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Kinetics and Mechanisms of Oxidation of Lactic Acid by Chromium(VI) and Chromium(V)

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Received November 27, 1984

The oxidation of lactic acid (H_2L) by chromium(VI) has been found to proceed in two measurable steps, both of which give pyruvic acid as the primary product: $2Cr(VI) + 2CH_3CHOHCOOH \xrightarrow{2k_6} 2CH_3COCOOH + Cr(V) + Cr(III)$; $Cr(V) + CH_3CHOHCOOH \xrightarrow{k_5} Cr(III) + CH_3COCOOH$. Buildup and decay of chromium(V) intermediates accompany the decay of chromium(VI). Analysis for the intermediate [Cr(V)] in runs with excess lactic acid gives first-order rate constants: $2k_6 = [H_2L](k_0 + k_H[H^+] + k_L[H_2L])$, with $k_0 = 0.0007\ M^{-1}\ s^{-1}$, $k_H = 0.013\ M^{-2}\ s^{-1}$ and $k_L = 0.0021\ M^{-2}\ s^{-1}$ at 298 K; $k_5 = [H_2L](k_A + k_B[H^+]^2)$, with $k_A = 0.0023\ M^{-1}\ s^{-1}$ and $k_B = 0.027\ M^{-3}\ s^{-1}$ at 298 K. Activated states and mechanisms have been deduced for each step and compared with similar oxidations of other α-hydroxy acids and oxalic acid and cooxidations of oxalic acid and alcohols. The significant buildup of chromium(V) has consequences for the interpretation of many previously studied chromium(VI) oxidations.[1]

Introduction

The oxidation of oxalic acid,[2] the cooxidation of alcohols with oxalic acid and α-hydroxy acids,[3-5] and the oxidation of several α-hydroxy acids by acid chromate ion ($HCrO_4^-$)[6-8] are reported to involve initial three-electron reductions of $HCrO_4^-$ by substrate (S), producing radicals (R·). The radicals reduce additional Cr(VI) to Cr(V), giving products (P):

$$Cr(VI) + 2S \rightarrow CrS_2 \rightarrow Cr(III) + P + R\cdot \qquad (I)$$

$$\cdot R + Cr(VI) \rightarrow Cr(V) + P \quad \text{fast} \qquad (II)$$

$$Cr(V) + S \rightarrow Cr(III) + P \qquad (III)$$

The kinetics and mechanisms of Cr(VI) decay in acid solutions of such substrates have been extensively studied. Rate laws for Cr(VI) decay usually involve terms first order in substrate at low concentrations where reaction I may require two steps

$$Cr(VI) + S \rightarrow Cr(IV) + P \quad \text{slow} \qquad (Ia)$$

$$Cr(IV) + S \rightarrow Cr(III) + R\cdot \quad \text{fast} \qquad (Ib)$$

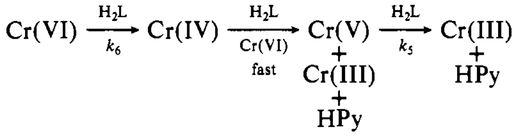
and terms second-order in substrate at high concentration in which reaction I may involve a one-step, three-electron reduction of Cr(VI) by two molecules of coordinated substrate.[2,6,7] Cooxidations involve a rate law that is first order in two different substrates.[3-5,9]

Growth and decay of [Cr(V)] intermediates has been observed, with "stability" for Cr(V) ascribed to complex formation with substrate.[9] Stable Cr(V) compounds with α-hydroxy acids having a tertiary alcohol group do form, and they have been isolated and characterized.[10] Studies of [Cr(V)] growth and decay have been sketchy[11,12] and not as yet revealing of mechanism except in cases where Cr(V) decay begins only after Cr(VI) disappears.[7-9] Buildup of [Cr(V)] ranges from small fractions of $[Cr(VI)]_0$[6] to a maximum of $^1/_2[Cr(VI)]_0$.[7-9]

This study using lactic acid as substrate was originally undertaken to fill in the series oxalic acid ($(COOH)_2$), glycolic acid ($CH_2OHCOOH$), lactic acid ($CH_3CHOHCOOH$), and 2-hydroxy-2-methylpropionic acid ($(CH_3)_2COHCOOH$). While this paper was in preparation, an article on the chromium(VI) oxidation of lactic acid appeared,[13] which did not include the growth and decay of Cr(V) in the kinetics study. This paper is the first to present *kinetics and mechanism of the reaction of Cr(V) intermediates with a reducing substrate*. Results here obtained indicate that a reexamination and/or reinterpretation of Cr(VI) and Cr(V) kinetics in the other systems should be undertaken. For studies[7-9] in which the Cr(VI) and Cr(V) reactions are clearly separable, we have been able to reinterpret published results and indicate simple criteria for detecting such separability. This study provides some clues for explanation of the widely differing product patterns and rate laws previously observed for very similar substrates.

Consecutive Reactions for the Formation and Decay of Cr(V) Intermediates

We have found it possible to follow the consecutive reactions



$$Cr(VI) \xrightarrow[k_6]{H_2L} Cr(IV) \xrightarrow[\substack{Cr(VI)\\ \text{fast}}]{H_2L} \begin{matrix} Cr(V) \\ + \\ Cr(III) \\ + \\ HPy \end{matrix} \xrightarrow[k_5]{H_2L} \begin{matrix} Cr(III) \\ + \\ HPy \end{matrix} \qquad (IV)$$

H_2L = lactic acid, $CH_3CHOHCOOH$
HPy = pyruvic acid, $CH_3COCOOH$

Two Cr(VI) are consumed in the formation of one Cr(V).

$$(\text{rate})_6 = \frac{-d[Cr(VI)]}{dt} = 2k_6[Cr(VI)] \qquad (1)$$

The integrated rate law for eq 1 is

$$[Cr(VI)]_t = [Cr(VI)]_0 e^{-2k_6 t} \qquad (2)$$

$$(\text{rate})_5 = \frac{d[Cr(V)]}{dt} = k_6[Cr(VI)] - k_5[Cr(V)] \qquad (3)$$

The integrated rate law for eq 2 is

$$[Cr(V)] = \frac{k_6[Cr(VI)]_0}{2k_6 - k_5}(e^{-k_5 t} - e^{-2k_6 t}) \qquad (4)$$

[Equation 4 is interesting in that k_6 appears in the numerator of the preexponential term and $2k_6$ appears in the denominator and in an exponential term as a consequence of only half of the Cr(VI) reaching Cr(III) by way of a Cr(V) intermediate.] We have been able to follow the growth and decay of Cr(V) as a function of $[H_2L]$ and $[H^+]$ to derive rate laws and mechanisms

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[1] Roček has made direct measurements of k_5 using $[Cr^VO(C_2H_5C(O)(CH_3)COO)_2]^-$ + $CH_3CH(OH)COOH$, finding a value of 0.0045 for k_A—about twice our value: Krumpolc, M.; Roček, J. *Inorg. Chem.* **1985**, *24*, 617-621.

