyzed Chromic Acid Oxidation of Tris(1,10-phenanthroline)iron(II)[1,2]

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Abstract: Oxalic acid accelerates the chromic acid oxidation of tris(1,10-phenanthroline)iron(II), $Fe(phen)_3{}^{2+}$, by factors up to 4×10^4. The reaction is first order in $Fe(phen)_3{}^{2+}$, $HCrO_4{}^-$, H^+, and $(CO_2H)_2$. The proposed mechanism involves formation of an oxalic acid–chromic acid complex, followed by its rate-limiting one-electron outer sphere reduction by $Fe(phen)_3{}^{2+}$. The chromic acid–oxalic acid complex is about 3000 times more reactive than H_2CrO_4. The reaction provides evidence that oxalic acid can accelerate the one-electron reduction of chromium(VI) to chromium(V). It is postulated that the rate acceleration results from a substantial increase in the Cr(VI)/Cr(V) reduction potential in the presence of oxalic acid due to the high stability of the Cr(V)–oxalic acid complex relative to the Cr(VI) complex. At high concentrations of $Fe(phen)_3{}^{2+}$ the reaction between $HCrO_4{}^-$ and $(CO_2H)_2$ tends toward becoming rate limiting ($k = 9.1 \times 10^3\ M^{-1}\ s^{-1}$).

Oxalic acid accelerates the rates of many chromic acid oxidations. For example, in the presence of oxalic acid alcohols react with Cr(VI) in a rapid cooxidation reaction yielding a ketone, CO_2, and $CO_2{}^-$ (or $\cdot CO_2H$), with Cr(VI) being reduced directly to Cr(III) in the rate-limiting step.[3,4] A similar rapid three-electron cooxidation reaction has been reported for oxalic acid acceleration of oxidation of malachite green.[5]

On the other hand, oxalic acid can also increase the rate of chromic acid oxidations without undergoing oxidation itself; it thus can act as an oxidation catalyst.[6] The most thoroughly investigated example within this class is the chromic acid oxidation of iodide.[2,8,9] However, because of the number of known and relatively stable valence states of iodine, it is difficult to determine whether oxalic acid accelerates a one-electron reduction of chromium(VI) to chromium(V), or a two-electron reduction to chromium(IV). A similar problem is encountered in the interpretation of the results of the oxalic acid catalyzed chromic acid oxidation of thiocyanate.[10]

It is therefore of interest to examine the mechanism of an oxalic acid catalyzed chromic acid oxidation reaction of a compound which exists in only two stable oxidation states. Eswara Dutt and Mottola[7] recently observed that oxalic acid greatly accelerates the redox reaction of chromic acid and tris(1,10-phenanthroline)iron(II), $Fe(phen)_3{}^{2+}$. However, their study was concerned primarily with the analytical utility of the rate enhancement, and kinetic measurements were confined to initial rates. The uncatalyzed reaction has been studied by Espenson and King,[11] who found that the reaction was highly complex with first- and second-order dependencies in $Fe(phen)_3{}^{2+}$, $HCrO_4{}^-$ as well as in H^+, and with the reaction going via four transition states of different composition with respect to numbers of chromium and iron atoms. Since they found that the oxidation product, $Fe(phen)_3{}^{3+}$, had no effect on the reaction rate, they concluded that the rate-limiting step for the simplest reaction path (via the transition state containing only one atom each of chromium and iron) was the reduction of chromium(VI) to chromium(V).

Experimental Section

Materials. Reagent grade oxalic acid (Fisher), sodium nitrate (B & A), nitric acid (Mallinckrodt), ceric ammonium sulfate (Fisher), and potassium dichromate (Baker) were used without further purification. Tris(1,10-phenanthroline)iron(II) sulfate (0.025 M) was obtained from G. F. Smith. Standard nitric acid solutions were prepared by dilution of Acculute standard volumetric solution (Anachemia Chemicals). Dowex 50W-X8 and Dowex 2-X8 exchange resins were used for ion-exchange product analysis.

Instruments. Stoichiometric measurements were performed with Zeiss PMQ II and Cary 14 spectrophotometers. Most kinetic experiments were performed with an Aminco-Morrow stopped flow apparatus; the slower reactions were carried out on a Zeiss PMQ II spectrophotometer, equipped with a Honeywell recorder. All kinetic experiments were thermostated to 25 °C with either Heto or Lauda constant temperature baths.

Stoichiometry and Product Analysis. Fe(III). The oxidation product, $Fe(phen)_3^{3+}$, was identified by its visible spectrum with maximum absorbance at 593 nm.[12] In addition, the spectrum of reaction products closely matched that of an authentic sample of $Fe(phen)_3^{3+}$ produced by oxidation with acidic ceric ammonium sulfate.[13] The molar absorptivity at 650 nm was 608 $M^{-1}\,cm^{-1}$; this wavelength was chosen instead of the absorption maximum at 593 nm in order to avoid significant absorption of tris(1,10-phenanthroline)iron(II) in solutions containing both iron(II) and iron(III).

