Three-Electron Oxidations. 17. The Chromium(VI) and Chromium(V) Steps in the Chromic Acid Cooxidation of 2-Hydroxy-2-methylbutyric Acid and 2-Propanol[1,2]

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Abstract: The chromic acid cooxidation of 2-hydroxy-2-methylbutyric acid (HMBA) and 2-propanol is a two-stage reaction. The stoichiometry of the first stage is HMBA + *i*-PrOH + 2Cr(VI) → $CH_3CH_2COCH_3$ + CO_2 + CH_3COCH_3 + Cr(V) + Cr(III); that of the slower second stage is HMBA + Cr(V) → $CH_3CH_2COCH_3$ + CO_2 + Cr(III). Kinetic, product, and isotope-effect studies of the first stage are consistent with a three-electron mechanism in which a termolecular complex formed of HMBA, *i*-PrOH, and $HCrO_4^-$ decomposes to acetone, carbon dioxide, a free radical, and Cr(III). Depending on the reaction conditions, either the decomposition or the formation of the termolecular complex may be rate limiting. The change in rate-limiting step results in a strong acidity dependence of the deuterium isotope effect in the cooxidation of 2-deuterio-2-propanol. The chromium(V) oxidation appears to proceed through a 3:1 complex of 2-hydroxy-2-methylbutyric acid and chromium(V) and results in the exclusive oxidation of the hydroxy acid even in a 20-fold excess of 2-propanol; in contrast to chromium(VI), chromium(V) thus shows a remarkable selectivity toward hydroxy acids.

In earlier papers of these series, we described a novel type of reaction in which chromium(VI) is reduced to chromium(III) in a three-electron oxidation–reduction step. Although we have recently found examples where a three-electron oxidation can take place in a 1:1 chromium(VI)–substrate complex,[2-4] the most common examples of three-electron oxidation proceed through a 1:2 chromium(VI)–substrate complex by a mechanism which in the most general form can be represented by Scheme I.

Scheme I

$$A + B + Cr^{VI} \rightleftarrows A\text{-}Cr^{VI}\text{-}B \quad (1)$$

$$A\text{-}Cr^{VI}\text{-}B \rightarrow C + Cr^{III} + \cdot R \quad (2)$$

$$\cdot R + Cr^{VI} \rightarrow D + Cr^{V} \quad (3)$$

$$A + Cr^{V} \rightarrow C' + Cr^{III} \quad (4)$$

$$B + Cr^{V} \rightarrow D' + Cr^{III} \quad (5)$$

In all known examples of three-electron oxidations following Scheme I, one of the substrate molecules is an organic acid carrying a second functional group (hydroxyl or carboxyl) allowing the formation of a relatively stable 1:1 chromium(VI)–substrate complex. The second substrate molecule is either identical with the first[5-7] or it may be a compound with a single functional group, e.g., an alcohol.[8-11] The latter case represents a cooxidation reaction in which two different substrates are oxidized simultaneously to yield at least two products. The chromium(V) intermediate formed in reaction 3 oxidizes one or both of the substrates A and B to products C′ and D′, which may but need not be identical with the products C and D obtained in the chromium(VI) oxidation.

Until now it has been impossible to separate the chromium(VI) and the chromium(V) oxidation steps and to gain thus more direct information on these two steps; the assignment of reaction products to individual oxidation reactions and mechanistic conclusions therefore had to be based on indirect information. Our recent work[7,12-15] has shown that tertiary α-hydroxy acids form complexes with chromium(V) which are sufficiently stable to permit their isolation in solid form; their nonaqueous and even aqueous solutions can be kept for prolonged periods of time. This ability of tertiary α-hydroxy acids to stabilize the chromium(V) state should permit the separation of the reactions of chromium(VI) (eq 1-3, Scheme I) from those of chromium(V) (eq 4 and 5). In this paper we wish to report the results of the investigation of the chromic acid cooxidation of 2-hydroxy-2-methylbutyric acid (HMBA) and of 2-propanol.