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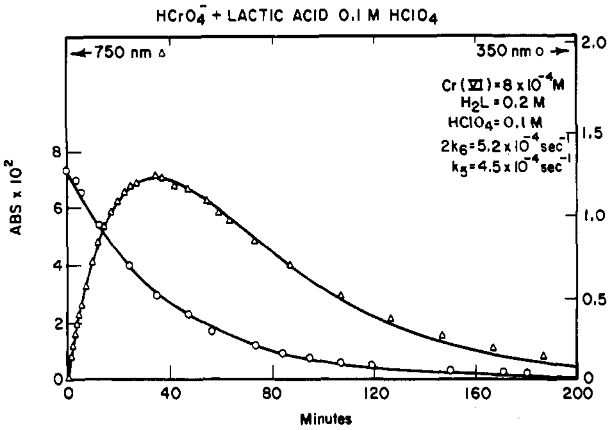

Figure 1. Spectrophotometric determination of $2k_6$ and k_5: absorbance vs. time curves for Cr(VI) + Cr(V) oxidation of lactic acid at 350 and 750 nm. Constants ($2k_6$ and k_5) calculated by least-squares fit of points at 750 nm were used to plot both curves. $\epsilon_{750}{}^6 = 38$; $\epsilon_{350}{}^5 = 1200$; $\epsilon_{350}{}^6 = 1560$. Cary 16 and Beckman Acta recording spectrophotometers were employed.

for the reactions of Cr(VI) as $HCrO_4^-$ and Cr(V) as $H_2CrO_4^-$ (postulated) with lactic acid.

Treatment of Absorbance vs. Time Curves at 350 and 750 nm

At 750 nm. Only Cr(V) absorbs.[6-9] ϵ^V has been estimated by Roček et al. in several α-hydroxy acid systems (38 in $C_2H_5C(CH_3)(OH)COOH$,[7] 34 in $C_1H_5CHOHCOOH$,[8] etc.). We used $\epsilon^V = 38$ to estimate k_6 from initial rates. Computer fits to data require initial estimates of k_6 and k_5 that will converge as the computer searches for minima in least-squares fits to eq 4.

(a) k_6 could be estimated from initial rates if ϵ^V is known.

(b) T_{max} (time of maximum absorbance) = $(\ln (2k_6/k_5))/(2k_6 - k_5)$. If $2k_6 = k_5$, $T_{max} = 1/k_5$. This gives the order of magnitude for $2k_6$ and k_5 when they are close. Then $2k_6 > 1/T_{max} > k_5$ or $2k_6 < 1/T_{max} < k_5$ can be explored for improved estimates.

(c) If the tails of absorbance vs. time curves show first-order characteristics, either $2k_6$ or k_5 can be estimated from an analysis of the tail and the other from T_{max}. Ten or more data points together with estimates of $2k_6$ and k_5 were fit by a least-squares program to the equation

$$A_5 = \frac{k_6\epsilon^V[\mathrm{Cr(VI)}]_0}{2k_6 - k_5}(e^{-k_5t} - e^{-2k_6t}) \qquad (5)$$

where A_5 = absorbance due to Cr(V) at 750 nm and ϵ^V is molar absorbance of Cr(V).

A simulated curve was then plotted along with the data points as in Figure 1.

At 350 nm with $\epsilon_{350}{}^{VI} = 1560$ and $\epsilon_{350}{}^V = 1200$ (Roček),[7,10] absorbance vs. time curves were fit to the equation

$$A = A_6 + A_5 = A_6{}^0e^{-2k_6t} + \frac{k_6\epsilon^V[\mathrm{Cr(VI)}]_0}{2k_6 - k_5}(e^{-k_5t} - e^{-2k_6t}) \qquad (6)$$

Figure 1 shows the kind of agreement obtained for one run recorded at each wavelength on two different spectrometers at the same time.

It should be noted that the two rate constants can be estimated by application of eq 4 or 5 in the absence of knowledge of ϵ^V, since the preexponential term is constant during any given run. However, the solution of eq 4 or 5 is ambiguous as to which constant is which. We have found the two constants to be quite different functions of the concentrations of substrate and hydrogen ion such that reversal of $2k_6 > k_5$ to $2k_6 < k_5$ can occur in this, the oxalic acid, and probably the glycolic acid systems, when [H^+] and [substrate] are varied over wide ranges. In the oxalic acid[2a] and the glycolic acid[6] studies previously reported, kinetics were derived from the linear tail of the curves for ln (A^{350}) vs. t when both [Cr(VI)] and [Cr(V)] are present. In the mandelic acid[9] and 2-hydroxy-2-methylbutanoic acid[7] studies, rapid Cr(V) decay did not occur until Cr(VI) decay was complete, allowing Cr(VI) decay, the primary object of each study, to be studied directly.

Experimental Section

Analytical grade sodium and potassium dichromate, perchloric acid, and ultrapure lactic acid were used without further purification. A sample of 85% syrupy lactic acid was diluted in water and allowed to hydrolyze to eliminate polymers. A reactive impurity that gave initial fast reduction of Cr(VI) was eliminated by vacuum distillation at 0.05 torr. The fraction boiling from 95 to 105 °C was collected and stored frozen at −20 °C. Crystallization was an indication of purity. Melting (17–20 °C) led to polymerization. Mol wt: 94 ± 3 by titration with NaOH. Results obtained with purified lactic acid agree with those obtained by using purchased "ultrapure" lactic acid.

Synthesis of α-Deuteriolactic Acid ($CH_3CD(OH)COOH$).[14] Methylmalonic acid in ether was treated with excess bromine and evaporated to dryness. The product was dissolved in D_2O, dried, and then refluxed in D_2O for 30 h to give 2-bromo-2-deuteriopropionic acid. Treatment with $ZnCO_3$ suspension in aqueous solution gave $Zn(CH_3CD(OH)COO)_2$, which precipitates on addition of ethanol. An aqueous solution of the zinc salt is converted to acid with Amberlite IR-120 ion-exchange resin in its acid form and the α-D lactic acid obtained by vacuum distillation (0.05 torr, 90–105 °C) and freezing. Analysis of the product by NMR indicated 90% α-D and 10% α-H lactic acid was formed. Measuring the deuterium isotope effect thus required application of eq 7 and 8 to calculate $2k_6{}^D$ and $k_5{}^D$ from observed rate constants.

$$2k_6{}^{obsd} = 0.1(2k_6{}^H) + 0.9(2k_6{}^D) \qquad (7)$$

$$k_5{}^{obsd} = 0.1k_5{}^H + 0.9k_5{}^D \qquad (8)$$

Analysis for Organic Oxidation Products. Reacting solutions were purged with nitrogen and CO_2 and CH_3CHO trapped in solutions of KOH and 2,4-dinitrophenylhydrazine,[6] respectively. Pyruvic acid was measured colorimetrically at 456 nm by using salicylaldehyde after removal of acetaldehyde.[15] Acetaldehyde was never detected among the products, and CO_2 was produced in small variable amounts up to 15% of the Cr(VI) consumed, in agreement with the recent findings of Mahapatro et al.[13] No attempt was made to analyze reaction mixtures for acetic acid.