Cr(III). Chromium(III) products were separated with Dowex 50W-X8 cation exchange resin. Anionic chromium(III) complexes, $Cr(ox)(OH_2)_4^+$, and $Cr(OH_2)_6^{3+}$ were eluted with 0.01 M HNO_3, 1.0 M HNO_3, and 3.0 M HNO_3, respectively. The anionic complexes eluted from the cation exchange column were then separated with Dowex 2-X8 anion exchange resin. $Cr(ox)_2(H_2O)_2^-$ was eluted with 1.0 M HNO_3 and $Cr(ox)_3^{3-}$ was eluted with 3.0 M HNO_3. Total chromium content of the eluted fractions was determined by spectrophotometric analysis of CrO_4^{2-} (ϵ_{372} 4.81 × 10^3 $M^{-1}\,cm^{-1}$) after oxidation of Cr(III) aliquots to chromate with alkaline hydrogen peroxide.[15]

Kinetics. All experiments were carried out with a large excess (more than tenfold) of oxalic acid and nitric acid. However, the relative concentrations of $Fe(phen)_3^{2+}$ and Cr(VI) in different experiments may be divided into three categories: (1) excess of Cr(VI); (2) nearly equivalent concentrations of Cr(VI) and $Fe(phen)_3^{2+}$; and (3) excess of $Fe(phen)_3^{2+}$. The reaction stoichiometry (vide infra) requires $3Fe(phen)_3^{2+}$ for each Cr(VI) reduced to Cr(III). The following relationship defines the experimental second-order rate constant,

$$\frac{-d[\mathrm{Fe(II)}]}{dt} = \frac{d[\mathrm{Fe(III)}]}{dt} = \frac{-3d[\mathrm{Cr(VI)}]}{dt} = k_{\mathrm{exptl}}[\mathrm{Cr(VI)}][\mathrm{Fe(II)}] \quad (1)$$

where Fe(II) and Fe(III) represent $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$, respectively.

When an excess of Cr(VI) was used, the reaction was monitored by the absorbance of $Fe(phen)_3^{2+}$ at 510 nm (ϵ 1.11 × 10^4 $M^{-1}\,cm^{-1}$) and the pseudo-first-order rate constant (k_{obsd}) obtained plots of $\ln(A - A_\infty)$ vs. time.

$$-d[\mathrm{Fe(II)}]/dt = k_{\mathrm{obsd}}[\mathrm{Fe(II)}] \quad (2)$$

$$k_{\mathrm{exptl}} = k_{\mathrm{obsd}}/[\mathrm{Cr(VI)}] \quad (3)$$

When the concentrations of Cr(VI) and $Fe(phen)_3^{2+}$ were within an order of magnitude, the reaction was monitored either at 510 or 650 nm and the rate constant k_{exptl} obtained from

$$\frac{1}{[\mathrm{Cr(VI)}]_0 - \frac{1}{3}[\mathrm{Fe(II)}]_0} \ln\left[\frac{[\mathrm{Fe(II)}]_0([\mathrm{Cr(VI)}]_0 - \frac{1}{3}[\mathrm{Fe(III)}])}{[\mathrm{Cr(VI)}]_0([\mathrm{Fe(II)}]_0 - [\mathrm{Fe(III)}])}\right] = k_{\mathrm{exptl}}t \quad (4)$$

When an excess of $Fe(phen)_3^{2+}$ was present, the reaction was monitored at 650 nm and rate constants (k'_{obsd}) were obtained from plots of $\ln(A_\infty - A)$ vs. time.

$$-\frac{d(\ln(A_\infty - A))}{dt} = \frac{-d[\mathrm{Cr(VI)}]}{dt} = k'_{\mathrm{obsd}}[\mathrm{Cr(VI)}] \quad (5)$$

$$k_{\mathrm{exptl}} = 3k'_{\mathrm{obsd}}/[\mathrm{Fe(phen)_3^{2+}}]_0 \quad (6)$$

Although the absorption at 650 nm is proportional to the concentration of $Fe(phen)_3^{3+}$, the magnitudes of A_∞ and $(A_\infty - A)$ are proportional to $[Cr(VI)]_0$ and [Cr(VI)], respectively.

Reactions were initiated by mixing two stock solutions, "A" ($Fe(phen)_3^{2+}$, $Cr_2O_7^{2-}$, and $NaNO_3$) and "B" (oxalic acid, HNO_3, and $NaNO_3$). Ionic strength was maintained at 1.0 M with sodium nitrate. No oxidation of tris(1,10-phenanthroline)iron(II) by dichromate could be detected even in solutions stored for several weeks. Very good straight line plots up to 3 half-lives for first-order plots or about 80% of the reaction for second-order plots were generally obtained.

