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 coworkers[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 $k_{II}(4 \times 10^5\ M^{-1}\ s^{-1})$.

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]

Miroslav Krumpolc and Jan Roček*

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680. *Received June 28, 1976*

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 $-d[Cr(VI)]/dt = [HCrO_4^-][HMBA](k_I + k_{II}[H^+] + k''[HMBA])$. 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

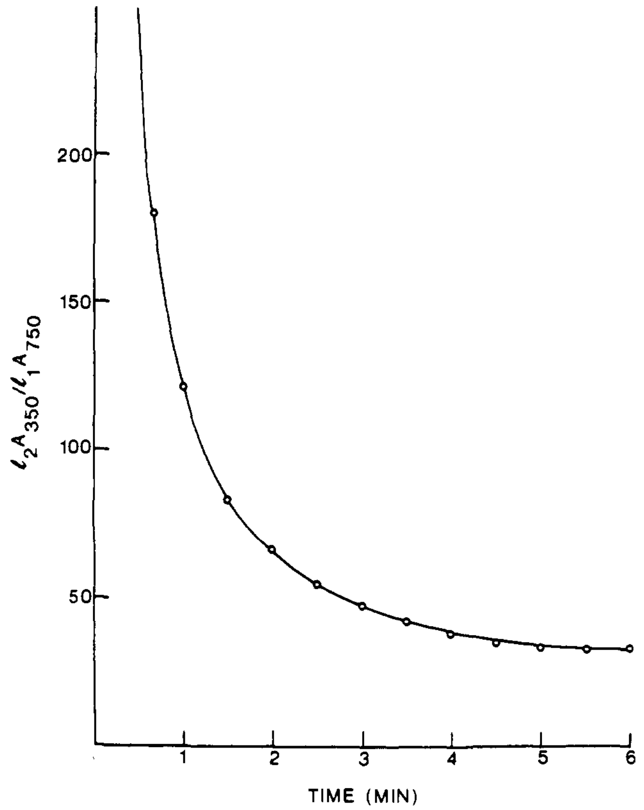


Figure 1. Determination of the ratio of molar extinction coefficients $\epsilon_{350}{}^{V}/\epsilon_{750}{}^{V}$ (eq 6). Conditions: 2-hydroxy-2-methylbutyric acid = 0.5 M, $HClO_4$ = 0.5 M, initial Cr(VI) = 7.75 × 10^{-4} M, 80 °C.

2:1 substrate–chromium(VI) complex or of a chromium(V) intermediate.

As we have shown in one preliminary communication,[8] the oxidation of 2-hydroxy-2-methylbutyric acid takes place in two steps which under some reaction conditions can be separated and investigated individually. In the first step, chromium(VI) is reduced to an equimolar mixture of chromium(V) and chromium(III) while 2-hydroxy-2-methylbutyric acid is oxidized to methyl ethyl ketone (MEK) and carbon dioxide:

$$2\text{Cr(VI)} + 2\text{HMBA} \rightarrow \text{Cr(V)} + \text{Cr(III)} + 2\text{MEK} + 2\text{CO}_2 \qquad (1)$$

The reduction of chromium(V) then occurs in the second phase of the reaction:

$$\text{Cr(V)} + \text{HMBA} \rightarrow \text{Cr(III)} + \text{MEK} + \text{CO}_2 \qquad (2)$$

This study deals primarily with the first step of this reaction sequence.

Experimental Section

Materials. 2-Hydroxy-2-methylbutyric acid (Aldrich) was crystallized from heptane (mp 72-3 °C) and the purity checked by GLC. Sodium dichromate (J. T. Baker, Reagent) was used without further purification; stock solutions prepared in distilled water were standardized iodometrically.[9] Perchloric acid solutions were prepared from 60% perchloric acid (B & A Reagent). Chromium(II) solutions were prepared[10] by dissolving metallic chromium in perchloric acid under nitrogen and were used on the same day. Kinetic measurements at pH 3 were carried out in potassium phthalate–hydrochloric acid buffer solutions,[11] and the pH was verified on a Fisher Accumet pH Meter Model 19.

Kinetic Measurements. Reaction rates of chromium(VI) oxidation of 2-hydroxy-2-methylbutyric acid were determined spectrophotometrically on a Cary Model 15 Recording Spectrophotometer equipped with a thermostated cell holder. The initial chromium(VI) concentrations were 7.75 × 10^{-4} M in kinetic studies and 7.75 × 10^{-3} M in product studies. The reaction rates were not influenced by methyl ethyl ketone (up to fivefold stoichiometric excess) and were insensitive to changes of the ionic strength (up to μ = 0.5 M); the first phase of the oxidation was not affected by the presence of air.

Due to the formation of large amounts of chromium(V), the reaction had to be followed at two different wavelengths, at 350 nm (in 1-cm cells) where both chromium(VI) and chromium(V) absorb,[12] and at 750 nm (in 5- or 10-cm cells) where chromium(V) is the only absorbing species.[3] Neglecting the small contribution of chromium(III) at 350 nm, the total absorbances are given by

$$A_{350} = A_{350}{}^{\text{VI}} + A_{350}{}^{\text{V}} = A_{350}{}^{\text{VI}} + l_1\epsilon_{350}{}^{\text{V}}[\text{Cr(V)}] \qquad (3)$$

$$A_{750} = l_2\epsilon_{750}{}^{\text{V}}[\text{Cr(V)}] \qquad (4)$$

Thus, the absorbance of chromium(VI) only is given by

$$A_{350}{}^{\text{VI}} = A_{350} - \frac{l_1\epsilon_{350}{}^{\text{V}}}{l_2\epsilon_{750}{}^{\text{V}}}A_{750} \qquad (5)$$

where l_1 and l_2 represent the length of the light path at 350 and 750 nm, respectively. The ratio of $\epsilon_{350}{}^{V}/\epsilon_{750}{}^{V}$ can be obtained from the limiting value of A_{350}/A_{750} under conditions when the concentration of chromium(VI) (and therefore the value of $A_{350}{}^{VI}$) approaches zero, and eq 5 is thus reduced to

$$\epsilon_{350}{}^{\text{V}}/\epsilon_{750}{}^{\text{V}} = l_2A_{350}/l_1A_{750} \qquad (6)$$