Chromium(V) intermediates were detected and measured spectrophotometrically at 750 nm on Beckman Acta and Cary 16 recording spectrometers and a Beckman DU with a Gilford recorder. An ESR signal for Cr(V) was studied with a Variant E-9 ESR spectrometer. Figure 2 shows a typical ESR spectrum obtained on a reacting solution and a typical growth and decay curve for peak to peak heights of Cr(V) EPR signals vs. time. The signal is characteristic of signals previously obtained in similar systems,[11,12] including satellites due to the natural abundance of ^{53}Cr. The decay is too steep in comparison with other [Cr^V] measurements, indicating peak to peak heights are increasingly too small. Buildup of paramagnetic Cr^{3+} broadens the Cr(V) signal as the reaction proceeds. The rising portion of the curve fits a variation of eq 4 quite well but T_{max} observed by this technique is usually early due to Cr(III) broadening of the Cr(V) ESR signal (Table II). Integrated signals will be necessary for quantitative Cr(V) measurement by this technique. Such were not accessible when these studies were made. Consequently, the quantitative measurements of [Cr(V)] vs. time were made spectrophotometrically.

Results

Observed rate constants ($2k_6{}^{obsd}$) and ($k_5{}^{obsd}$) were deduced from data obtained at both 750 and 350 nm. For a few runs at high (>1.0 M) [lactic acid] and high acidity (>0.3 M H^+) the decay of Cr(V) was biphasic. However, at low acidities, runs from 0.05 to 1.0 M lactic acid gave values of $2k_6{}^{obsd}$ and $k_5{}^{obsd}$ that fit experimental curves at both wavelengths extremely well over the full course of the reaction (Figure 1). Table I summarizes values of $2k_6{}^{obsd}$ and $k_5{}^{obsd}$ for various concentrations of lactic acid and hydrogen ion. Runs exhibiting biphasic Cr(V) decay showed slow first-order decay of Cr(V) after Cr(VI) was completely consumed. Values of $k_5{}^{slow}$ for several runs, together with those of $2k_6{}^{obsd}$ and $k_5{}^{obsd}$ at varying concentrations of H^+ and lactic acid (H_2L), are found in Table I.

Kinetics and Mechanism of Chromium(VI) Decay.

$$2\mathrm{Cr(VI)} + 2\mathrm{H_3CHOHCOOH} \xrightarrow{2k_6} \mathrm{Cr(V)} + \mathrm{Cr(III)} + 2\mathrm{CH_3COCOOH} \quad \mathrm{(V)}$$

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Table I. Variation of $2k_6$ and k_5 with $[H^+]$ and $[H_2L]$[a]

$[H_2L]$, M	$[H^+]$, M	$10^3(2k_6^{obsd})$, s^{-1}	$10^3(2k_6^{calcd})$, s^{-1}	$10^3k_5^{obsd}$	$10^3k_5^{calcd}$	$10^3k_5^{slow}$
1.0	0.1	4.4	4.3	2.4	2.3	
1.0	0.01	3.1	2.9	2.7	2.3	
1.0	0.36	7.9	8.0	5.5	5.9	
1.0	0.86		12.4[b]	[c]	22.3[b]	4.4
1.0	0.46	9.2	9.5	4.0	8.0	4.0
1.50	0.102	8.8	8.2	6.2	4.0	3.5
1.44	0.102	7.8	7.4	3.4	3.9	2.5
0.83	0.10	2.8	3.1	2.2	2.0	
0.67	0.10	2.6	2.4	1.6	1.6	
0.5	0.10	1.6	1.6	1.31	1.29	
0.47	0.10	1.5	1.5	1.76	1.32	
0.33	0.10	0.81	0.95	0.84	0.86	
0.20	0.10	0.52	0.51	0.52	0.52	
0.17	0.10	0.31	0.42	0.41	0.43	
0.10	0.10	0.19	0.23	0.34	0.26	
0.05	0.10	0.10	0.12	0.15	0.13	
1.90	0.016	9.8	9.4	6.8	4.5?	3.5
0.20	0.30	1.13	1.10	1.15	0.94	
0.20	0.84	2.60	2.64	3.90	4.30	3.9
0.946[d]	0.10	5.2[f]		3.2[f]		
0.946[e]	0.10	1.11[f]		0.62[f]		
0.473[d]	0.10	1.11[g]		2.50[g]		
0.473[e]	0.10	0.25[g]		0.49[g]		

[a] $10^3[Cr(VI)]_0 = 0.8–1.0$ M; T = 20 °C. [b] $T_{max}^{calcd} = 59$ s; $T_{max}^{obsd} < 90$ s. [c] too fast to measure. [d] α-Lactic acid. [e] α-Deuteriolactic acid. [f] At 25 °C. [g] $[Cr(VI)]_0 = 0.0125$ M.

Table II. T_{max} for Cr(V) Heights of ESR Signals[a]

$[H_2L]$, M	μ, M	$[H^+]$, M	$2k_6^{calcd\,b}$	$k_5^{calcd\,b}$	$T_{max}^{calcd,b}$, min	$T_{max}^{obsd,b}$, min
0.33	0.33	0.007	5.3×10^{-4}	7.6×10^{-4}	26	27
0.092	0.50	0.10	2.5×10^{-4}	8.2×10^{-4}	72	60
0.115	0.5	0.10	2.54×10^{-4}	2.65×10^{-3}	64	65
0.184	0.95	0.10	4.79×10^{-4}	4.4×10^{-4}	36	28
0.368	0.5	0.10	1.06×10^{-3}	8.8×10^{-4}	18	11
0.460	0.5	0.10	1.47×10^{-3}	1.1×10^{-3}	13	11

[a] $[Cr(VI)] = 5 \times 10^{-4}$ M. [b] $2k_6$ and k_5 calculated from eq 6 and 8; $T_{max}^{calcd} = \ln(2k_6/k_5)/(2k_6 - k_5)$.