A few preliminary kinetic runs were made by mixing a stock solution containing $Fe(phen)_3^{2+}$ and oxalic acid with a stock solution containing chromic acid and nitric acid. The solution of tris(1,10-phenanthroline)iron(II) and oxalic acid was found to be somewhat unstable, probably because of acid hydrolysis of the iron complex.[16] The kinetics observed under these conditions were not completely reproducible, and are not reported here.

A relatively slow secondary reaction takes place under conditions of excess tris(1,10-phenanthroline)iron(II)[7,17]

$$2Fe(phen)_3^{3+} + (CO_2H)_2 \rightarrow 2Fe(phen)_3^{2+} + 2CO_2 + 2H^+ \quad (7)$$

Under most experimental conditions, the oxidation of oxalic acid by $Fe(phen)_3^{3+}$ is orders of magnitude slower than the Cr(VI) oxidation of $Fe(phen)_3^{2+}$.

Results and Discussion

Products. The only oxidation product was $Fe(phen)_3^{3+}$. The stoichiometry described by eq 8 was established from a series of experiments in which the concentrations of oxalic acid were varied over three orders of magnitude.

$$\mathrm{Cr(VI)} + 3\mathrm{Fe(phen)_3^{2+}} \xrightarrow{\mathrm{H^+,(CO_2H)_2}} \mathrm{Cr(III)} + 3\mathrm{Fe(phen)_3^{3+}} \quad (8)$$

Stoichiometric ratios of 2.9 to 3.0 (Table I, column 5) indicate that $Fe(phen)_3^{2+}$ is the only species oxidized; oxalic acid is not oxidized, even if it is present in large excess over chromic acid and tris(1,10-phenanthroline)iron(II).

Chromium(III) is formed as a mixture of oxalate complexes. At low concentrations of oxalic acid (0.01 M) and nitric acid (0.013 M), 38 ± 2% of Cr(III) was present as $Cr(ox)(H_2O)_4^+$, 59 ± 2% as $Cr(ox)_2(H_2O)_2^-$, and only about 3% consisted of $Cr(ox)_3^{3-}$. At higher concentrations of oxalic acid (0.2 M) and nitric acid (0.27 M), $Cr(ox)(H_2O)_4^+$ comprised 30% of the product, while anionic complexes accounted for the remainder. $Cr(H_2O)_6^{3+}$ accounted for less than 1% of the Cr(III) product at both high and low concentrations.

Kinetics. In contrast to the uncatalyzed reaction,[11] which has a complicated rate law involving terms first and second order in all reactants, the oxalic acid catalyzed reaction obeys simple kinetics at least at lower concentrations. The reaction is first order in $Fe(phen)_3^{2+}$, $HCrO_4^-$, H^+, and $(CO_2H)_2$ over wide concentration ranges.

The first-order dependence on $Fe(phen)_3^{2+}$ was revealed by good first-order plots up to 3 half-lives of the reaction for runs with Cr(VI) in excess and by equally satisfactory second-order plots for runs with $Fe(phen)_3^{2+}$ and Cr(VI) of comparable concentration. It is significant to note that there is no decrease in reaction rates toward the end of the runs, where the concentration of $Fe(phen)_3^{3+}$ is considerably higher than that of $Fe(phen)_3^{2+}$. The oxidation product thus exhibits no retarding effects on the oxidation rate, indicating that the Cr(VI) → Cr(V) reduction is irreversible and rate limiting.

Table I. Stoichiometry of $Fe(phen)_3^{3+}$ Formation[a]

$Fe(phen)_3^{2+}$, 10^4 M	$(CO_2H)_2$, 10^4 M	Cr(VI), 10^5 M	$Fe(phen)_3^{3+}$, 10^4 M[b]	Fe(III)/Cr(VI)
8.65	1.82	8.96	2.44	2.88[c]
8.65	2.73	8.96	2.49	2.90[c]
8.65	4.54	8.96	2.63	2.94
8.65	9.08	8.96	2.62	2.93
8.65	26.0	8.96	2.63	2.94
8.21	454.	8.52	2.48	2.91
7.79	908.	8.07	2.41	2.99
6.93	1820.	7.17	2.03	2.83

[a] $[HNO_3] = 0.182$ M. [b] Yield of $Fe(phen)_3^{3+}$ determined spectrophotometrically at 650 nm. [c] Extrapolated to $t = 0$ in order to correct for hydrolysis[16] of $Fe(phen)_3^{3+}$; no correction is necessary at higher concentrations, as the reduction becomes much faster than hydrolysis.

Table II. Effect of $[Fe(phen)_3^{2+}]$ on Oxidation Rates[a]

Cr(VI), 10^5 M	$Fe(phen)_3^{2+}$, 10^3 M	k'_{obsd}, s^{-1}	$k_{expll} = 3k'_{obsd}/[Fe(phen)_3^{2+}]_0$, 10^{-3} M^{-1} s^{-1}
5.89	0.0190		5.2
	0.0380		4.9
	0.0570		4.7
	0.0760		4.9
	0.0950		4.8
	0.190		5.6
	0.380		4.8
2.46	0.683	0.94	4.2
	1.37	1.9	4.2
	2.73	3.3	3.6
	4.10	5.2	3.8
	5.46	6.1	3.3
	6.83	7.6	3.3
	8.19	9.2	3.4

[a] $(\text{Oxalic acid})_{total} = 5.00 \times 10^{-3}$ M, $HNO_3 = 0.200$ M, corresponding to $[(CO_2H)_2] = 3.86 \times 10^{-3}$ M and $[H^+] = 0.201$ M; $\mu = 1.0$ M ($NaNO_3$), $T = 25$ °C. The rate of formation of $Fe(phen)_3^{3+}$ was monitored at 650 nm.