The numerical value of this ratio was determined graphically by plotting A_{350}/A_{750} vs. time (Figure 1) and from the direct measurement of A_{350}/A_{750} in solutions essentially free of unreacted chromium(VI). The best value of this ratio obtained by using both methods was 31.7.

Thus, pseudo-first-order rate constants for the disappearance of chromium(VI) could be determined by plotting log ($A_{350} - 31.7 \times l_1A_{750}/l_2$) vs. time. In most cases very good straight-line plots were obtained, usually over 3 half-lives (Figure 2a). Only under conditions when the reaction was studied at very low acidity ($[H^+] < 0.02$ M), a small deviation from linearity was observed usually after the second half-life. This deviation was probably caused by the formation of a chromium(III)–HMBA complex which also absorbs at 750 nm.[13]

In those cases when the buildup of chromium(V) during the reaction approached nearly the theoretical amount predicted by the stoichiometry of eq 1, it was also possible to determine rate constants from plots of log ($A_{750}{}^{\max} - A_{750}$) vs. time. The agreement between the rate constants obtained from two methods of treatment of experimental data was found within experimental errors (±6%).

Product Analysis. Chromium(V). In order to monitor the formation of chromium(V) in the course of chromic acid oxidation of 2-hydroxy-2-methylbutyric acid, an analytical method for the determination of chromium(V) in the presence of chromium(VI) was required. The approach which proved successful was based on a considerably higher reactivity of iodide ions toward chromium(V) than chromium(VI). We developed a procedure in which potassium iodide was first allowed to react with chromium(V) at moderate acidities and then with chromium(VI) at high acidities. In a typical experiment, a 6 × 10^{-3} M solution of potassium iodide in 2 ml of a potassium hydrogen phthalate–hydrochloric acid buffer[11] (pH 2.2) was placed in a 1-cm cell, purged with nitrogen for about 3 min, 5–20 μl of a sample containing both chromium(V) and chromium(VI) injected, and the amount of triiodide ions formed determined spectrophotometrically[14] at 350 nm. Under these conditions the oxidation of potassium iodide by chromium(VI) is negligibly slow; the total absorbance A_1 (Figure 3) is thus given by

$$A_1 = A_{\text{Cr(VI)}} + A_{\text{I}_3^-} = \epsilon_{350}{}^{\text{Cr(VI)}}[\text{Cr(VI)}] + \epsilon_{350}{}^{\text{I}_3^-}[\text{Cr(V)}] \qquad (7)$$

where $A_{\text{Cr(VI)}}$ is the absorbance of chromium(VI) and $A_{\text{I}_3^-}$ that of the triiodide ion formed from chromium(V). After recording the first part of the curve the acidity of the sample was increased by adding about three drops (~50 μl) of concentrated perchloric acid. The additional triiodide ion formed corresponded to the amount of chromium(VI) present. The total absorbance A_2 (Figure 3) expressed in terms of chromium(V) and chromium(VI) concentrations is given by

$$A_2 = \epsilon_{350}{}^{\text{I}_3^-}\{[\text{Cr(V)}] + 1.5[\text{Cr(VI)}]\} \qquad (8)$$

Substituting the concentration of chromium(VI) from eq 7, solving for [Cr(V)] gives

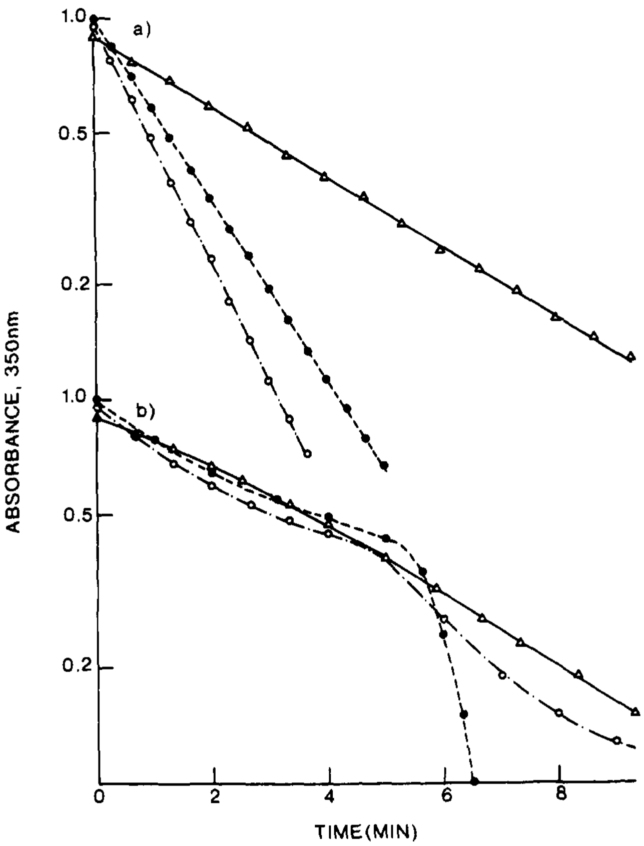


Figure 2. First-order rate plots for chromic acid oxidation of 2-hydroxy-2-methylbutyric acid: (a) absorbance of chromium(VI) calculated from eq 5 and corrected for the amount of chromium(V); (b) uncorrected total absorbance of chromium(VI) and chromium(V). Conditions: Initial Cr(VI) = 7.75 × 10^{-4} M, 80 °C; (○) HMBA = 1 M, $HClO_4$ = 0.1 M; (●) HMBA = 0.5 M, $HClO_4$ = 0.5 M; (△) HMBA = 0.05 M, $HClO_4$ = 1.86 M.