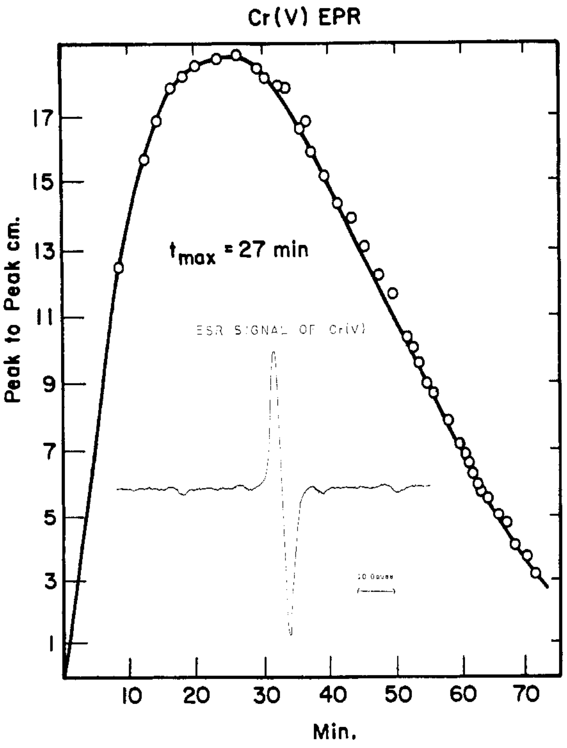


Figure 2. Peak to peak heights of ESR signals due to Cr(V) vs. time. $[Cr(VI)]_0 = 5 \times 10^{-4}$ M; $[H_2L] = 0.33$ M; $[NaClO_4] = 0.33$ M. Inset: ESR signal recorded at T_{max} for a run with $[HCrO_4^-] = 5 \times 10^{-4}$ M, $[H_2L] = 0.092$ M, $[H^+] = 0.1$ M, $\mu = 0.5$ M ($NaClO_4$), $g = 1.9780$, and half-width = 4.1 G. Signals gradually broaden as [Cr(III)] builds up during a run.

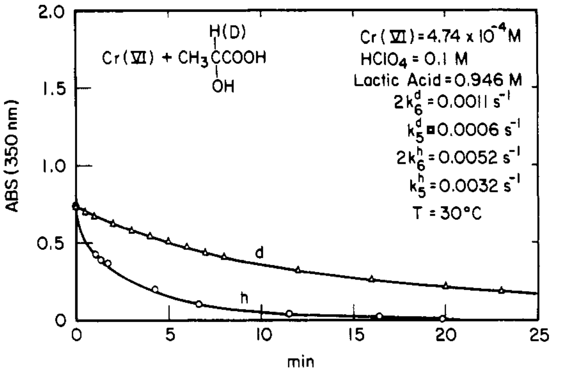


Figure 3. Deuterium isotope effect. 90% percent α-deuteriolactic acid was used to obtain curve d.

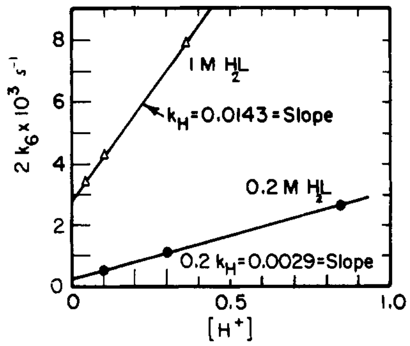


Figure 4. Dependence of $2k_6$ on $[H^+]$ in 1.0 and 0.2 M lactic acid. $2k_6 = [H_2L](k_0 + k_H[H^+] + k_L[H_2L])$. Intercepts: $2.8 \times 10^{-3} = k_0 + k_L$; $2.2 \times 10^{-4} = 0.2(k_0 + 0.2k_L)$. $k_0 = 0.0007$ M^{-1} s^{-1}; $k_H = 0.015$ M^{-2} s^{-1}; $k_L = 0.0021$ M^{-2} s^{-1}.

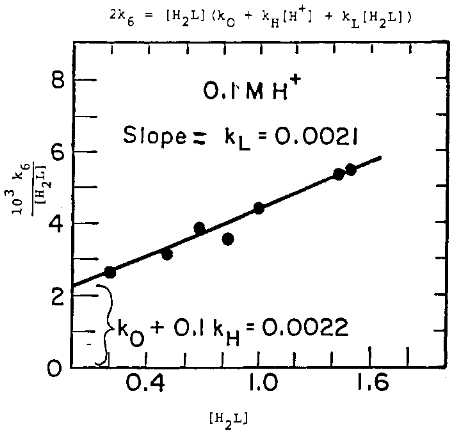


Figure 5. Test of eq 9: $2k_6$ as a function of [lactic acid] at 0.1[H^+]. Intercept = 0.0022 = $k_0 + 0.1k_H$; slope = k_L = 0.0021 M^{-2} s^{-1}; k_0 = 0.0007 M^{-1} s^{-1}; k_H = 0.015 M^{-2} s^{-1}.

Variations of $2k_6$ with concentrations of lactic acid and hydrogen ion, shown graphically in Figures 4 and 5, fit the equation

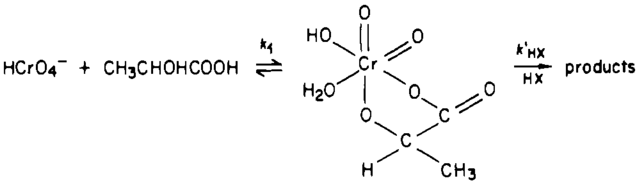
$$2k_6 = [H_2L](k_0 + k_H[H^+] + k_L[H_2L]) \qquad (9)$$

and the complete rate law for reaction I is

$$d[Cr(VI)]/dt = 2k_6[Cr(VI)] = [Cr(VI)][H_2L](k_0 + k_H[H^+] + k_L[H_2L]) \qquad (10)$$

Equation 10 is of the same form as found by Mahapatro et al.[13] in a study that monitored Cr(VI) iodometrically and reported first-order behavior of "chromium(VI)". We observed deviations from first-order decay of absorbance at 350 nm at short times and significant chromium(V) formation under all conditions of reaction. Values of rate constants k_0 = 0.0007 M^{-1} s^{-1}, k_H = 0.014 M^{-2} s^{-1}, and k_L = 0.0021 M^{-2} s^{-1} were used to find $2k_6^{calcd}$ in Table I and may be compared with values of 0.0002, 0.044, and 0.0053 found when the presence of Cr(V) was ignored.[13]

The deuterium isotope effect was measured for only two experiments—one at 350 nm, Figure 3, and the other at 750 nm using $[Cr(VI)]_0$ = 0.0125 M in a 1.0-cm cell. Allowance had to be made for $Cr_2O_7^{2-}$ formation. $k_6^{H/D}$ was found to be 7.2 and 8.0 for 0.473 M lactic acid (750 nm) and 0.946 M (350 nm) lactic acid, respectively, in 0.1 M $HClO_4$, characteristic of a primary isotope effect involving one hydrogen. We can thus assume that the hydrogen atom on the α-carbon dissociates as the activated state decays to the products, Cr(IV) + propionic acid. It is not presently possible to determine if the effect is the same in each of the three terms of the rate law. We postulate that the three terms be ascribed to different bases assisting the removal of proton from the α-carbon atom. This should give approximately the same isotope effect in each term. From the rate law we deduced the mechanism