Table III. Effect of [Cr(VI)] on Oxidation Rates[a]

Cr(VI),[b] 10^3 M	$HCrO_4^-$,[c] 10^3 M	k_{obsd}, s^{-1}	$k_{expll} = k_{obsd}/[HCrO_4^-]_0$, 10^{-3} M^{-1} s^{-1}
0.00197	0.00197		5.4
0.00296	0.00296		5.9
0.0197	0.0197		4.6
0.0246	0.0246		4.7
0.0512	0.0512		4.6
0.0589	0.0589		5.2
0.0719	0.0709	0.33	4.7
0.0983	0.0965	0.45	4.7
0.196	0.189	0.95	5.0
0.256	0.244	1.3	5.3
0.388	0.362	2.0	5.5
0.510	0.467	2.6	5.6
0.785	0.691	3.8	5.5
1.96	1.51	8.2	5.4
3.93	2.61	13.8	5.3

[a] $Fe(phen)_3^{2+} = 1.90 \times 10^{-5}$ M, oxalic acid $= 5.00 \times 10^{-3}$ M, $HNO_3 = 0.200$ M, $\mu = 1.0$ M ($NaNO_3$), $T = 25$ °C. [b] $[Cr(VI)] = [HCrO_4^-] + 2[Cr_2O_7^{2-}]$ = total concentration of Cr(VI). [c] Corrected for formation of dichromate,[18] $K_d = [Cr_2O_7^{2-}]/[HCrO_4^-]^2 = 98$ M^{-1}.

The data in Table II show the effect of the initial concentration of $Fe(phen)_3^{2+}$ at constant chromic acid concentration. The results are consistent with the first-order dependence on $Fe(phen)_3^{2+}$ except at high concentrations of iron(II) where a trend toward a lower order can be noted. The absence of any indication of a second-order dependence in $Fe(phen)_3^{2+}$ confirms the above conclusion that the reduction of chromium(VI) to chromium(V) is irreversible and rate limiting. In this respect the oxalic acid catalyzed oxidation parallels the uncatalyzed oxidation,[11] but differs from a number of other chromium(VI) oxidations of one-electron metal ion reductants.[18]

The good linearity of the first-order plots for runs with an excess of $Fe(phen)_3^{2+}$ indicates that the reaction is first order in chromium(VI). The results in Table III show that the first-order dependency is actually on $HCrO_4^-$ rather than on the total chromium(VI) concentration and that $Cr_2O_7^{2-}$ is kinetically inactive. In contrast, $Cr_2O_7^{2-}$ appeared to be more effective than $HCrO_4^-$ in the uncatalyzed oxidation.[11]

The kinetic order in oxalic acid and hydrogen ions was determined from the data of Table IV. The table contains four sets of experiments. In the first two we examined the effect of changing concentrations of oxalic acid at constant nitric acid concentration; in the other two sets the concentration of nitric acid was changed while the amount of oxalic acid was kept constant. As oxalic acid is a moderately strong acid (K_a = 0.059),[19] the concentration of hydrogen ions and of undissociated oxalic acid present in the solution after mixing depended on both the amounts of oxalic acid and nitric acid added. Although both concentrations changed in all sets, the main change occurred in the concentration of undissociated oxalic acid in the first two sets, and in the concentration of hydrogen ions in the latter two.

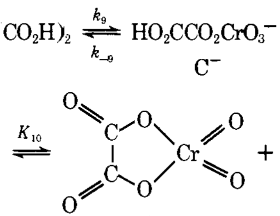
Inspection of the data makes it clear that the reaction is first order in both undissociated oxalic acid and hydrogen ions.[20] This is confirmed by the approximately constant values of $k_{obsd}/([(CO_2H)_2][H^+][Cr(VI)])$ (column 7), where [Cr(VI)] is the total concentration of hexavalent chromium. The decrease of these values at high oxalic and nitric acid concentrations is attributable to a partial conversion of Cr(VI) into the oxalato complex.[21] As is shown in the last column, this trend toward lower values disappears when the concentration of the monochromate anion, $[HCrO_4^-]$, is used instead of [Cr(VI)].

Mechanism. The above data can be reconciled with the reaction scheme given in Scheme I.