Experimental Section

Materials. Sodium dichromate dihydrate (Baker, Reagent), 2-propanol (Baker Analyzed, spectroscopic grade), and lithium aluminum deuteride (Aldrich, minimum 99% D) were used as received. Perchloric acid solutions were prepared from 70% perchloric acid (Mallinckrodt, analytical reagent). Stock solutions of sodium dichromate in distilled water were standardized iodometrically. Chromium(II) solutions were prepared[16] by dissolving metallic chromium (Ventron) in perchloric acid under nitrogen and were used on the same day. 2-Hydroxy-2-methylbutyric acid (Aldrich) was crystallized from heptane (mp 72 °C, lit.[13] 72-73 °C). Acetone (Fisher, spectroscopic grade) was dried over molecular sieves (Fisher, Type 4A). 2-Methoxyethyl ether (Aldrich) was dried over calcium hydride (Alfa Inorganics) for 2 days and then over lithium aluminum hydride (Alfa Inorganics) for 1 day. Low-acidity measurements were carried out in potassium phthalate–hydrochloric acid[17] and 2-hydroxy-2-methylbutyric acid–sodium 2-hydroxy-2-methylbutyrate buffers and the pH was checked on a Fisher Accumet pH meter.

2-Propanol-*d* (8.3 g, 0.138 mmol, 99.1% pure, isotopic purity 99%) was prepared[18] by the reduction of acetone (8.7 g, 0.15 mmol) by lithium aluminum deuteride (2.0 g, 0.048 mmol) in 40 mL of 2-methoxyethyl ether (diglyme) under nitrogen and isolated by fractional distillation on a small column (20-cm length, 1-cm i.d.) filled with glass helices. Substantially improved yields (92 vs. 72% reported[19]) were obtained by using rigorously anhydrous conditions: the 2-methoxyethyl ether, after drying over lithium aluminum hydride, was directly distilled onto lithium aluminum deuteride on a vacuum line.

Kinetic Measurements. The cooxidation of 2-hydroxy-2-methylbutyric acid and 2-propanol by chromic acid was followed spectrophotometrically using a Cary Model 15 recording spectrophotometer equipped with a thermostated cell holder. The reaction rates were determined[7] by following the change in the absorbance at two different wavelengths, 350 nm (A_{350}), where both chromium(VI) and chromium(V) absorb, and 750 nm (A_{750}), where chromium(V) is the only absorbing species. The absorbance of chromium(VI) at 350 nm, A^{VI}_{350}, was calculated[7] using the equation

$$A^{VI}_{350} = A_{350} - 32.0A_{750}(l_1/l_2) \quad (6)$$

where l_1 and l_2 denote the length of the light path at 350 (usually 1 cm) and 750 nm (5 or 10 cm), respectively, and the factor of 32.0 is a limiting value of the $\epsilon^{V}_{350}/\epsilon^{V}_{750}$ ratio determined graphically by plotting l_2A_{350}/l_1A_{750} vs. time. Complications were encountered at high alcohol concentrations (0.5 M) where the ratios of A_{350}/A_{750} tended to be higher and did not lead to constant values toward the end of the reaction.

Pseudo-first-order rate constants (k_{obsd} s^{-1}) for the disappearance

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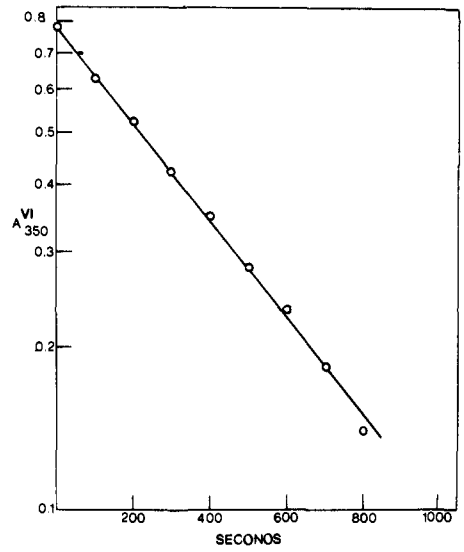


Figure 1. Determination of chromium(VI) oxidation rates: log plot of A^{VI}_{350} (from eq 6) vs time. [HMBA] = 0.1 M; [*i*-PrOH] = 0.1 M; $[HClO_4]$ = 0.1 M; [Cr(VI)] = 5×10^{-4} M; 25 °C.