(VI)

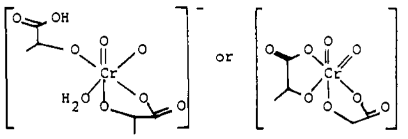
where $k_0 = K_1k'_{H_2O}$, $k_H = K_1k'_{H_3O^+}$, and $k_L = K_1k'_{H_2L}$. Rate constants for general-acid catalysis are given by

$$k_0 = k'_0K_1(H^+)(OH^-) = k'_0K_1K_w$$

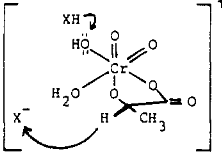
$$k_H = k'_HK_1 \quad K_a \text{ for } H^+ = 1$$

$$k_L = k'_LK_1[H^+][HL^-] = k'_LK_1K_{a(H_2L)}$$

k'_0K_1 can be estimated as 7 × 10^{10}. K_1 is not kinetically detectable and so has an upper limit of ~0,1 M, giving a lower limit for k'_0 of 7 × 10^{11} s^{-1} near the upper limit for proton-transfer rates. Limiting values of k'_H and k'_L then become 0.015 s^{-1} and 0.21 s^{-1}, respectively. Relative effectiveness of base attack on the α-H of lactic acid is $OH^- >>> HL^- > H_2O$, which is quite reasonable. H_2L can conceivably form



suitable for three-electron transfer to Cr as has been suggested for other rate laws involving terms second order in substrate.[6-9] We prefer substrate (H_2L) acting as a general acid because of its weak tendency toward coordination and the plausible need for the assistance of a conjugate base of a general acid to remove a proton from the α-carbon in the activated state for a two-electron process.



The postulate of base-assisted deprotonation of α-C–H is the simplest of several alternatives. H· or H^- transfer to Cr(VI) has been suggested. Such is consistent with the deuterium isotope effect but requires another assumption regarding the term second order in substrate. Such a term results from formation of a 1:2 active complex, CrL_2, in other systems.[3-5] Our postulate has the nondefinitive virtue of simplicity cum plausibility in the absence of criteria for choice among alternatives.

Following the rate-determining step, two rapid reactions (eq VII and VIII) give the Cr(V) observed.

$$Cr(IV) + CH_3CH(OH)COOH \rightarrow Cr(III) + CH_3C(H)(\dot{O})COOH \text{ or } CH_3\dot{C}(OH)COOH \qquad (VII)$$

$$CH_3CH(\dot{O})COOH + HCrO_4^- \rightarrow CH_3C(O)COOH + Cr(V) \qquad (VIII)$$

Cr(IV) has most commonly been postulated to oxidize α-hydroxy acids by breaking C–C bonds to give CO_2^- radicals. CO_2 is virtually not a product of the reaction under study. Alcohols may be oxidized to radicals by Cr(IV).[11] One may also conjecture the possibility of Cr(IV) and Cr(VI) effecting a two-electron oxidation of substrate:

$$Cr^{IV}L + Cr(VI) \rightarrow Cr(III) + Cr(V) + HPy \qquad (IX)$$

Such a process has been observed in the oxidation of N_2H_4 by VO_2^+, in which an activated state of $(VO_2)_2N_2H_4$ produces $2VO^{2+}$ (one electron each) and $^1/_2N_2$, the two-electron oxidation product of N_2H_4.[16] Cr(IV) is known to trap substrate on its way to Cr(III) in similar systems.[17]

Kinetics and Mechanism of Cr(V) Oxidation of Lactic Acid. Values for k_5^{obsd} obtained at various concentrations of hydrogen ion and lactic acid (Table I) are plotted in Figure 5 where $k_5^{obsd}/[H_2L]$ vs. $[H^+]^2$ gives a straight line with an intercept from which the rate law is derived:

$$k_5^{obsd} = H_2L(k_A + k_B[H^+]^2) \qquad (11)$$

$$d[Cr(V)]/dt = [H_2CrO_4^-][H_2L](k_A + k_B[H^+]^2) \qquad (12)$$

where k_A = 2.3 × 10^{-3} s^{-1} M^{-1} and k_B = 2.7 × 10^{-2} s^{-1} M^{-3}. Deviations from this rate law occur at high [H_2L] and low [H^+], where two runs suggest a third term $k_C[H_2L]^2$, with k_C ~ 4 × 10^{-4}. More data are required to confirm the need for and the form of this term.

A primary deuterium isotope effect is observed (Figure 3) with $k_5^{H/D}$ ≅ 10 in 0.946 M lactic acid and 0.1 M $HClO_4$, indicating

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(17) Cooper, J. N.; Staudt, G. E.; Smalser, M. L.; Settzo, L. M.; Haight, G. P. *Inorg. Chem.* **1973**, *12*, 2075–2079.

Table III. Chromium(V) Decay

substrate	probable $k_5/2k_6$	products	mechanism	ref
oxalic acid	≥ 1	$2CO_2$	one step, $2e^-$	2
glycolic acid	≥ 1	$H_2COCOOH$	one step, $2e^-$	6
lactic acid	~ 1	$CH_3COCOOH$	one step, $2e^-$	13, *a*
lactic acid	<1	CO_2, CH_3CHO?[c]	radical chain, $1e^-$?	13, *a*
mandelic acid	$<<1$[d]	$PhC(H)(O) + CO_2$	radical chain, $1e^-$	8, *b*
$C_2H_5C(CH_3)(OH)COOH$	$<<1$[d]	$C_2H_5COCH_3 + CO_2$	radical chain, $1e^-$	7, *b*
$C_2H_5C(CH_3)(OH)COOH + (CH_3)_2CHOH$	$<<1$[d]	$C_2H_5COCH_3 + CO_2$	radical chain, $1e^-$	9, *b*
$(CH_3)_2CHOH$	>1	$(CH_3)_2C{=}O$	one step, $2e^-$	11

[a] This work. [b] Mechanism proposed in this paper. [c] Not observed. [d] Cr(V) oxidation of mandelic acid and 2-methyl-2-hydroxybutyric acid begins only after Cr(VI) disappears. The value of k_5 may in fact be higher than $2k_6$, but the reaction is inhibited by Cr(VI), a proven radical trap.[17]

