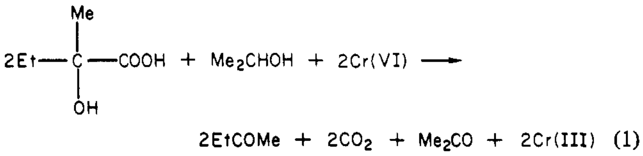
Three-Electron Oxidations. 18. Carbon-13 and Deuterium Isotope Effects in the Cooxidation of 2-Hydroxy-2-methylbutyric Acid and 2-Propanol. Evidence for a Two-Step Mechanism[1,2]

S. Ramesh,[3a] Surendra N. Mahapatro,[3a] Juei H. Liu,[3b] and Jan Roček*[3a]

Contribution from the Department of Chemistry, Department of Criminal Justice, University of Illinois at Chicago Circle, Chicago, Illinois 60680. Received January 19, 1981

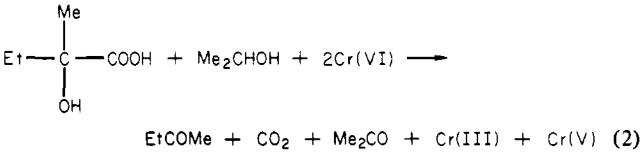
Abstract: The mechanism of the chromic acid cooxidation of 2-hydroxy-2-methylbutyric acid (HMBA) and 2-propanol (ROH) was investigated by using deuterium and carbon-13 isotope effects. The carbon isotope effect associated with the oxidative decarboxylation of HMBA was determined from the mass ratio 44:45 ($^{12}CO_2$:$^{13}CO_2$), the deuterium isotope effect from kinetic measurements. When the acidity is increased from $[H^+] = 0.02$ or 0.05 M to $[H^+] = 1.86$ M, the deuterium isotope effect, k_H/k_D, increases from 1.1 to 5.7 while the carbon isotope effect, $^{12}k/^{13}k$, decreases from 1.027 to 1.0048. The magnitude of the carbon-13 isotope effect is dependent on the concentration of HMBA. The change in deuterium isotope effect indicates that the rate-limiting step changes from formation of a Cr(VI)-HMBA-ROH complex at low acidities to its decomposition into oxidation products at high acidities. This interpretation is buttressed by the observation that the less readily oxidized and more rapidly esterified methanol exhibits a large deuterium isotope effect throughout the entire acidity range. The existence of a significant carbon isotope effect at low acidities, where complex formation is rate limiting, strongly suggests that the oxidative decomposition of the Cr(VI)-HMBA-ROH complex take place in two steps. The first step results in the oxidation of the alcohol and formation of a Cr(IV)-HMBA intermediate; this intermediate must be sufficiently long lived to equilibrate with free HMBA before undergoing oxidative decomposition in the second step. The overall three-electron reduction of chromium(VI) by HMBA and ROH thus consists of a two-electron oxidation of the carbon-hydrogen bond of the alcohol followed by a one-electron oxidation of the carbon-carbon bond of the hydroxy acid. The observation of a carbon-13 isotope effect in the chromium(V) oxidation of HMBA is consistent with a mechanism of reversible complex formation between Cr(V) and HMBA and rate-limiting oxidation. In the cooxidation of oxalic acid (OX) and 2-propanol significant deuterium and carbon-13 isotope effects were observed throughout the entire acidity range, leaving open the possibility that in this case the oxidative decomposition of the complex Cr(VI)-OX-ROH may take place in a single three-electron transfer step.

We have shown[2] that the cooxidation of 2-hydroxy-2-methylbutyric acid (HMBA) and 2-propanol with chromic acid

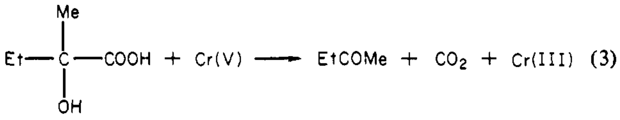


$$2\mathrm{Et}{-}\overset{\mathrm{Me}}{\underset{\mathrm{OH}}{\mathrm{C}}}{-}\mathrm{COOH} + \mathrm{Me_2CHOH} + 2\mathrm{Cr(VI)} \longrightarrow 2\mathrm{EtCOMe} + 2\mathrm{CO_2} + \mathrm{Me_2CO} + 2\mathrm{Cr(III)} \quad (1)$$

takes place in two distinct stages, I (eq 2) and II (eq 3). The



$$\mathrm{Et}{-}\overset{\mathrm{Me}}{\underset{\mathrm{OH}}{\mathrm{C}}}{-}\mathrm{COOH} + \mathrm{Me_2CHOH} + 2\mathrm{Cr(VI)} \longrightarrow \mathrm{EtCOMe} + \mathrm{CO_2} + \mathrm{Me_2CO} + \mathrm{Cr(III)} + \mathrm{Cr(V)} \quad (2)$$