$$[Cr(V)] = \frac{1.5A_1 - A_2\dfrac{\epsilon_{350}^{Cr(VI)}}{\epsilon_{350}^{I_3^-}}}{1.5\epsilon_{350}^{I_3^-} - \epsilon_{350}^{Cr(VI)}} \qquad (9)$$

Introducing molar extinction coefficients ($\epsilon_{350}^{Cr(VI)} = 1560\ M^{-1}\ cm^{-1}$, $\epsilon_{350}^{I_3^-} = 22\,300\ M^{-1}\ cm^{-1}$) into eq 9 gives

$$[Cr(V)] = \frac{1.5A_1 - 0.070A_2}{31\,890} \qquad (10)$$

Similarly, eq 7 and eq 8 can be solved for [Cr(VI)]

$$[Cr(VI)] = \frac{A_2 - A_1}{1.5\epsilon_{350}^{I_3^-} - \epsilon_{350}^{Cr(VI)}} = \frac{A_2 - A_1}{31\,890} \qquad (11)$$

This method gives well reproducible results for solutions containing an excess of chromium(V) over chromium(VI). However, some irregular fluctuations in the heights of the first peak (A_1) were obtained when chromium(VI) was in excess.

Chromium(III). Solutions containing chromium(VI), chromium(V), and chromium(III) were passed through an anion-exchange column (Dowex 2-X8, ion form Cl^-, 50-100 Mesh), which completely removed chromium(VI) and chromium(V). The concentration of chromium(III) was then determined spectrophotometrically at 580 nm [λ_{max} for Cr(III)].

Methyl Ethyl Ketone. The addition of a saturated solution of 2,4-dinitrophenylhydrazine in 2 M hydrochloric acid to the reaction mixture gave the 2,4-dinitrophenylhydrazone of methyl ethyl ketone as the sole product, which was identified by comparison of the NMR and mass spectra with an authentic sample. In kinetic and stoichiometric experiments methyl ethyl ketone was determined by GLC on a Fisher-Victoreen Gas Chromatograph Series 4400 on a 10-ft 10% Carbowax 20M LP36 column at 80 °C. In a typical experiment, a 1-ml sample of the reaction mixture was quenched with few drops of about 2 M solution of chromium(II) perchlorate,[15] extracted with 1 ml of *p*-xylene for 2 min, and the extract analyzed by GLC using acetone as an internal standard. The yield of methyl ethyl ketone was determined from the ratio of peaks using the method of relative response factors.[16]

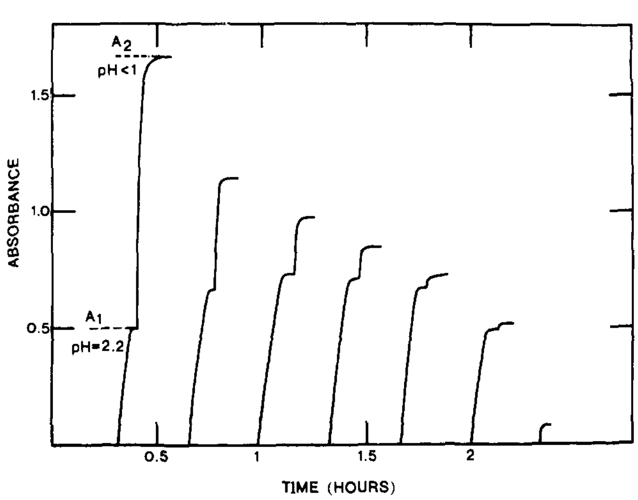


Figure 3. Spectrophotometric determination (at 350 nm) of I_3^- formed by chromium(V) and chromium(VI) oxidation of iodide at pH 2.2 (A_1) and pH <1 (A_2), respectively. Conditions: HMBA = 0.5 M, $HClO_4$ = 0.5 M, initial Cr(VI) = 7.75 × 10^{-3} M, 50 °C.

Table I. Products of the Chromic Acid Oxidation of 2-Hydroxy-2-methylbutyric Acid at 80 °C (Chromium(VI) = 7.75 × 10^{-3} M, 3.10 × 10^{-5} mol)

		Products, yields			
		Methyl ethyl ketone		Carbon dioxide	
Substrate, M	$[H^+]$, M	10^5 mol	%	10^5 mol	%
2.0	0.001	4.56	98	4.56	98
0.1	1.86	4.51	97	4.65	100
0.02	0.001	4.65	100	4.51	97

Carbon Dioxide. The yield of carbon dioxide was determined manometrically in a Warburg apparatus[17] using Fast Green FCF dissolved in ethyl lactate as the manometric fluid. Reaction solutions were saturated with carbon dioxide at room temperature, then equilibrated for about 40-50 min at 80 °C and a sodium dichromate solution injected from a microliter syringe into the flask through a side arm with a serum cap. The apparatus was calibrated by carbon dioxide generated from known amounts of sodium dichromate in excess oxalic acid under the same conditions.