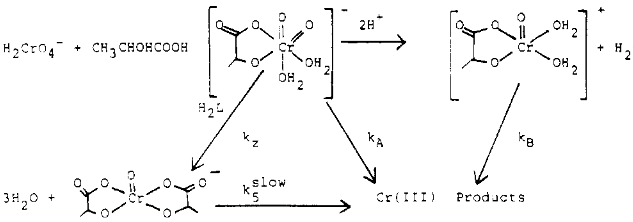
Table IV. Products of Oxidation of α-Hydroxy Acids by Cr(VI) and Cr(V)

substrate acid	radicals	mol/mol of Cr(VI) reduced			
		RCOCOOH	RCHO or R_2CO	RCOOH	CO_2
$CH_2OHCOOH$	CO_2^-	1.5–1	0–0.5	0	0–0.5
$CH_3CHOHCOOH$	$CH_3C(OH)COOH$	1.5	0	0	0–0.16
$C_6H_5CHOHCOOH$	$C_6H_5C{=}O$	0.25	0.75	0.25	1.0
	$C_6H_5CH{-}OH$	0.44	0.97	0.04	0.94
	(extrema)	0.01	0.61	0.64	(1.25)
$C_2H_5C(CH_3)(OH)COOH$	$C_2H_5C(CH_3)OH$ or $CO_2^-\cdot$		1.5[a]		1.5
$HOOCCOOH$	$CO_2^-\cdot$				3.0

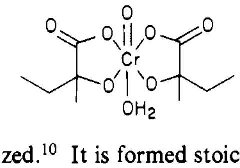
[a] $CH_3COC_2H_5$.

α-C–H bond scission in the active state for the two-electron oxidation.

The second term ($k_B[H^+]^2$) in the rate law is thought to involve the conversion of Cr(V) from a CrO_2^+ octahedral center to CrO^{3+} square-pyramidal center characteristic of d^1 systems (cf. VO^{2+}). The monolactate of each undergoes rapid internal redox to Cr(III) and pyruvic acid in the mechanism



A second phase of [Cr(V)] decay is observed at high $[H_2L]$ and/or high $[H^+]$, where slow disappearance of Cr(V) is observed after [Cr(VI)] reaches zero. The rate may be independent of concentrations of $HClO_4$ and lactic acid, suggesting first-order decay by internal redox of a completely formed Cr(V) complex. Data are not sufficient to make a firm conclusion on this point. These results suggest the above mechanism for Cr(V) reactions with lactic acid. The stable complex



has been characterized.[10] It is formed stoichiometrically during chromium(VI) oxidations involving 2-methyl-2-hydroxybutanoic acid (HMBA) and decays only after Cr(VI) disappears. By analogy, it appears reasonable that a similar complex with Cr(V) and lactic acid would be responsible for the delayed lactic acid reductions of Cr(V).

Discussion

Chromium(V) Formation and Decay during Cr(VI) Oxidations of Alcohols and Carboxylates. The observation in this study that reduction of Cr(V) may proceed at rates comparable to that of Cr(VI) and that steady-state concentrations of Cr(V) may be up to 20% of the total chromium present in solution casts doubt on the validity of many studies of chromate oxidation where [Cr(VI)] has been monitored at 350 nm or by iodimetry on quenched solutions. The recent study[13] of chromium(VI) oxidation of lactic acid reported first-order loss of *oxidizing equivalents*. Chromium(V) formation was observed but was ignored because a maximum concentration of "only" 10% of the total [Cr] was obtained. However, 10% of the total could be a much higher percentage of the oxidizing equivalents remaining at the time of quenching. We have found up to 20% of the total chromium as chromium(V) and close to equal concentrations of chromium(VI) and chromium(V) in latter stages of several runs. It is interesting, therefore, that the rate law for chromium(VI) oxidation of lactic acid is found to be of the same form in the two studies, albeit with rather different values for the three rate constants.

In the chromium(VI) oxidations of oxalic acid[2a] and glycolic acid[6] first-order decay of absorbance at 350 nm occurred after an initial buildup of Cr(V). The rate constants obtained were ascribed to $2k_6$ for chromium(VI) decay—a valid assumption only if $2k_6 < k_5$. [$2k_6$ is our notation, assuming $2Cr(VI) \xrightarrow{2k_6} Cr(III) + Cr(V) \xrightarrow{k_5} Cr(III)$ for the stepwise progress of Cr(VI) to Cr(III).] Reversal of this inequality occurs at conditions of low [lactic acid] and high acidity in the present study. A similar study of [Cr(V)] growth and decay in oxalic acid and glycolic acid should be made in dilute aqueous acid solutions. Such a study of the oxidation of oxalic acid has been made in 50% acetic acid without detailed analysis of the effects of changing acid and substrate concentrations on k_5^{obsd}.[12] Similarly, Wiberg and Schäfer[11] determined k_6^{obsd} and k_5^{obsd} from the growth and decay of Cr(V) during the oxidation of 2-propanol in 85% acetic acid. Esters $ROCrO_3^-$ and $(RO)_2CrO_2$ are formed in detectable amounts in the essentially nonaqueous medium. Mechanisms of Cr(V) oxidations were not addressed, but the detection of the diester of Cr(VI) suggests that ester formation with Cr(V) should also occur and that the oxidation of alcohols by chromium(VI) and chromium(V) proceeds according to eq I–III for the diester and eq Ia,b, II, and III for the monoester. Ester formation is not detectable when alcohols are oxidized in dilute perchloric acid solutions.[18]

Chromium(V) decay proceeds by two processes in the present study that may be compared with Cr(V) reactions (A) with glycolic acid[6] and oxalic acid[1] on the one hand and (B) with mandelic acid[8] and HMBA[7] and the Cr(V) cooxidation of 2-propanol and HMBA[9] on the other, as shown in Tables III and IV. Reactions A obey eq 4 throughout each kinetics run, whereas reactions B do not show Cr(V) decay until Cr(VI) disappears and do not obey eq 4 (Table V).

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(18) Haight, G. P.; Smentowski, F.; Rose, M.; Heller, C. *J. Am. Chem. Soc.* **1968**, *90*, 6325–6328.

Table V. T_{max} for Delayed Cr(V) Decay

	T_{max}^{obsd}, s	T_{max}^{calcd},[b] s	$10^3(2k_6)$[a]	10^3k_5[a]	ref
HMBA +	1300	1100	1.95	0.32	9
$(CH_3)_2CHOH$	2800	1800	1.05	0.24	9
HMBA	270	65	9.5	23	7
	3600	650	6.4	3.9	7
MA	840	389	3.0	2.18	8
	3600	553	0.64	3.95	8

[a] Estimated from data in references. [b] T_{max}^{calcd} would be observed if the reduction of Cr(V) occurred concurrently with Cr(VI) and eq 4 would be applicable.