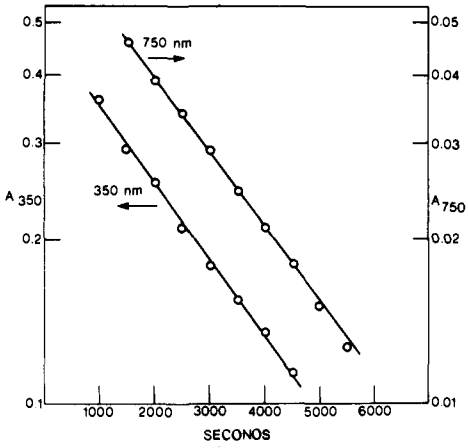


Figure 2. Determination of chromium(V) oxidation rates: log plot of A_{350} (1-cm cell) and of A_{750} (5-cm cell) vs. time for the last phase of the reaction. Conditions as in Figure 1.

of chromium(VI) were determined by plotting log A^{VI}_{350} vs time. The reaction obeyed good first-order kinetics, usually over 2-3 half-lives (Figure 1). A large excess (10-1000-fold) of substrates was used for all kinetic measurements. When the chromium(V) maximum at 750 nm is well developed, the rates of reduction of chromium(VI) can also be determined from initial slopes of log ($A^{max}_{750} - A_{750}$) vs. time plots. Except at high alcohol concentrations, agreement within about 5% was generally obtained between the rate constants determined by both methods. The rate constants from log A^{VI}_{350} plots are of higher precision and are therefore used throughout this paper with the exception of a few measurements at high alcohol concentrations and low acidities. Under these conditions the determination of rate constants from measurements at 350 nm became unreliable because of changes in the value of $\epsilon^{V}_{350}/\epsilon^{V}_{750}$ and values determined from log ($A^{max}_{750} - A_{750}$) plots were used instead.

Rate constants for the cooxidation reaction, k_{coox} (s^{-1}), were obtained from k_{obsd} by subtracting the oxidation rates by which each of the substrates would react in the absence of the other:

$$k_{coox} = k_{obsd} - (k_{HMBA} + k_{i\text{-PrOH}}) \quad (7)$$

The rate constants k_{HMBA} (s^{-1}) and $k_{i\text{-PrOH}}$ (s^{-1}) were determined experimentally at several concentrations, particularly at those where they were large enough to lead to significant correction; for the remaining reaction conditions they were calculated from known rate laws.[7,19]

Plots of log A_{750} vs. time for the last phase of the reaction (Figure 2) give reasonably good straight lines and permit the approximate determination of the rates for the chromium(V) oxidation. Similar

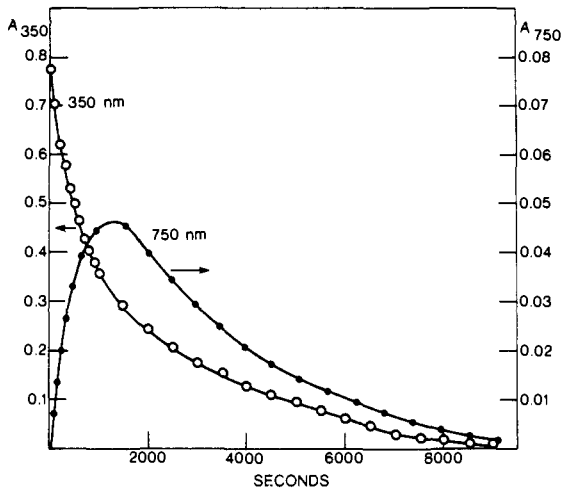


Figure 3. Absorbance vs. time plot at 350 (1-cm cell) and 750 nm (5-cm cell). Conditions as in Figure 1.