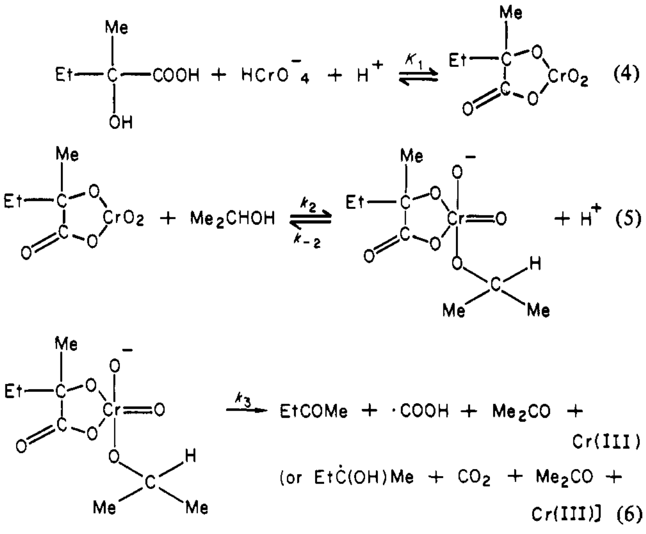


$$\mathrm{Et}{-}\overset{\mathrm{Me}}{\underset{\mathrm{OH}}{\mathrm{C}}}{-}\mathrm{COOH} + \mathrm{Cr(V)} \longrightarrow \mathrm{EtCOMe} + \mathrm{CO_2} + \mathrm{Cr(III)} \quad (3)$$

reaction can be stopped when the first phase is completed, i.e., when chromium(VI) is reduced to an equimolar mixture of chromium(V) and chromium(III). The ability to separate the chromium(VI) oxidation step from the chromium(V) step offers the potential for gaining a better insight into the cooxidation mechanism than can be obtained in systems where the chromium(VI) and chromium(V) oxidations occur simultaneously.

From a combination of kinetic and product studies, we concluded that the chromium(VI) cooxidation of 2-propanol and 2-hydroxy-2-methylbutyric acid takes place by the sequence of reactions in Scheme I.

Scheme I



$$\cdot\mathrm{CO_2H}\ [\text{or } \mathrm{Et\dot{C}(OH)Me}] + \mathrm{Cr(VI)} \longrightarrow \mathrm{CO_2}\ (\text{or } \mathrm{EtCOMe}) + \mathrm{Cr(V)} \quad (7)$$

Based on the observed strong acidity dependence of the deuterium isotope effect in the cooxidation of 2-deuterio-2-propanol (high k_H/k_D at high acidities, low at low acid concentrations), it was concluded that reaction 6, the oxidative decomposition of the intermediate termolecular complex, is rate limiting at high acidities whereas reaction 5, the formation of the complex, becomes rate limiting at low acidities.

An important question, which remained unresolved, was the timing of the two bond-breaking processes in the oxidative decomposition of the termolecular complex. Does the breaking of the carbon-carbon bond in the hydroxy acid residue take place

---

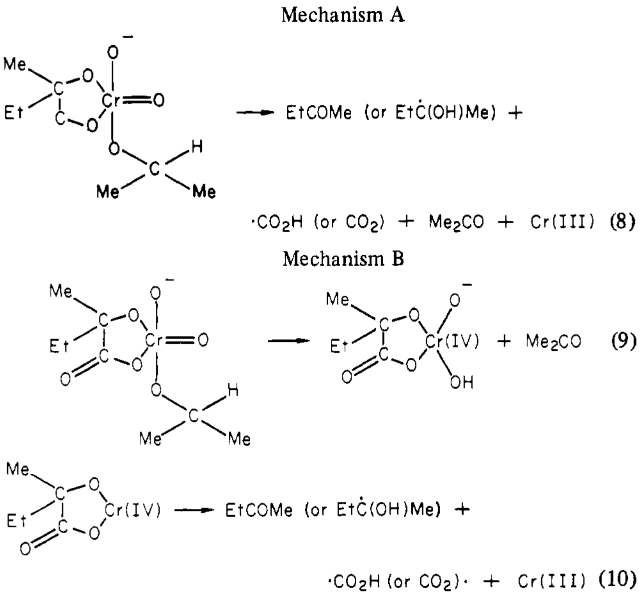
(1) The support of this investigation by a grant of the National Science Foundation is gratefully acknowledged.