Roček[9] has proposed a mechanism for chromium(V) oxidation of HMBA based on the isolation of a complex $[Cr^VO(HMBA\text{-}2H)_2^-]$[10] and an observation that the reaction appears first order in HMBA. We suggest the following alternative mechanism to explain the rapid decay of Cr(V) only after Cr(VI) has been consumed:

$$\mathrm{Cr(VI)} + \mathrm{HMBA} \xrightarrow{2k_6} \mathrm{Cr(IV)} + CO_2 + CH_3COC_2H_5 \qquad \text{(II-1)}$$

$$\mathrm{Cr(IV)} + \mathrm{HMBA} \xrightarrow{\text{fast } k_4} \mathrm{Cr(III)} + CO_2^- + CH_3COC_2H_5 \qquad \text{(II-2)}$$

$$\mathrm{Cr(VI)} + CO_2^- \xrightarrow{k^r_6} \mathrm{Cr(V)} \qquad \text{(II-3)}$$

$$\mathrm{Cr(V)} + 2\mathrm{HMBA} \rightleftharpoons [\mathrm{Cr^VO(HMBA\text{-}2H)_2}] \qquad \text{(II-4)}$$

$$CO_2^- + [\mathrm{Cr^VO(HMBA\text{-}2H)_2}] \xrightarrow{k^r_5} \mathrm{Cr(IV)} + CO_2 \qquad \text{(II-5)}$$

$$\mathrm{Cr(IV)} + \mathrm{HMBA} \xrightarrow{k_4} \mathrm{Cr(III)} + CO_2^- + CH_3COC_2H_5 \qquad \text{(II-2)}$$

$$k^r_6 >> k^r_5, \text{ or Cr(VI) inhibits (II-5)}$$

If the steady-state concentration of radical CO_2^- (or HCO_2) is given by $[CO_2^-] = 2k_6[\mathrm{Cr(VI)}][\mathrm{HMBA}]/k^r_6[\mathrm{Cr(VI)}] = (2k_6/k^r{}_6^-)[\mathrm{HMBA}]$, the first-order dependence on HMBA is understood. When Cr(V) becomes competitive as a radical trap, then the chain reaction proceeds. The disappearance of Cr(V) has features similar to autocatalytic processes as would be the case if an inhibitor (Cr(VI)) were being removed at the start of the process.

The oxidation of mandelic acid (MA) by chromium(V) follows the same radical-chain mechanism shown above. The presence of the phenyl group stabilizes radicals on the α-carbon atom. (CO_2^- is not trapped by acrylonitrile, etc.[8]) Reactions II-1ma and II-3ma compete with (II-1) and (II-2). Step II-1 is virtually

$$\mathrm{Cr(VI)} + \mathrm{MA} \xrightarrow{2k_6} \mathrm{Ph\dot{C}O} + CO_2 + \mathrm{Cr(III)} \quad \text{(3 e)} \quad \text{(II-1ma)}$$

$$\mathrm{Ph\dot{C}O} + \mathrm{Cr(VI)} \rightarrow \mathrm{PhCOOH} + \mathrm{Cr(V)} \quad \text{(II-3ma)}$$

eliminated with α-deuteriomandelic acid in favor of (II-1ma).

Mandelic acid, though more reactive with Cr(VI), prefers C–C scission to C–H scission at the α-carbon and can stabilize Cr(V) sufficiently to prevent oxidation by Cr(V) to phenylglyoxylic acid. Actually the C–C bond scission is effected by Cr(IV) if the radical-chain mechanism is correct, in keeping with previous perceptions that Cr(IV) is an effective agent for that process.[6–9,13]

For the cooxidation of HMBA and 2-propanol, the mechanism is modified by the process

$$\mathrm{HMBA} + (CH_3)_2CHOH + \mathrm{Cr(VI)} \rightarrow (CH_3)_2C{=}O + C_2H_5(CH_3)C{=}O + CO_2^{-}\cdot \quad \text{(II-1cox)}$$

taking place instead of (II-1) and (II-2). We feel the preference of Cr(V) for C–C bond scission in this case is due in part to the blocking of 2-propanol interaction with chromium(V) by the formation of the stable complex $CrO(MBA)_2^-$, which can be oxidized only by C–C bond scission. This is a subtle point since oxalic acid (C–C rupture) and 2-propanol (C–H rupture) are both oxidized competitively by Cr(V) during their cooxidation,[3] and the α-C on mandelic acid is *not* oxidized by C–H scission with Cr(V).[8] Clearly a combination of factors is operating in the variable preferences shown for alternative pathways in the several cases studied so far, and one cannot use C–H vs. C–C bond scission to distinguish one- and two-electron processes.

Table VI. Rate Constants for $2k_6$ Terms

substrate	10^4k_0	10^2k_H	10^3k_L	ref	pK_a[16]
lactic acid[a]	7 (2)	1.4 (4.4)	2.1 (5.3)	12, *b*	3.86
mandelic acid[a]	9.2	7.6	7.2	8	3.41
HMBA[c]	15	3.4	7.2	9	3.54

[a] At 25 °C. [b] This work. [c] At 80 °C.

We propose that the radical-chain mechanism (eq II-5 and II-2) describes the minor second phase (k_5^{slow} in Scheme I) in chromium(V) oxidation of lactic acid. If such is the case, the radical-chain mechanism for that phase could account for the small but positive yield of CO_2. The meager evidence described here indicates that the rate of decay of a $Cr^VOL_2^-$ complex may be independent of $[H_2L]$ and $[H^+]$.

Three-Electron Oxidations by Cr(VI). Recent investigations of chromate oxidations of α-hydroxy acids were undertaken by Roček and co-workers following their discovery of "cooxidation" of oxalic acid and primary or secondary alcohols in which complexes $[\mathrm{Cr^{VI}(OCHR_2)(C_2O_4)}]$ appeared to undergo internal transfer of three electrons to give Cr(III), $R_2C{=}O$, CO_2, and CO_2^- radicals, which reduced a second Cr(VI) to Cr(V). The very favorable potentials for Cr(VI) + 3e⁻ → Cr(III) vs. those for Cr(VI) + e⁻ → Cr(V) and Cr(VI) + 2e⁻ → Cr(IV) makes the one-step, three-electron processes very attractive in comparison to pathways requiring production of unstable Cr(V) and Cr(IV) intermediates of high energy.

In general it is not possible to use kinetic tests to distinguish the one-step, three-electron process involving two substrate molecules (eq I) from the two-step, two-electron and one-electron process (eq Ia and IIa).