Results and Discussion

Reaction Products. The overall stoichiometry of the reaction is simple. Essentially quantitative yields of methyl ethyl ketone and carbon dioxide were obtained whenever the reaction was allowed to proceed to completion (Table I):

$$2Cr(VI) + 3HMBA \rightarrow 2Cr(III) + 3MEK + 3CO_2 \qquad (12)$$

However, following the change in the concentrations of reactants and products as a function of time shows a rather unusual pattern. Monitoring the reaction spectrophotometrically at the $HCrO_4^-$ maximum (350 nm) led, instead of the expected logarithmic decrease with time, to an anomalous behavior (Figure 2b and 4). The absorbance started to decrease as expected, but instead of forming a smooth curve approaching asymptotically a zero value, it appeared to reach a relatively stable value corresponding to about 40% of the initial absorbance; this phase of the reaction was followed by a sudden new start of the reaction which led to zero absorbance.

We suspected that this unusual behavior was due to the formation of a stabilized chromium(V) species in the first

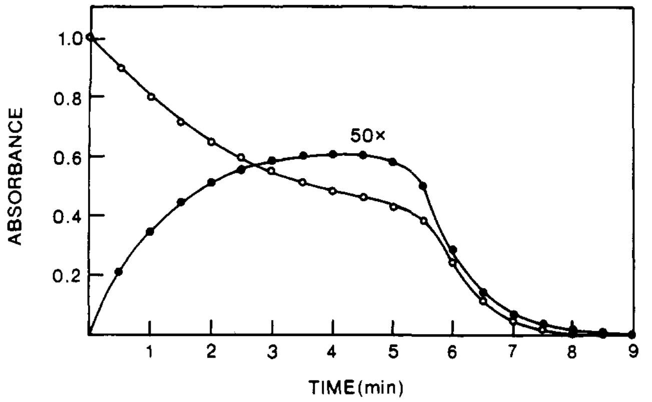


Figure 4. Time dependence of absorbance at 350 nm (○) and 750 nm (●). Conditions same as in Figure 1. Absorbance at 750 nm multiplied 50 times. Only Cr(V) absorbs at 750 nm, both Cr(VI) and Cr(V) absorb at 350 nm.

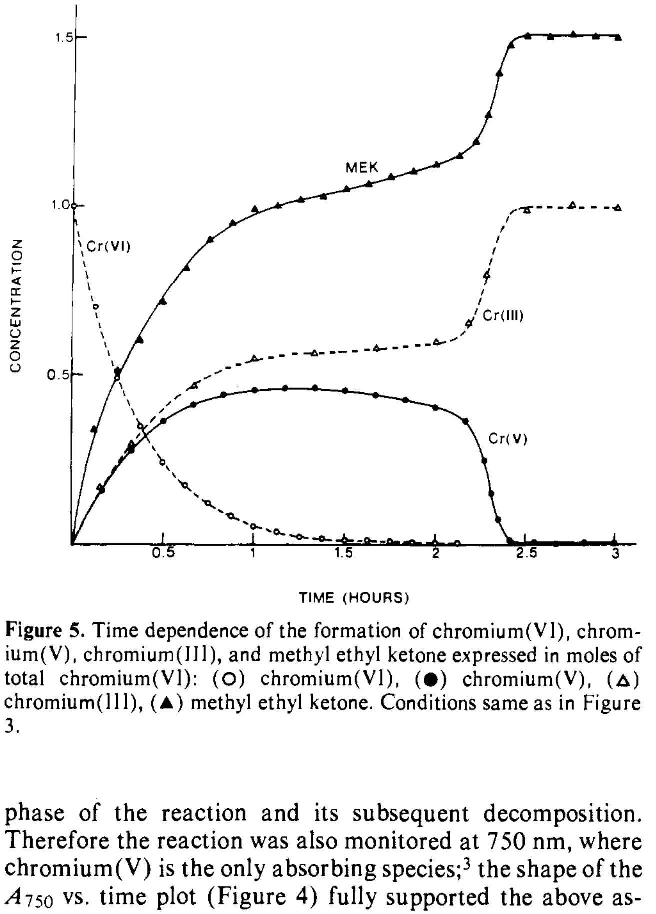


Figure 5. Time dependence of the formation of chromium(VI), chromium(V), chromium(III), and methyl ethyl ketone expressed in moles of total chromium(VI): (○) chromium(VI), (●) chromium(V), (△) chromium(III), (▲) methyl ethyl ketone. Conditions same as in Figure 3.

phase of the reaction and its subsequent decomposition. Therefore the reaction was also monitored at 750 nm, where chromium(V) is the only absorbing species;[3] the shape of the A_{750} vs. time plot (Figure 4) fully supported the above assumption.

Further evidence for the presence of high concentrations of chromium(V) was obtained from iodometric studies. We found that the solutions suspected of containing chromium(V) reacted extremely rapidly with potassium iodide under conditions when the oxidation of iodide ions by chromium(VI) was slow. This result is consistent with the high reactivity of chromium(V) toward the iodide ion revealed by studies of induced oxidations of iodides.[18,19]

The difference in reactivity of chromium(V) and chromium(VI) toward iodide ions is high enough to permit a complete separation of the two reactions. At moderate acidities (pH 2.2 in a buffer solution) chromium(V) is reduced rapidly and quantitatively, while no appreciable reduction of chromium(VI) takes place. Acidification with an excess of mineral acid (pH <1) then leads to a rapid reduction of chromium(VI).