(2) Part 17: Mahapatro, S. N.; Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1980**, *102*, 3799.

(3) (a) Department of Chemistry; (b) Department of Criminal Justice.

0002-7863/81/1503-5172$01.25/0 © 1981 American Chemical Society

Scheme II



simultaneously with (mechanism A, reaction 8, Scheme II) or subsequently to (mechanism B, reactions 9 and 10) the oxidation of the carbon–hydrogen bond in the alcohol?

In order to distinguish between these two mechanisms, we decided to study the carbon-13 isotope effect associated with the oxidation of the carbon–carbon bond in the hydroxy acid by determining the $^{13}C/^{12}C$ ratio in the carbon dioxide formed during the oxidation of the carboxyl group by chromium(VI). The determinations were carried out under conditions where only a minimal amount of carbon dioxide is formed by chromium(V) oxidation (reaction 3).

Experimental Section

Sodium dichromate dihydrate (Baker, reagent), 2-propanol (Baker analyzed, spectroscopic grade), methanol (Fisher, spectroscopic grade), methanol-d_4 (Aldrich, 99.5 atom % D), and lithium aluminum deuteride (Aldrich, min 99% D) were used as received. Perchloric acid solutions were prepared from 70% acid (Mallinckrodt, analytical reagent). Stock solutions of sodium dichromate in distilled water were standardized iodimetrically. Chromium(II) perchlorate solutions were prepared[4] by dissolving metallic chromium (Ventron) in perchloric acid under oxygen-free nitrogen and were used on the same day. 2-Hydroxy-2-methylbutyric acid (Aldrich) was recyrstallized from heptane (mp 72 °C). 2-Deuterio-2-propanol (isotopic purity 99.1) was prepared according to the procedure of Wiberg and Schäfer.[5]

Deuterium Isotope Effect. Deuterium isotope effects were determined from kinetic measurements of the cooxidation of the 2-hydroxy-2-methylbutyric acid with the protio and deuterio alcohols, respectively.

Carbon-13 Isotope Effect. The carbon-13 isotope effects were determined from the $^{13}C/^{12}C = R$ ratios in the carbon dioxide formed during the cooxidation of 2-hydroxy-2-methylbutyric acid and 2-propanol with chromium(VI) and the natural abundance $^{13}C/^{12}C = R_0$ in the carboxylic group of the hydroxy acid. When only a few percent (<5%) of the hydroxy acid are allowed to react, changes in the isotopic composition of the hydroxy acid in the course of the reaction are neglected and the ratio R_0/R corresponds directly to the carbon-13 isotope effect.

A single sample of recrystallized 2-hydroxy-2-methylbutyric acid was used in all the measurements. The reactions were carried out in a 50-mL cyclindrical (o.d. 25 mm) reaction vessel (A) with a 14/35 joint and two side arms (B and C) (15 mL, o.d. 10 mm), one of which (C) was attached through a joint (10/30) and a 4 mm bore stopcock. The vessel was connected to a vacuum line manifold through a 4 mm bore stopcock. In a typical experiment, 20 mL of a solution of 2-hydroxy-2-methylbutyric acid (0.1 M, 2 mmol) and 2-propanol (0.045 M, 0.9 mmol) containing perchloric acid (0.02 to 1.86 M) was placed in the larger arm A of the reaction vessel, and 0.1 mL of a 0.5 M (0.1 mmol chromium(VI)) sodium dichromate solution was placed in the smaller arm B. Approximately 10 mL of a freshly prepared solution of chromium(II) perchlorate (0.15 M, ~1.5 mmol) was placed in arm C. After three freeze–evacuation–thaw cycles, the reaction vessel was removed from the vacuum line, the contents were thermally equilibrated in a thermostat at 25 °C for 0.5 h, and the reaction was started by mixing the contents of arms A and B. After 2 to 3 half-lives of the chromium(VI) oxidation, the reaction was quenched by addition of chromium(II) from arm C. The reaction vessel was reattached to the vacuum line and the carbon dioxide formed in the reaction was collected in a liquid nitrogen trap, purified by distillation through a column of silica gel and a dry ice–acetone trap, and condensed into another liquid nitrogen trap. After determining quantitatively the amount of carbon dioxide formed by transferring it to a manometer, the carbon dioxide was transferred to bulbs which could be attached directly to the isotope ratio mass spectrometer inlet system.