Neither can product patterns be used to distinguish one-, two-, and three-electron pathways. Firm conclusions as to which pathways are favored must be made on a system-by-system basis. Oxidation of *alcohols alone* gives direct >C=O formation from one two-electron step and also formation of intermediate radicals $R_2CH{-}O\cdot$ or $R_2\dot{C}{-}OH$ and then $R_2C{=}O$ by using two one-electron steps. Oxidations of oxalic acid or HMBA, which *require* C–C bond scission, each involve two-electron oxidation by Cr(VI) to give CO_2, as well as one-electron oxidation by Cr(IV). Cr(V) is reported to oxidize mandelic acid to benzaldehyde[8] (one-electron preference) and glycolic acid to glyoxylic acid (two-electron preference).[6] At high concentrations of glycolic acid and in most of the lactic acid runs described here, no CO_2 is formed, indicating that if there are one-electron steps, they oxidize alcohol (H–C bond scission) in preference to carboxylate (C–C bond scission) in those cases. Of the four species above, only mandelic acid is oxidized by a three-electron step involving only one molecule of substrate (eq II-3ma). Radicals formed are different with the different acids. Acrylonitrile traps CO_2 as CO_2^- from glycolic acid and HMBA but not from mandelic acid.

Steps Involving Chromium(VI). In each reaction system in which the Cr(V) reaction can be separated from the chromium(VI) reaction, the observed rate constant $2k_6$, involves the three terms we have reported in eq 6. In the cases of oxalic acid and glycolic acid,[6] the somewhat different rate laws involving denominator terms indicate that significant complex formation between $HCrO_4^-$ and substrate occurs. *We have observed no effect of substrate on the absorbance of Cr(VI) at 350 nm* in the presence of any of these substances in dilute aqueous perchloric acid such as has occurred in many systems in which Cr(VI) esters are formed.[19] *It appears that Cr(VI) is largely $HCrO_4^-$ in the*

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[19] Haight, G. P.; Richardson, D. C.; Coburn, N. H. *Inorg. Chem.* **1964**, *3*, 1777–1780.

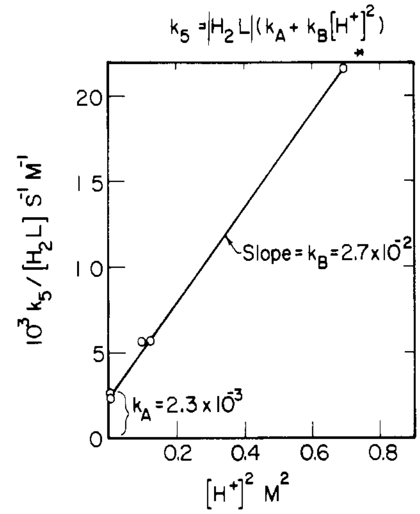

Figure 6. Dependence of k_5 on varying concentrations of H_2L and H^+. $k_5/[H_2L]$ at constant $[H^+]$ is invariant in the range 0.05 M < $[H_2L]$ < 1.00 M.

reacting systems with no spectral evidence of significant ester formation and no kinetic evidence in the present study nor in studies of HMBA and MA. H_2CrO_4 ($[H^+] > 0.5$ M) and $Cr_2O_7^{2-}$ (Cr(VI) > 10^{-3} M) are the only other forms of Cr(VI) that affect reaction rates—both as less reactive or inert forms of Cr(VI) in equilibrium with $HCrO_4^-$.

The magnitude of k_L/k_H or k_L/k_0 is smaller for mandelic acid than for lactic acid, with mandelate ion being the weaker base for assisting α-H transfer. The fact that a mandelic acid molecule can be oxidized by 3 equiv removes the need for a $[Cr^{VI}(MA)_2]^*$ active complex to effect a three-electron oxidation and indicates that the second MA molecule in the activation process functions as a general acid and not as an electron donor (Table VI).

This study presents compelling evidence that monitoring chromium(V) intermediates is essential to mechanistic studies of chromate oxidations. General-acid catalysis of chromium(VI) oxidations is suggested: $d[Cr(VI)]/dt = [HCrO_4^-][S](k_0 + \sum k_{HX}[HX])$ includes the substrate in HX if it is an acid. Three chromium(V) lactates undergo internal redox to form products. $CrO_2L(H_2O)_2^-$ and $CrOL(OH_2)_2^+$ are comparable to chromium(VI) $(CrO_2L(OH)(OH_2)^-)$ in reactivity. $CrOL_2^-$ is inert but reacts with radicals after Cr(VI) is consumed.

Acknowledgment. The authors wish to thank Dr. J. K. Beattie of the University of Sydney for laboratory facilities and helpful discussions and Professor Jan Roček for helpful discussions and for providing, with many studies, the context for interpretation of our results.

Registry No. H_2L, 50-21-5; Cr, 7440-47-3.

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EPR Properties of a Cobalt(II) Complex Containing a Low-Symmetry Porphyrin-like Ligand

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Received October 1, 1984

The single-crystal EPR spectrum of the low-spin, strongly rhombic (hemiporphyrazinato)cobalt(II) (Co(hp)) diluted into the isomorphous Ni(II) complex gives $g_x = 3.567$, $g_y = 1.821$, $g_z = 1.728$, $A_x = 247.6 \times 10^{-4}$ cm^{-1}, $A_y \simeq 4 \times 10^{-4}$ cm^{-1}, and $A_z = 33.5 \times 10^{-4}$ cm^{-1}. With respect to the related porphyrin and phthalocyanine complexes, loss of the axial symmetry strongly affects the spectrum but does not change the ground-state orbital, which remains $(x^2 - y^2)^2(z^2)$. An extended Hückel MO calculation predicts the correct ground state; the right ordering of the excited states can be obtained from a ligand field type calculation. Fitting of the spin-Hamiltonian parameters indicates that, among these low-lying excited states, two doublets and one quartet give important contributions to the ground-state wave function. The quartet state lies at a few hundred wavenumbers from the doublet ground state. Model calculations predict that a ground-state inversion may occur upon small structural changes. Experimentally this is confirmed by the EPR spectra of Co(hp) diluted in a range of nonisomorphous host lattices. A rationalization of the different ground states possible for Co(II) complexes is given in terms of simple MO arguments.

Introduction

A large amount of work, both theoretical and experimental, has been reported in the past years with the aim to clarify the electronic properties of planar low-spin Co(II) complexes.[1-6] The main problem in these compounds is that several doublet and quartet states are clustered together at low energies and strongly interact with each other through spin–orbit coupling.

However, careful EPR and ENDOR studies have allowed determination of the ordering of the levels in a number of cases. The general result is that two spin doublets, namely $(x^2 - y^2)^2(yz)$ and $(x^2 - y^2)^2(z^2)$, are lowest in energy and possible candidates for the ground state. The EPR spectrum is strongly influenced by the energy separation of these two states, but definitive assignment of the ground state is not unambiguous. In spite of this, detailed analysis of the theoretical g-value expressions has shown that the actual ground state can be obtained from the relative values of the g_z and g_y components.[1,7]

This criterion, which seems to be generally valid, requires single-crystal data to be available for a definitive assignment of the magnetic axes.

The results reported up to now show that high-symmetry compounds, such as the D_{4h} porphyrin and phthalocyanine derivatives[8] or the quasi-D_{4h} complexes with bidentate S-containing

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