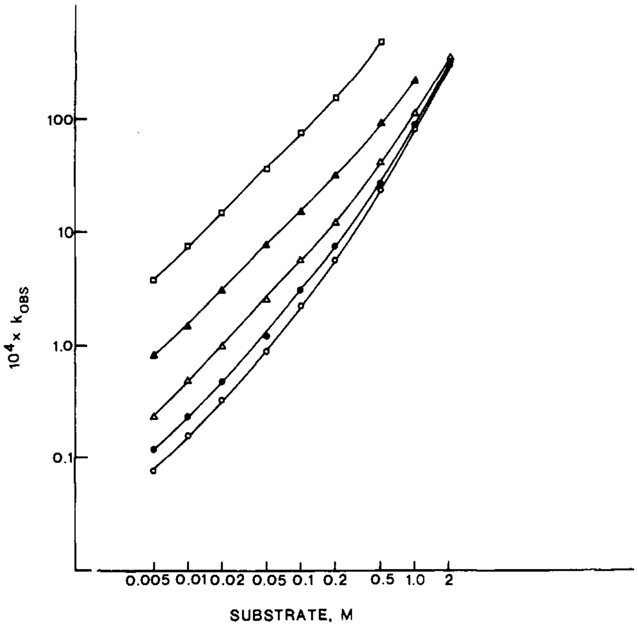


Figure 6. Effect of 2-hydroxy-2-methylbutyric acid concentration on rates of chromic acid oxidations. Conditions: initial Cr(VI) = 7.75 × 10^{-4} M, 80 °C, (○) H^+ = 0.001 M, (●) H^+ = 0.02 M, (△) $HClO_4$ = 0.1 M, (▲) $HClO_4$ = 0.5 M, (□) $HClO_4$ = 1.86 M.

Figure 3 gives the results of a number of such analyses carried out on samples removed from a reaction mixture of chromic acid and 2-hydroxy-2-methylbutyric acid at regular time intervals. On each curve the first plateau (A_1) is the absorption (at 350 nm) in the buffer solution after all chromium(V) has been reduced. The final absorption (A_2) is reached after acidification and complete reduction of chromium(VI). The gradual decrease of chromium(VI) and the formation and decay of chromium(V) are clearly visible.

Finally, an ESR spectrum (sharp single signal, $g = 1.9784$) consistent with those reported from other chromium(V) containing solutions[12,20] has been obtained.[13]

Figure 5 gives the time dependence of the concentrations of chromium(VI), chromium(V), chromium(III), and of methyl ethyl ketone. The concentrations of chromium(VI) and chromium(V) were determined spectrophotometrically from measurements at 350 and 750 nm, respectively. The concentration of chromium(VI) was calculated from $A_{350}{}^{VI}$ (eq 5) ($\epsilon_{350}{}^{VI} = 1560\ M^{-1}\ cm^{-1}$); the concentration of chromium(V) was obtained using eq 4 ($\epsilon_{750}{}^{V} = 38\ M^{-1}\ cm^{-1}$). The concentration of chromium(III) was determined independently at 580 nm after both chromium(VI) and chromium(V) were removed by passing the reaction mixture through an anion-exchange column. It should be noticed that the concentration of chromium(III) is always higher than or equal to the concentration of chromium(V). Methyl ethyl ketone was determined by GLC.

The plot indicates that the reaction consists of two separate phases. In the first phase, chromium(VI) is reduced to an equimolar mixture of chromium(V) and chromium(III) with the formation of 1 mol of methyl ethyl ketone for every mole of chromium(VI) reduced. The stoichiometry of this phase therefore must be that of eq 1. The second phase of the reaction is the reduction of chromium(V) to chromium(III) which leads to the formation of an additional mole of methyl ethyl ketone (eq 2). Thus, only one-half of the chromium(VI) gives chromium(V), while the other half is reduced directly to chromium(III).

Kinetics. The present kinetic study deals only with the first phase of the reaction (eq 1). Figure 6 shows the dependence of the reaction rate on the concentration of 2-hydroxy-2-

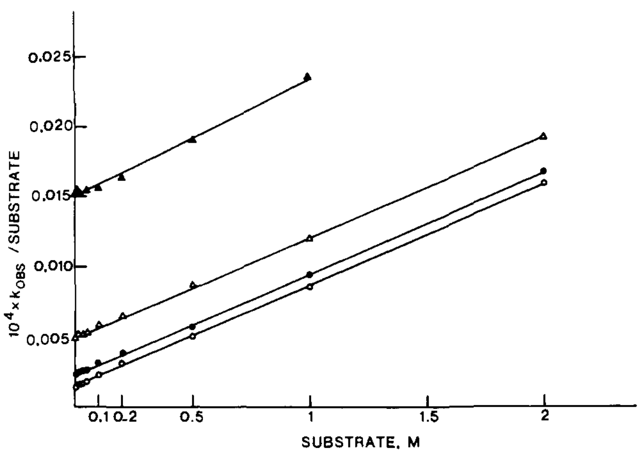


Figure 7. Determination of rate constants k' and k'' (eq 13); conditions same as in Figure 6.