Scheme I

$$HCrO_4^- + (CO_2H)_2 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} \underset{C^-}{HO_2CCO_2CrO_3^-} + H_2O \quad (9)$$

$$C^- + H^+ \overset{K_{10}}{\rightleftharpoons}$$



$$+ H_2O \quad (10)$$

C_I

$$C_I + Fe(phen)_3^{2+} \xrightarrow{k_{11}} Cr(V) + Fe(phen)_3^{3+} \quad (11)$$

$$Cr(V) + Fe(phen)_3^{2+} \xrightarrow{k_{12}} Cr(IV) + Fe(phen)_3^{3+} \quad (12)$$

$$Cr(IV) + Fe(phen)_3^{2+} \xrightarrow{k_{13}} Cr(III) + Fe(phen)_3^{3+} \quad (13)$$

Reaction 10 is assumed rapid compared to k_9 and k_{11}; Vandegrift and Roček[2] found this to be true in the oxalic acid catalyzed oxidation of iodide. At low $Fe(phen)_3^{2+}$ concentrations reaction 11 will be rate limiting and reaction 9 fully reversible. Under these conditions the following rate law will apply

Table IV. Effect of Oxalic and Nitric Acid Concentrations on Oxidation Rates[a]

Reactant			Mixed solution					
Cr(VI), 10^4 M	Oxalic acid,[b] M	HNO_3, M	$(CO_2H)_2$, M	H^+, M	k_{obsd}, s^{-1}	$\frac{10^{-6}\,k_{obsd}}{[(CO_2H)_2][H^+][Cr(VI)]}$	$HCrO_4^-$ 10^4 M	$\frac{10^{-6}\,k_{obsd}}{[(CO_2H)_2][H^+][HCrO_4^-]}$
2.50	0.00200	0.200	0.00154	0.200	0.54[c]	7.0	2.38	7.4
	0.00500		0.00386	0.201	1.25[c]	6.4	2.38	6.8
	0.0100		0.00774	0.202	2.8[c]	7.3	2.37	7.7
	0.0500		0.0390	0.211	13.9[c]	6.8	2.30	7.3
	0.100		0.0789	0.221	29.[c]	6.6	2.20	7.5
	0.200		0.160	0.240	52.[c]	5.4	2.01	6.8
	0.300		0.244	0.256	78.[c]	5.0	1.83	6.8
1.25	0.040	0.400	0.0349	0.405	12.8[d]	7.2	1.14	7.9
	0.100		0.0874	0.413	27.[d]	6.0	1.03	7.3
	0.200		0.176	0.424	51.[d]	5.5	0.88	7.8
	0.300		0.264	0.436	67.[d]	4.7	0.77	7.6
	0.400		0.353	0.447	81.[d]	4.1	0.68	7.5
4.93	0.0400	0.0050	0.0138	0.0312	1.28[e]	6.0	4.52	6.6
		0.0100	0.0149	0.0351	1.57[e]	6.1	4.52	6.6
		0.0150	0.0159	0.0391	1.85[e]	6.0	4.52	6.6
		0.0200	0.0169	0.0431	2.1[e]	5.8	4.51	6.3
		0.0300	0.0186	0.0514	2.8[e]	5.9	4.51	6.5
		0.0600	0.0227	0.0773	5.1[e]	5.8	4.49	6.4
		0.100	0.0263	0.114	8.5[e]	5.8	4.47	6.4
		0.250	0.0325	0.257	26.[e]	6.3	4.36	7.1
		0.400	0.0349	0.405	45.[e]	6.4	4.26	7.4
		0.500	0.0358	0.504	58.[e]	6.5	4.19	7.6
2.50	0.0400	0.0100	0.0149	0.0351	0.86[c]	6.5	2.38	6.9
		0.0200	0.0169	0.0431	1.28[c]	7.0	2.38	7.4
		0.0400	0.0202	0.0598	2.0[c]	6.6	2.37	7.0
		0.100	0.0263	0.114	5.0[c]	6.6	2.35	7.0
		0.150	0.0292	0.161	8.1[c]	6.9	2.33	7.4
		0.200	0.0312	0.209	10.8[c]	6.6	2.31	7.2
		0.300	0.0336	0.306	18.2[c]	7.1	2.27	7.8
		0.400	0.0349	0.405	25.[c]	7.1	2.24	7.9
		0.500	0.0358	0.504	30.[c]	6.6	2.20	7.5

[a] All measurements at μ = 1.0 M ($NaNO_3$) at 25 °C; concentrations of $(CO_2H)_2$ and H^+ calculated for $K_a = 0.059$.[19] [b] [Oxalic acid] = $[(CO_2H)_2] + [HO_2CCO_2^-]$ = total concentration of oxalic acid. [c] $Fe(phen)_3^{2+} = 9.50 \times 10^{-6}$ M. [d] $Fe(phen)_3^{2+} = 1.00 \times 10^{-5}$ M. [e] $Fe(phen)_3^{2+} = 4.87 \times 10^{-5}$ M.