Table I. Acidity Dependence of Carbon-13 and Deuterium Isotope Effects in the Cooxidation of 2-Hydroxy-2-methylbutyric Acid (HMBA) and 2-Propanol[a]

[HMBA], M	[H⁺], M	$^{12}k/^{13}k$	k_H/k_D
0.5	0.05	1.027	1.49
	0.10	1.026	1.97
	0.50	1.024	3.77
	1.26	1.012	4.82
	1.50	1.007	5.15
	1.86	1.005	5.70
0.1	0.02	1.024	1.26
		1.022	
		1.024	
		1.030[b]	
		1.032[b]	
	1.86	1.0043	5.99
		1.0059	
		1.011[b]	
		1.011[b]	
		1.0047[c]	
		1.0072[c]	

[a] [2-Propanol] = 0.045 M; 25 °C. [b] Reaction allowed to go to completion. [c] With 2-deuterio-2-propanol.

In some experiments the reaction was allowed to proceed to completion by omitting the addition of chromium(II); in these experiments, the carbon dioxide formed was due to the oxidation by both chromium(VI) and chromium(V).

The quantitative determination of the yield of carbon dioxide was used to check the completeness of quenching. A higher yield of carbon dioxide than that corresponding to the stoichiometry of reaction 2 indicated that quenching was incomplete due to either to too late addition (in very fast reactions) or to an insufficient amount of chromium(II). Results from these runs were rejected; they led to anomalously high values of $^{13}C/^{12}C$ isotope effects, due to the contribution from chromium(V) oxidation (reaction 3).

The collected carbon dioxide was analyzed for its 44 and 45 peaks on a Nuclide 6-60 RMS spectrometer equipped with a double inlet system. Isotope ratios of m/e 45:44 were measured alternately for the sample and a standard; at least six such cycles were used for calculation of the isotope ratio. All measurements were made at approximately the same pressure. Data obtained were corrected for instrumental errors (mixing and tailing) and ^{17}O contents.[6] Carbon dioxide generated from Grenville Calcite was used as the working standard and the results were reported in relation to PDB standard as parts per million ($\delta^{13}C$).[7]

We observed that traces of 2-propanol could constitute a serious error in the $^{13}C/^{12}C$ ratios due to its dominant m/e 45 ion ($CH_3C^+(H)OH$).[8] While a column of silica gel removed most of it, repeated distillation of the carbon dioxide from dry ice/methanol and dry ice/acetone cooled traps removed final traces and led to stable and reproducible 44:45 ratios.

The natural abundance of carbon-13 (R_0) in the carboxyl group of the hydroxy acid was determined from the $^{13}CO_2/^{12}CO_2$ ratio in the carbon dioxide obtained from the quantitative oxidation of the 2-hydroxy-2-methylbutyric acid with excess periodic acid;[9] periodic acid (2 mL, 0.01

---

(4) Holah, D. G.; Fackler, J. P., Jr. *Inorg. Synth.* **1967**, *10*, 26.

(5) Wiberg, K. B.; Schäfer, H. *J. Am. Chem. Soc.* **1969**, *91*, 927.

(6) Graig, H. *Geochim. Cosmochim. Acta* **1957**, *12*, 133.