Table II. Chromic Acid Oxidation of 2-Hydroxy-2-methylbutyric Acid; Acidity Dependence; 80 °C

$[H^+]$, M	k', $M^{-1} s^{-1}$	$\frac{k'(K_a + h_o)^b}{K_a}$	k'', $M^{-2} s^{-1}$
1.86^a	0.075	0.170	
0.5	0.0152	0.0170	0.0077
0.1	0.0048	0.0050	0.0070
0.02	0.00225	0.00225	0.0072
0.003	0.00150	0.00150	0.0072

^{a} $h_o = 5.0.^{25}$ ^{b} $K_a = 4.0^{22}$ M.

methylbutyric acid for five different acidities. The reaction order in 2-hydroxy-2-methylbutyric acid changes from first toward second order as the concentration of the substrate is increased; this change is most pronounced at low acidities. At any given acidity the relationship between the experimental pseudo-first-order rate constants and the concentrations of the substrate was found to fit the following equation:

$$k_{obsd} = k'[HMBA] + k''[HMBA]^2 \qquad (13)$$

A plot of $k_{obsd}/[HMBA]$ vs. [HMBA] gave good straight lines (Figure 7) from which the values of k' and k'' at five different acidities were determined (Table II). The second-order rate constants k'' are clearly acidity independent over the whole range of hydrogen ion concentrations. On the other hand, the first-order rate constants k' can be expressed as consisting of an acidity independent and an acidity dependent term. A plot of k' vs. $[H^+]$ (at higher acidities the value of k' had to be corrected for the concentration of the monochromate[18,21] anion $HCrO_4^-$) gives a straight line (Figure 8) showing that the acidity dependence of k' can be written as

$$\frac{k'(K_a + [H^+])}{K_a} = k_I + k_{II}[H^+] \qquad (14)$$

where $k_I = 1.5 \times 10^{-3}\ M^{-1} s^{-1}$, $k_{II} = 3.4 \times 10^{-2}\ M^{-2} s^{-1}$, and K_a is the equilibrium constant for the dissociation of chromic acid

$$H_2CrO_4 \overset{K_a}{\rightleftarrows} HCrO_4^- + H^+$$

$$K_a{}^{22} = 4.0\ M \qquad (15)$$

Equation 14 is valid even at the highest perchloric acid concentrations used (1.86 M), provided that the h_o function[25] is used instead of $[H^+]$.

The complete rate law for the chromic acid oxidation of 2-hydroxy-2-methylbutyric acid thus is given by

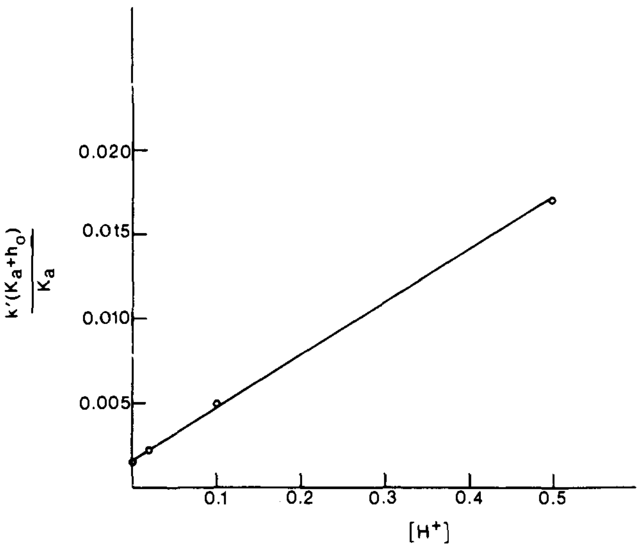
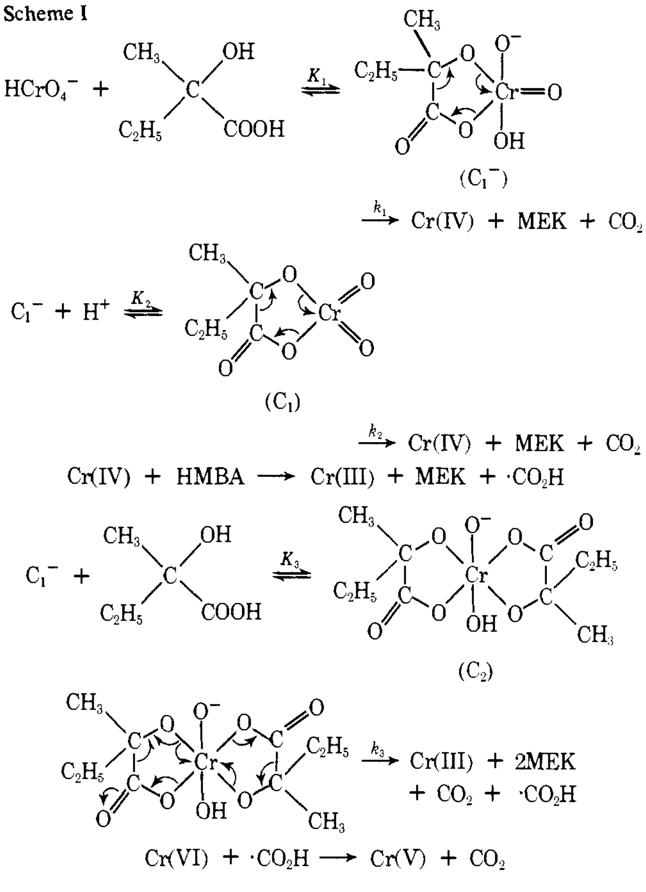


Figure 8. Determination of rate constants k_I and k_{II} (eq 14); conditions same as in Figure 6.