values (within 8%) can be obtained from the last part of the log A_{350} vs. time plot; at this point of the reaction chromium(VI) has been practically completely reduced and the absorption at 350 nm therefore becomes proportional to the concentration of chromium(V).[20]

Product Analysis. Chromium(V). The concentration of chromium(V) was calculated from time-absorbance curves monitored at 750 nm using the previously reported[13] value of ϵ 38.0. The concentration of chromium(V) at the highest point of the A_{750} vs. time curve was also determined iodometrically. A satisfactory agreement (within 5%) between the iodometric and spectrophotometric determinations was obtained.

Acetone and 2-butanone were analyzed by LC using a Waters Associates Model 6000A liquid chromatograph equipped with a Model 440 absorbance detector (254 nm), C_{18} reverse phase column, and a water-acetonitrile-acetic acid (760:145:45 v/v) solvent system. Product analyses were carried out either after the completion of the reaction or at an earlier time after quenching. In a typical experiment, 10 μL of a 1 M solution of chromium(VI) was injected into 1 mL of a reaction solution, the oxidation stopped by 2-3 drops of a chromium(II) solution, and the analytical result corrected for the volume change. The concentration of ketones was calculated from a calibration graph.

Carbon dioxide was determined manometrically in a Warburg apparatus. The instrument was calibrated by the carbon dioxide generated by the chromic acid oxidation of oxalic acid.[7]

Results and Discussion

Rate Studies. Figure 3 shows a typical example of an absorption vs. time plot for the reaction of chromium(VI) with a mixture of 2-hydroxy-2-methylbutyric acid and 2-propanol at 350 and at 750 nm. The buildup and later reduction of chromium(V) can be seen most directly at 750 nm, where chromium(V) is the only species with a significant absorption. The 350-nm curve which reflects the sum of chromium(VI) and chromium(V) shows the fairly rapid initial decrease corresponding to the reduction of chromium(VI) followed by a considerably slower reaction, the reduction of chromium(V). Figure 4 shows the concentration vs. time dependence for the chromium(VI) and chromium(V) species obtained from the data shown in Figure 3 using eq 6. The results show that the two oxidation steps, the chromium(VI) oxidation and the chromium(V) oxidation, are sufficiently separated in time to permit their independent investigation.

Tables I-V summarize the kinetic results obtained for the chromium(VI) oxidation step. The observed pseudo-first-order rate constants, k_{obsd}, are obtained from measurements at two wavelengths (cf. Experimental Section), in order to correct for the absorption changes due to the formation of chromium(V). The rate constants are further corrected for the rates of oxidation by which each of the two substrates would react in the

Table I. Dependence of Rates on Concentration of $HCrO_4^-$ [a]

10^4[Cr(VI)], M	10^4[$HCrO_4^-$], [b] M	10^3k_{obsd}	10^3k_{obsd}[Cr(VI)]/[$HCrO_4^-$]
1.0	0.99	1.95	1.97
2.5	2.43	2.07	2.13
5.0	4.72	2.03	2.15
25	19.9	1.71	2.15
50	34.7	1.47	2.12
100	57.7	1.05	1.82

[a] [$HClO_4$] = 0.1 M; [2-propanol] = 0.1 M; [2-hydroxy-2-methylbutyric acid] = 0.1 M; 25 °C. [b] $[HCrO_4^-] = (\sqrt{1 + 8K_d[Cr(VI)]} - 1)/4K_d$, where $K_d = [Cr_2O_7^{2-}]/[HCrO_4^-]^2 = 63.6$. While this value was obtained[21] at somewhat higher acidity ([H^+] = 0.17 M), it gives better results than the value 57.3 obtained by extrapolation[21] to 0.1 M $HClO_4$.