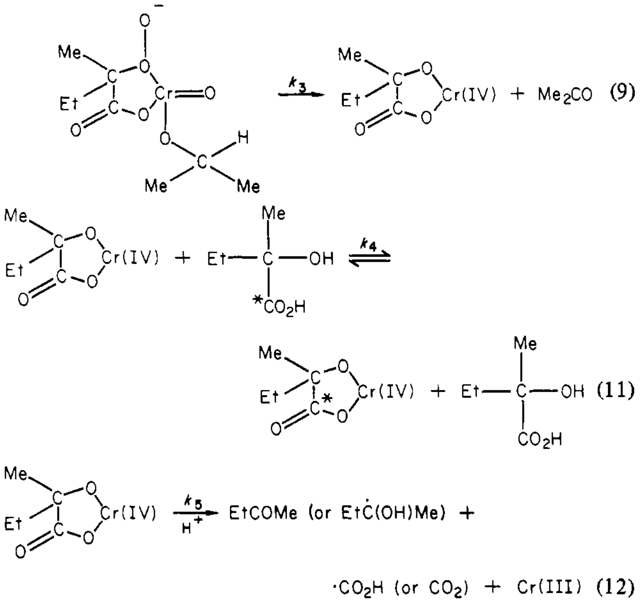
(7) $\delta^{13}C = [(R_{sample}/R_{standard}) - 1]1000$.

(8) "Mass Spectral Data," American Petroleum Institute Research Project 44, 1975; Vol. I, Serial No. 426.

(9) At higher temperatures, the decarboxylation of 2-hydroxy-2-methylbutyric acid was quantitative and seems specific and the further oxidation of the ketone very slow: Dryhurst, Glenn "Periodate oxidation of Diol and Other Functional Groups;" Pergamon Press: Oxford, 1966.

Scheme III

Mechanism C



M; 0.02 mmol) was placed in arm A while a solution of 2-hydroxy-2-methylbutyric acid (1 mL, 0.005 M; 0.005 mmol) containing perchloric acid (0.1 M) was placed in arm B. After deaeration by repeated freeze–evacuation–thaw cycles, the reaction was started by mixing and allowed to go to completion overnight at 40 °C.

The R values obtained have a standard deviation of ±0.5 in $\delta^{13}C$ units, which corresponds to an error of ±0.001 in the carbon-13 isotope effect measurements.

Results and Discussion

Table I summarizes the carbon-13 and deuterium isotope effects for the chromium(VI) cooxidation of 2-hydroxy-2-methylbutyric acid and 2-propanol at several acidities. Four experiments in which the reaction was not quenched but allowed to proceed to completion are also included; the observed carbon-13 isotope effects then reflect both the chromium(VI) cooxidation and the chromium(V) oxidation of 2-hydroxy-2-methylbutyric acid. The deuterium isotope effect study, which has been repeated in order to have measurements of both the deuterium and carbon-13 isotope effects under comparable conditions, gave results which are in excellent agreement with those reported previously.[2] The observed acidity dependence of the deuterium isotope effect is consistent with the mechanism shown in Scheme I, with a change in the rate-limiting step from complex formation at low acidities to oxidative decomposition of the complex at high acid concentrations.

The carbon-13 isotope effect exhibits an entirely different pattern. The carbon dioxide isolated from cooxidation is significantly enriched in ^{12}C at all acidities except at the very highest ones. This result is inconsistent with that expected from either mechanisms A or B. If the termolecular intermediate complex decomposed in a single three-electron transfer step according to mechanism A, the carbon-13 isotope effect shold parallel the behavior of the deuterium isotope effect. If the reactin proceeded by mechanism B, no carbon isotope effect should be observed.

In order to explain the existence of a carbon-13 isotope effect even under conditions when the formation of the termolecular Cr(VI)–HMBA–alcohol complex is rate limiting, one must modify mechanism B. In mechanism C (Scheme III) the chromium(IV) intermediate can exchange selectively with the free hydroxy acid present in the solution (reaction 11; one carbon atom has been arbitrarily marked by an asterisk to indicate ligand exchange) prior to undergoing oxidative decomposition. The decrease of the carbon isotope effect at the highest acidities can be understood if one makes the plausible assumption that the oxidative decomposition of the chromium(IV) complex (reaction 12) is catalyzed by acid, while the ligand exchange (reaction 11) is not. Thus k_4 would be larger than $k_5[H^+]$ at low acidities, but smaller at high hydrogen ion concentrations.[10]

Table II. Effect of Concentration of 2-Hydroxy-2-methylbutyric Acid (HMBA) on the Carbon-13 Isotope Effect[a]

HMBA, M	$^{12}k/^{13}k$	HMBA, M	$^{12}k/^{13}k$
0.06	1.0074	0.85	1.016
0.2	1.0084	1.00	1.017
0.5	1.012		

[a] [2-Propanol] = 0.045 M, [$HClO_4$] = 1.26 M, 25 °C.