$$-d[Fe(II)]/dt = k_{obsd}[Fe(II)] = 3k_{11}[C_1][Fe(II)] \tag{14}$$

where

$$[C_1] = K_9K_{10}[HCrO_4^-][(CO_2H)_2][H^+] \tag{15}$$

At higher oxalic acid concentrations the concentration of C_1 will become comparable to that of $HCrO_4^-$, so that

$$[Cr(VI)] = [C_1] + [HCrO_4^-] \tag{16}$$

Combining eq 3, 14, 15, and 16 gives

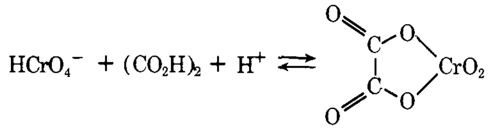
$$k_{exptl} = \frac{3k_{11}K_9K_{10}[(CO_2H)_2][H^+]}{1 + K_9K_{10}[(CO_2H)_2][H^+]} \tag{17}$$

and

$$\frac{1}{k_{exptl}} = \left(\frac{1}{3k_{11}K_9K_{10}}\,\frac{1}{[(CO_2H)_2][H^+]}\right) + \frac{1}{3k_{11}} \tag{18}$$

Figure 1 shows a plot of $1/k_{exptl} = [Cr(VI)]/k_{obsd}$ vs. $1/([CO_2H)_2][H^+])$ for the set of measurements in 0.40 M nitric acid. A satisfactory straight line with a slope $1/(3k_{11}K_9K_{10}) = 1.33 \times 10^{-7}$ and an intercept $1/(3k_{11}) = 0.7 \times 10^{-6}$, corresponding to a value of $k_{11} = 4.8 \times 10^5$ M^{-1} s^{-1} and $K_9K_{10} = 5.3$ M^{-2}, is obtained.

The value 5.3 for the equilibrium constant of reaction 19 in



(19)

a solution of nitric acid with an ionic strength μ = 1.0 M is in reasonable agreement with the values of 7.5 and 9.5 M^{-2} obtained earlier in perchloric acid solutions at μ = 0.63 and 0.1 M, respectively. Since two ions of opposite charge combine to form a neutral product, the decrease of the equilibrium constant with increasing ionic strength is expected.

At high $Fe(phen)_3^{2+}$ concentrations, reaction 11 may reach rates comparable to those of reaction 9. Then the following rate expressions apply

$$-d[Cr(VI)]/dt = k'_{obsd}[Cr(VI)] = k_{11}[C_1][Fe(II)] \tag{20}$$

$$k'_{obsd} = \frac{k_9k_{11}K_{10}[Fe(II)][(CO_2H)_2]\,[H^+]}{k_{-9} + k_{11}K_{10}[Fe(II)][H^+]} \tag{21}$$

$$\frac{1}{k'_{obsd}} = \left(\frac{k_9}{k_9k_{11}K_{10}[(CO_2H)_2][H^+]}\,\frac{1}{[Fe(II)]}\right) + \frac{1}{k_9[(CO_2H)_2]} \tag{22}$$

These equations will hold only if the concentration of oxalic acid is kept low enough to make the concentration of C_1 negligible in comparison with $HCrO_4^-$; the data given in Table II meet this condition. A plot (Figure 2) of $1/k'_{obsd}$ vs. $1/[Fe(phen)_3^{2+}]$ allows the determination of k_9. The value $k_9 = 9.1 \times 10^3$ M^{-1} s^{-1} thus obtained for the rate-limiting formation of the oxalylchromate complex agrees moderately well with that determined by Vandegrift and Roček[2] in a study of the oxalic acid catalyzed chromic acid oxidation of iodide (1.24×10^4 M^{-1} s^{-1}). The order of magnitude of k_9 also is in

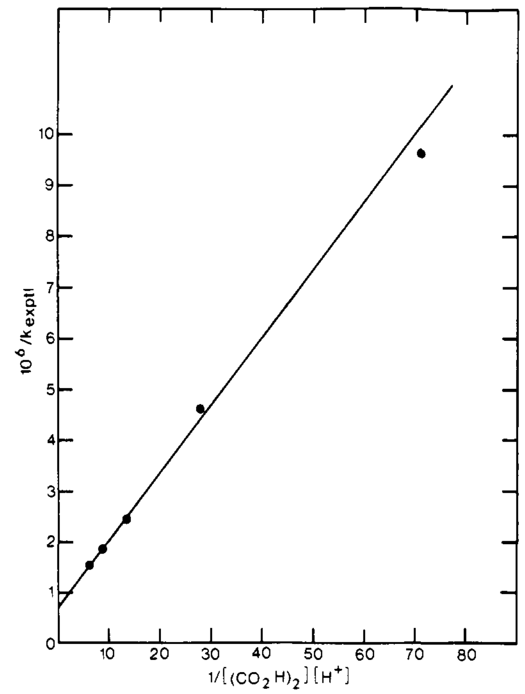


Figure 1. Reciprocal plot of k_{exptl} vs. $[(CO_2H)_2][H^+]$; data from Table IV.