Scheme I



$$v = k_{obsd}[Cr(VI)] = [HCrO_4^-][HMBA] \times (k_I + k_{II}[H^+] + k''[HMBA]) \qquad (16)$$

where [Cr(VI)] stands for the total analytical concentration of chromium(VI).[26]

Mechanism. A mechanism consistent with all experimental data is given in Scheme I. The first step represents the formation of an anionic complex (C_I^-) between chromic acid and the hydroxy acid. The complex is written in a cyclic form which we consider most likely and consistent with the behavior of other α-substituted carboxylic acids. The anionic complex is protonated to form a new complex (C_I) in the second step. This

Table III. Observed and Calculated (Eq 22) Pseudo-First-Order Rate Constants (10^4k, s^{-1}) for the Chromic Acid Oxidation of 2-Hydroxy-2-methylbutyric Acid in Perchloric Acid at 80 °C

Substrate, M	[H+], M									
	1.86 (h_o = 5.0)		0.5		0.1		0.02		0.001[a]	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
2.0					380	380	330	330	320	320
1.0			230	230	120	120	93	93	85	87
0.5	(≈500)	400	95	100	43	42	28	29	24.5	25.7
0.2	158	156	33	36	12.8	12.5	7.5	7.2	5.8	5.8
0.1	78	77	15.7	17.3	5.8	5.5	3.1	2.9	2.23	2.23
0.05	37	38	7.8	8.5	2.6	2.6	1.20	1.28	0.90	0.95
0.02	15.2	15.3	3.1	3.3	1.02	1.00	0.48	0.47	0.33	0.34
0.01	7.7	7.7	1.53	1.67	0.50	0.48	0.238	0.228	0.157	0.160
0.005	3.8	3.8	0.82	0.83	0.237	0.243	0.118	0.112	0.077	0.077

[a] In potassium hydrogen phthalate–hydrochloric acid buffer.

Table IV. Yield of Chromium(V)[a] and the Contribution of Individual Kinetic Terms of Eq 22 (in %) for the Chromic Acid Oxidation of 2-Hydroxy-2-methylbutyric Acid at 80 °C (Chromium(VI) = 7.75×10^{-4} M)

Substrate, M	[H+], M																			
	1.86 (h_o = 5.0)				0.5				0.1				0.02				0.001			
	Cr(V)	Terms[b]			Cr(V)	Terms[b]			Cr(V)	Terms[b]			Cr(V)	Terms[b]			Cr(V)	Terms[b]		
	max[a]	*A*	*B*	*C*	max[a]	*A*	*B*	*C*	max[a]	*A*	*B*	*C*	max[a]	*A*	*B*	*C*	max[a]	*A*	*B*	*C*
2.0									75	8	17	75	80	9	4	87	79	9	0	91
1.0					71	6	66	28	71	12	28	60	78	16	7	77	77	17	0	83
0.5	79	1	97	2	68	7	76	17	71	17	39	44	75	26	12	62	74	29	1	70
0.2	59	1	98	1	63	7	85	8	68	23	53	24	71	42	19	39	70	51	1	48
0.1	34	1	98	1	43	8	88	4	56	27	60	13	64	52	23	25	65	67	2	31
0.05	15	1	99	0	23	8	90	2	33	28	64	8	40	59	27	14	45	79	2	19
0.02	0	1	99	0	5	8	91	1	12	30	67	3	20	64	29	7	26	88	2	10
0.01	0	1	99	0	0	8	91	1	6	30	69	1	10	66	30	4	12	94	2	4
0.005	0	1	99	0	0	9	91	0	0	30	69	1	0	68	30	2	5	96	2	2

[a] $\mathrm{Cr(V)_{max}}$ = maximum yield of Cr(V) in percent; yield based on stoichiometry $2\mathrm{Cr(VI)} \rightarrow \mathrm{Cr(V)} + \mathrm{Cr(III)}$ (eq 1). [b] $A = 100k_{\rm I}/k_{\rm T}$; $B = 100k_{\rm II}[\mathrm{H^+}]/k_{\rm T}$; $C = 100k''[\mathrm{HMBA}]/k_{\rm T}$; $k_{\rm T} = k_{\rm I} + k_{\rm II}[\mathrm{H^+}] + k''[\mathrm{HMBA}]$.

complex is written in the simplest tetracoordinated form, although the coordination sphere of chromium(VI) may well be expanded to five or six by hydration. Both species, the negatively charged C_1^- and the neutral C_1, decompose with the formation of the same products, chromium(IV), methyl ethyl ketone, and carbon dioxide. The decomposition of the second complex (C_1) is responsible for the acid-catalyzed term in the rate law (eq 16).

The third reaction in Scheme I indicates the formation of a 2:1 HMBA-chromium(VI) complex (C_2) explaining thus the second-order dependence in the substrate (eq 16). This complex is represented by a bicyclic structure. In analogy with our previous studies[21] we assume that it decomposes by a one-step three-electron oxidation-reduction mechanism directly to one molecule of chromium(III), one molecule of carbon dioxide, two molecules of methyl ethyl ketone, and a ·COOH free radical. The equilibrium constant for the formation of the complexes must be relatively low compared with that observed for oxalic acid[28] or glycolic acid,[3] since we were never able to observe a decrease in reaction order with respect to a substrate at high substrate concentrations. Unlike in earlier studies with the more reactive oxalic or glycolic acid, we were unsuccessful in our attempts to trap the intermediate free radical by acrylamide or acrylonitrile. This is probably due to the fact that at the relatively high temperature required for the reaction to proceed at measurable rates, the oxidation of the free radical by chromium(VI) is so fast that acrylamide or acrylonitrile are unable to compete for it effectively.