Table III. Deuterium Isotope Effects in the Cooxidation of 2-Hydroxy-2-methylbutyric Acid and Methanol or Methanol-d_3[a]

$[H^+]$, M	10^4k_H, s^{-1}	10^4k_D, s^{-1}	k_H/k_D
0.02	2.88	0.16	17.6
0.05	3.14	0.21	14.7
0.10	3.38	0.23	14.4
0.50	3.84	0.28	13.5
1.26	6.96	0.56	12.4

[a] [HMBA] = 0.12 M, [CH_3OH] or [CD_3OH] = 0.12 M, 25 °C. CD_3OH was introduced as CD_3OD; the small amount of DOH formed in the solution by its hydrolysis was neglected.

Mechanism C implies that one should be able to observe competition between ligand exchange (reaction 11) and oxidative decomposition of the chromium(IV) intermediate (reaction 12) at moderate acidities. Under these conditions, the magnitude of the carbon isotope effect should depend on the concentration of the free hydroxy acid present in the solution: higher concentration should favor ligand exchange and lead to an increase in isotope effect. Such a concentration dependence of the isotope effect has been observed at $[H^+] = 1.26$ M where a concentration change in 2-hydroxy-2-methylbutyric acid from 0.06 to 1.0 M results in a change in the isotope effect from 1.0074 to 1.017 (Table II). *The results of this study thus lead to the conclusion that the oxidative decomposition of the chromium(VI) intermediate complex of 2-propanol and 2-hydroxy-2-methylbutyric acid in the cooxidation reaction is a two-step process. To reconcile this result with the stoichiometry of the reaction (reaction 1), one must conclude that chromium(VI) is remarkably selective toward the oxidation of the carbon–hydrogen bond of the alcohol while chromium(IV) is equally selective toward the carbon–carbon bond of the hydroxy acid.* In this preference for reacting with the hydroxy acid, chromium(IV) resembles chromium(V).[2]

The assumption that the acidity dependence of the deuterium isotope effect is due to a change in the rate-limiting step from complex formation (reaction 5) to oxidative decomposition (reaction 6) is crucial to the conclusions reached in this study. We have therefore subjected it to an additional test.

The change in the rate-limiting step is obviously due to the circumstance that for 2-propanol, the rate of hydrolysis ($k_{-2}[H^+]$) of the Cr(VI)–HMBA–alcohol complex is comparable to the rate of oxidation (k_3). The rate of hydrolysis should be governed primarily by steric factors, while the rate of oxidation should be determined principally by electronic factors influencing the stability of the carbonyl compound relative to the corresponding alcohol. Methanol[11] is known to be much less reactive toward oxidation than 2-propanol and its ester-like intermediate should be more easily hydrolyzed. Therefore, complex formation (reaction 5) should be reversible and oxidative decompositin (reaction 6) rate limiting at all acidities. Consequently, the cooxidation of methanol should exhibit a deuterium isotope effect at all acidities. This expectation has been confirmed experimentally (Table III). Although the isotope effect shows some depedence on acidity, it is in the opposite direction to that of 2-propanol and the magnitude of the isotope effect is very large throughout the entire range of acidities. The unusually high values are almost certainly due to

---

(10) It is likely that equilibration reaction 11 will lead to a mixture of chromium(IV) intermediates containing one or several hydroxy acid ligands; consequently, reaction 12 will result in the formation of a mixture of chromium(III) products containing from zero to two hydroxy acid ligands.

(11) Roček, J. *Collect. Czech. Chem. Commun.* **1960**, *25*, 1052.

Table IV. Acidity Dependence of the Carbon-13 and Deuterium Isotope Effects in the Cooxidation of Oxalic Acid and 2-Propanol[a]

[*i*-POH], M	[$(CO_2H)_2$], M	[H^+], M	$^{12}k/^{13}k$	k_H/k_D
2.29	0.05	0.086	1.025	
		0.096	1.025	4.14
2.60	0.06	0.5	1.020	4.08
		1.5	1.019	4.28
		1.84	1.016	4.25
		1.86	1.017	

[a] 25 °C.

a combination of primary with secondary isotope effects.