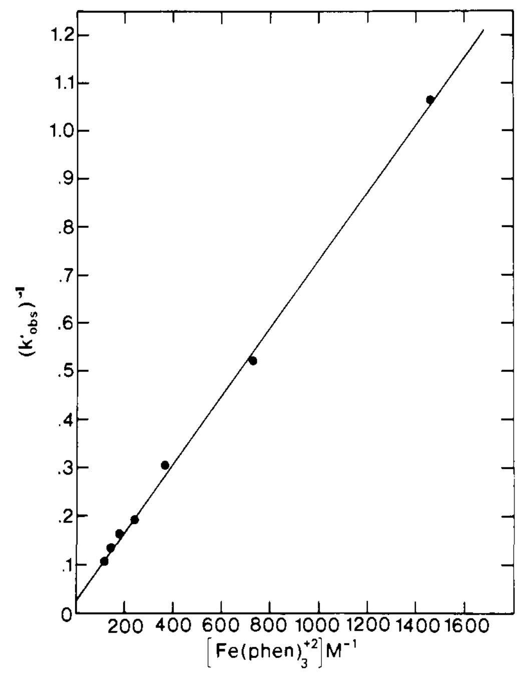


Figure 2. Reciprocal plot of k_{obsd} vs. $[Fe(phen)_3{}^{2+}]$; data from Table II.

agreement with rates of chromium(VI) complex formation with other substrates.[22,23] The rate of reduction of C_1 by $Fe(phen)_3{}^{2+}$ (k_{11}) can be calculated from the slope of the plot and from the value $K_9K_{10} = 5.3\ M^{-2}$. The value of $3.5 \times 10^5\ M^{-1}\ s^{-1}$ obtained in this way is in acceptable agreement with the value of $4.8 \times 10^5\ M^{-1}\ s^{-1}$ from eq 18.

In the more general case which includes reactions at high oxalic acid, nitric acid, and chromium(VI) concentrations, a significant fraction of chromium(VI) will be present as the complex C_1 or the dimeric ion $Cr_2O_7{}^{2-}$. The total concentration of chromium(VI) then can be expressed as

$$\begin{aligned}[Cr(VI)] &= [HCrO_4{}^-] + [C_1] + 2[Cr_2O_7{}^{2-}] \\ &= [HCrO_4{}^-](1 + K_9K_{10}[(CO_2H)_2]\,[H^+]) \\ &\qquad + 2K_d[HCrO_4{}^-]^2 \end{aligned} \tag{23}$$

from which

$$[HCrO_4{}^-] = -A + \sqrt{A^2 - 8K_d[Cr(VI)]}/4K_d \tag{24}$$

where

$$A = 1 + K_9K_{10}[(CO_2H)_2][H^+]$$

and[18]

$$K_d = [Cr_2O_7{}^{2-}]/[HCrO_4{}^-]^2 = 98\ M^{-1}$$

Equation 24 was used to calculate the values for $[HCrO_4{}^-]$ in Table IV (column 8).

Overall oxidation rates are increased by the presence of oxalic acid by factors of up to about 4×10^4 over the uncatalyzed reaction. It is further of interest to compare the rates of the individual rate-limiting steps in the catalyzed and uncatalyzed reactions. In the catalyzed reaction the rate-limiting step is shown in reaction 11, where $k_{11} \approx 4 \times 10^5\ M^{-1}\ s^{-1}$. The path going through the transition state with one chromium and one iron atom in the uncatalyzed reaction can be assumed to have a rate-limiting step

$$H_2CrO_4 + Fe(phen)_3{}^{2+} \xrightarrow{k_{25}} Cr(V) + Fe(phen)_3{}^{3+} \tag{25}$$

From Espenson and King's rate data and using[24] $K_a = 8.0$ M for the dissociation constant of H_2CrO_4 at $\mu = 1.5$ M a value of $k_{25} \approx 1.3 \times 10^2\ M^{-1}\ s^{-1}$ can be estimated. The chromic acid-oxalic acid complex thus reacts about 3000 times faster than H_2CrO_4.

It is this selective effect of oxalic acid on a single reaction path, namely that going via the simplest transition state containing only one atom each of chromium and iron, which makes the kinetics of the catalyzed reaction so simple compared with the uncatalyzed oxidation.