According to Scheme I the full rate law for the chromic acid oxidation of 2-hydroxy-2-methylbutyric acid can be written as

$$-\frac{\mathrm{d[Cr(VI)]}}{\mathrm{d}t} = k_{\mathrm{obsd}}[\mathrm{Cr(VI)}] = k_1[\mathrm{C_1^-}] + k_2[\mathrm{C_1}] + k_3[\mathrm{C_2}] \quad (17)$$

As the intermediates are present only in very small concentrations, the total concentration of chromium(VI) can be expressed as

$$[\mathrm{Cr(VI)}] = [\mathrm{HCrO_4^-}] + [\mathrm{H_2CrO_4}] \quad (18)$$

and for C_1^-, C_1, and C_2 one obtains

$$[\mathrm{C_1^-}] = K_1[\mathrm{HCrO_4^-}][\mathrm{HMBA}] \quad (19)$$

$$[\mathrm{C_1}] = K_2[\mathrm{C_1^-}][\mathrm{H^+}] = K_1K_2[\mathrm{HCrO_4^-}][\mathrm{HMBA}][\mathrm{H^+}] \quad (20)$$

$$[\mathrm{C_2}] = K_3[\mathrm{C_1^-}][\mathrm{HMBA}] = K_1K_3[\mathrm{HCrO_4^-}][\mathrm{HMBA}]^2 \quad (21)$$

The full rate law derived from eq 17–21 is thus summarized by

$$k_{\mathrm{obsd}} = \frac{[\mathrm{HMBA}](k_{\rm I} + k_{\rm II}[\mathrm{H^+}] + k''[\mathrm{HMBA}])}{1 + [\mathrm{H^+}]/K_{\rm a}} \quad (22)$$

where $k_{\rm I} = k_1K_1 = 1.5 \times 10^{-3}\ \mathrm{M^{-1}\,s^{-1}}$, $k_{\rm II} = k_2K_1K_2 = 3.4 \times 10^{-2}\ \mathrm{M^{-2}\,s^{-1}}$, $k'' = k_3K_1K_3 = 7.2 \times 10^{-3}\ \mathrm{M^{-2}\,s^{-1}}$. At very high acidities the concentration of hydrogen ions must be replaced by acidity function h_o. Pseudo-first-order rate constants calculated from eq 22 and compared with experimental data in Table III give an excellent agreement over a wide range of concentrations.

Table IV shows how the maximum yield of chromium(V) (based on the stoichiometry of eq 1) depends on reaction conditions. It is clear that the yield of the stable chromium(V) species is determined almost entirely by the excess of HMBA and is very approximately proportional to its concentration. It is essentially independent of the dominant kinetic term. As we have obtained no kinetic evidence for the formation of the HMBA-Cr(VI) complex in substantial concentrations, it seems most likely that chromium(V) is formed first as the free acid, H_3CrO_4, which subsequently reacts with HMBA to form a stable complex.

The stability of chromium(V) formed in the course of the chromic acid oxidation of 2-hydroxy-2-methylbutyric acid is much higher than that of any previously observed chromium(V) compound. There is little doubt that chromium(V) exists in the form of a complex with the hydroxy acid, and it is quite probable that the complex is cyclic. Ordinarily, one would expect that a cyclic complex between a two-electron oxidant and substrate which can easily react in a two-electron oxidation leading to carbon–carbon bond cleavage should be extremely unstable. In fact, a similar complex derived from chromium(VI) is held responsible for the very rapid chromic acid oxidation of ditertiary α-glycols.[29,30] Why the complex with a tertiary hydroxy acid should be so particularly stable is unclear. It is not clear whether this is due to a particularly low ability of chromium(V) to react by a cyclic reaction mechanism, or whether the principal factor is ligand stabilization of the chromium(V) species.

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Chromic Acid Oxidation of Iodide[1]

George F. Vandegrift and Jan Roček*

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680.

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Abstract: The chromic acid oxidation of iodide follows the rate law given in eq 26 of the text over a range of iodide concentrations from 4×10^{-4} to 2.0 M and of hydrogen ion (nitric acid) concentration from 0.3 to 1.0 M. The proposed mechanism postulates four reaction paths involving $ICrO_3H$, $ICrO_3H_2^+$, $I_2CrO_3H^-$, and I_2CrO_2 as reactive intermediates. Kinetic evidence has been obtained for the reaction $HCrO_4^- + I^- + H^+ \rightleftarrows ICrO_3^-$ with an equilibrium constant $K_1 = [ICrO_3^-]/([HCrO_3^-]\cdot[I^-]h_0) = 1.4 \pm 0.5$ at 25 °C and 2.0 M ionic strength ($NaNO_3$).

Of all the oxidation reactions routinely performed in chemical laboratories, few are used as commonly as the oxidation of iodide to iodine by chromic acid.

There have been several attempts to unravel the Cr(VI)–I^- redox reactions; none so far completely satisfactory. The earliest recorded work on the kinetics of this system was in 1903 by DeLury, who found that the reaction was first order in $Cr_2O_7^{2-}$, ca. second order in acid, and a mixture of first and second order in iodide ion.[2]

$$\text{Rate} = [Cr_2O_7^{2-}][H^+]^2(k_1[I^-] + k_2[I^-]^2) \qquad (1)$$

Beard and Taylor used chloride ion to keep constant ionic strength[3] and observed an interesting effect of chloride ion, which reduced the rate at low concentrations but accelerated it at concentrations higher than 0.7 M; for a solution 1.5 M in chloride they proposed the rate law:

$$\text{Rate} = 14.6[H^+][I] + 5.3 \times 10^4[H^+]^2[I^-]^2[\text{Cr(VI)}] \qquad (2)$$

Edwards[4] noted that their data fit equally well in the form:

$$\text{Rate} = k_1[CrI^-] + k_2[H^+][CrI^-] + k_3[I^-][CrI^-] + k_4[H^+][I^-][CrI^-] \qquad (3)$$

Howlett and Sarsfield[5] found a similar ionic strength effect with perchlorate with a minimum at 0.7 M. They also performed a study of the initial rate vs. dielectric constant of the solvent and obtained an excellent correlation of $\log(k)$ vs. $1/D$.