Earlier[12] we reported the existence of a significant carbon-13 isotope effect and of a sizable deuterium isotope effect in the cooxidation of oxalic acid and 2-propanol; these findings were interpreted as providing support for a synchronous mechanism analogous to that shown in mechanism A. The results obtained in this present study demonstrate that the existence of a carbon-13 isotope effect in itself cannot be accepted as evidence for the synchronous mechanism A. It is therefore quite possible that the cooxidation of oxalic acid and alcohol also reacts by a mechanism of type C and that the observed carbon-13 isotope effect is due to ligand exchange between the chromium(IV) intermediate and oxalic acid in the solution. This interpretation would be consistent with the necessity to assume a relatively stable chromium(IV)–oxalic acid intermediate in the oxalic acid catalyzed chromium(VI) oxidation of tris(phenanthroline)iron(II)[13] and perhaps also in the oxalic acid catalyzed oxidation of iodine.[14] In order to check this possibility, we measured the deuterium and carbon-13 isotope effects at varying acidities (Table IV). Although some decrease in the carbon-13 isotope effect can be observed, it is far less than that observed for 2-hydroxy-2-methylbutyric acid. The deuterium isotope effect is essentially constant, indicating that the oxidative decomposition of the termolecular complex is rate limiting throughout the entire range of acidities.

This may mean that the relative rate of ligand exchange to oxidative decomposition in the chromium(IV) intermediate complex is simply higher for oxalic acid than for 2-hydroxy-2-methylbutyric acid.[17] However, based on these results, the synchronous mechanism of type A cannot be ruled out. It is conceivable that oxalic acid is sufficiently more reactive toward chromium(IV) than 2-hydroxy-2-methylbutyric acid to make the chromium(IV)–oxalic acid intermediate so unstable toward oxidative decomposition that its formation and decomposition are fused into a single reaction. If this interpretation were correct, then one could view the tertiary hydroxy acids as representing an intermediate case between the reactive oxalic acid on one hand and the unreactive picolinic acid on the other hand. While picolinic acid does not undergo oxidation, it does accelerate the oxidation of alcohols to the same extent as oxalic acid and 2-hydroxy-2-methylbutyric acid; also, the rate law for the oxidation catalyzed by picolinic acid is the same as that found for the 2-hydroxy-2-methylbutyric acid cooxidation.[15] If the cooxidation of oxalic acid and alcohol reacted indeed by the synchronous mechanism A, then one can regard the three reactions as members of a series reacting essentially by the same mechanism in which the carbon–hydrogen bond of the alcohol is always broken in the oxidative decomposition step of the tertiary complex, while the fate of the carbon–carbon bond of the acid ligand depends on its reactivity toward chromium(IV). It could be broken simultaneously (mechanism A) in oxalic acid, subsequently (mechanism C) in a less reactive ligand like 2-hydroxy-2-methylbutyric acid, or not at all as in picolinic acid. The considerably higher reactivity of oxalic acid compared with the reactivity of 2-hydroxy-2-methyl-butyric acid toward chromium(VI) and chromium(V) is consistent with this interpretation. This interpretation also makes it easier to understand the high yield of $Cr(H_2O)_6^{3+}$ formed in the cooxidation of oxalic acid.[16]

From the carbon-13 isotope effects observed when the cooxidation of 2-hydroxy-2-methylbutyric acid and 2-propanol was allowed to go to completion, we can compute the isotope effect due to chromium(V) oxidation alone (reaction 3): $^{12}k/^{13}k = 1.036$ at $H^+ = 0.02$ M and 1.017 at $H^+ = 1.86$ M. These results are consistent with the earlier proposed mechanism for the chromium(V) oxidation of 2-hydroxy-2-methylbutyric acid consisting of a reversible complex formation between chromium(V) and the hydroxy acid followed by rate-limiting oxidative cleavage.[2] The observed shift in isotope effect with acidity is similar to that observed for chromium(IV) in this study and might mean that the oxidation step is acid catalyzed while the equilibration is not.

---

(12) Ramesh, S.; Roček, J.; Schoeller; D. A. *J. Phys. Chem.* **1978**, *82*, 2751.

(13) Hintze, R. E.; Roček, J. *J. Am. Chem. Soc.* **1977**, *99*, 132.

(14) Vandegrift, G. F.; Roček, J. *J. Am. Chem. Soc.* **1976**, *98*, 1371.

(15) Roček, J.; Peng, T-Y. *J. Am. Chem. Soc.* **1977**, *99*, 7622.

(16) Hasan, F.; Roček, J. *J. Am. Chem. Soc.* **1972**, *94*, 3181.

(17) Higher acidities apparently affect the stoichiometry of the reaction, as smaller than expected amounts of carbon dioxide were collected.