Except for very high concentrations of $Fe(phen)_3{}^{2+}$, the rate-limiting step of the reaction is the reduction of chromium(VI). It is highly unlikely that $Fe(phen)_3{}^{2+}$ would be oxidized to a higher oxidation state than $Fe(phen)_3{}^{3+}$ because of the instability of higher valence states of iron. Moreover, no outer-sphere reducing agent has been found to react by a two-electron transfer.[25] We therefore conclude that chromium(VI) is reduced in the rate-limiting step in a one-electron reaction to chromium(V) (reaction 11). *Oxalic acid thus acts as a catalyst for the reaction by lowering the activation energy of the chromium(VI) → chromium(V) transition.*

The decrease in activation energy may be due to an increase in the thermodynamic stability of chromium(V) in the presence of bidentate ligands such as oxalic acid[26] and α-hydroxy acids.[27] These acids complex strongly with chromium(V), but only weakly with chromium(VI), and therefore selectively stabilize chromium(V). The relative increase in the thermodynamic stability of chromium(V) will result in an increase in the reduction potential of the chromium(VI)/chromium(V) couple in the presence of oxalic acid. Considering that the reduction potential of $Fe(phen)_3{}^{3+}$ is 1.12 V,[28] whereas that of chromium(VI)/chromium(V) in the absence of oxalic acid is only 0.5-0.65 V,[29] we believe that the addition of oxalic acid must result in an increase of the reduction potential by at least 0.3 V for a smooth oxidation process to occur.

No evidence of accumulation of chromium(V) or chromium(IV) intermediates was found. The absence of detectable intermediates indicates that $Fe(phen)_3{}^{2+}$ is oxidized even more rapidly by chromium(V) and chromium(IV) than by chromium(VI).

From the ion-exchange product studies, it is known that a large fraction of Cr(III) has more than one coordinated oxalate (60-70%). Since no evidence for a second-order term in oxalic acid is present in the rate law, considerable anation must take place on either one or both intermediate oxidation states of chromium.

Little is known of the rates or equilibria of chromium(V) and chromium(IV) substitution reactions. Cooper and co-workers[30] studied the chromium(III) products after initiating reduction of chromium(VI) with one- and two-electron initiators (VO^{2+} and $N_2H_5^+$, respectively) in the presence of various potential ligands. Oxalate complexes of chromium(III) were found in these studies, but stoichiometric measurements indicated that significant amounts of oxalate were also oxidized, thus making quantitative interpretation of Cooper's results in terms of equilibrium concentrations of $Cr^{V}(ox)_n$ and $Cr^{IV}(ox)_n$ difficult.

Our Cr(III) product data are consistent with oxalate anation being of comparable rate to the Cr(V) or Cr(IV) reduction by $Fe(phen)_3^{2+}$. Since these reductions must be considerably faster than the rate-limiting reduction of Cr(VI), the substitution reactions of either or both Cr(V) and Cr(IV) must be at least an order of magnitude greater than $k_{11}(4 \times 10^5\ M^{-1}\ s^{-1})$.

Chromium(IV) is known to be reduced by oxalic acid.[30,31] Hasan and Roček[31] found in a competitive rate study that oxalic acid reduces chromium(IV) 1.83 times as fast as VO^{2+}, which is known to reduce chromium(IV) in a very fast reaction.[32] It is therefore somewhat surprising that no oxalic acid is oxidized even when oxalic acid is 10^3 more concentrated than $Fe(phen)_3^{2+}$. Thus, $Fe(phen)_3^{2+}$ must be at least 10^4 more reactive toward chromium(IV) than oxalic acid.

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Three-Electron Oxidations. 12. Chromium(V) Formation in the Chromic Acid Oxidation of 2-Hydroxy-2-methylbutyric Acid[1,2]

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Abstract: The chromic acid oxidation of 2-hydroxy-2-methylbutyric acid (HMBA) proceeds in two steps: (1) $2HMBA + 2Cr(VI) \rightarrow 2C_2H_5COCH_3 + 2CO_2 + Cr(V) + Cr(III)$; (2) $HMBA + Cr(V) \rightarrow C_2H_5COCH_3 + CO_2 + Cr(III)$. The first step of the reaction leads to the formation of an unusually stable chromium(V) intermediate complex and obeys the rate law $-d[Cr(VI)]/dt = [HCrO_4^-][HMBA](k_1 + k_{11}[H^+] + k''[HMBA])$. The reaction thus proceeds through a 1:1 and a 2:1 HMBA-Cr(VI) complex. A three-electron oxidation-reduction mechanism is proposed for the decomposition of the 2:1 complex. An iodometric analytical method for the determination of chromium(V) in the presence of chromium(VI), based on the high reactivity of iodide toward chromium(V), has been developed.

In a recently reported study of the chromic acid oxidation of glycolic acid,[3] we have shown that the reaction proceeds by two different mechanistic pathways, namely through intermediate complexes formed from chromic acid and either one or two molecules of the substrate. We proposed that the reaction going through the 2:1 glycolic acid–chromic acid complex proceeds by a three-electron oxidation mechanism in which chromium(VI) is reduced directly to chromium(III). The observation of a deuterium kinetic isotope effect of $k_H/k_D = 36$ indicating the simultaneous breaking of two carbon-hydrogen bonds in the rate-limiting step provided strong evidence in support of this proposal.

In this paper we wish to report the results of an investigation of the chromic acid oxidation of a tertiary hydroxy acid, 2-hydroxy-2-methylbutyric acid (HMBA), which obviously must react by a different mechanism. The only previous investigation of the chromic acid oxidation of tertiary 2-hydroxy acids reported in the literature[4-7] failed to reveal the formation of a