Table II. Dependence of Oxidation Rates on Concentration of 2-Hydroxy-2-methylbutyric Acid (HMBA)[a]

[$HClO_4$], M	[HMBA], M	[*i*-PrOH], M	10^3k_{obsd}	10^3k_{coox} [b]	k_{coox}/[HMBA]·[*i*-PrOH]·[H^+]
0.02	0.1	0.045	0.173	0.172	1.91
	0.2	0.045	0.374	0.370	2.05
	0.5	0.048	0.990	0.973	2.03
0.1	0.01	0.045	0.083	0.077	1.71
	0.02	0.053	0.190	0.183	1.74
	0.05	0.053	0.504	0.497	1.89
	0.1	0.048	0.990	0.989	2.06
	0.1	0.100	2.03	2.02	2.02
	0.2	0.048	2.00	1.99	2.07
	0.5	0.045	4.42	4.39	1.95
	1.0	0.045	8.66	8.56	1.90
0.2	0.1	0.046	1.78	1.75	1.89
	0.5	0.048	7.87	7.80	1.62
0.5	0.001[c]	0.045	0.142	0.027	1.20
	0.002[c]	0.045	0.173	0.058	1.29
	0.005[c]	0.048	0.286	0.163	1.36
	0.01	0.045	0.433	0.314	1.40
	0.02	0.045	0.729	0.613	1.36
	0.05	0.043	1.98	1.86	1.73
	0.1	0.045	3.72	3.59	1.60
	0.2	0.045	7.20	7.06	1.57
	0.5	0.050	19.30	19.10	1.70

[a] [Cr(VI)] = 5×10^{-4} M; 25 °C. [b] From eq 7. [c] At these low concentrations of HMBA, the amount of chromium(V) formed is considerably reduced.

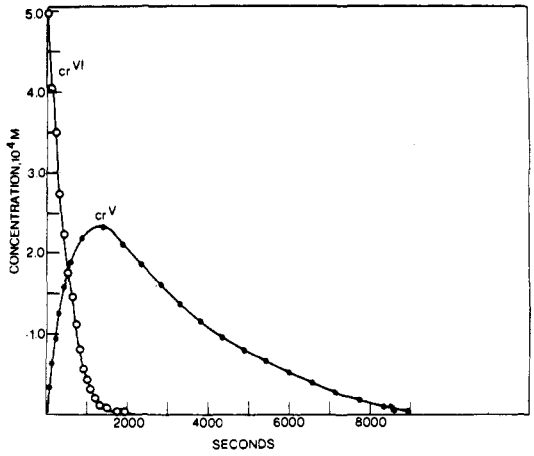


Figure 4. Concentration vs. time dependence for chromium(VI) and chromium(V) calculated from data of Figure 3.

Table III. Dependence of Oxidation Rates on Concentration of 2-Propanol[a]

[$HClO_4$], M	[*i*-PrOH]	10^3k_{obsd}	10^3k_{coox}	k_{coox}/[HMBA]·[*i*-PrOH][H^+]
0.02	0.0019	0.0597	0.0429	2.25
	0.021	0.490	0.473	2.25
	0.048	0.990	0.973	2.03
	0.1	2.31	2.29	2.29
	0.2	4.95[b]	4.93	2.46
	0.4	8.66[b]	8.64	2.16
	0.5	11.6[b]	11.5	2.30
	1.0	24.8[b]	24.7	2.47
0.1	0.004	0.420	0.394	1.97
	0.008	0.910	0.883	2.21
	0.02	2.10	2.07	2.07
	0.045	4.42	4.39	1.95
	0.1	10.5	10.4	2.08
	0.2	19.5	19.5	1.94
	0.5	42.0	41.9	1.68
0.5	0.002	0.914	0.837	1.67
	0.008	3.55	3.45	1.73
	0.019	8.40	8.27	1.74
	0.05	19.3	19.10	1.74
	0.1	41.1	40.7	1.63
	0.2	85	84	1.70

[a] [Cr(VI)] = 5×10^{-4} M; [HMBA] = 0.5 M; 25 °C. [b] From log $(A^{max}_{750} - A_{750})$ plots.

absence of the other ($k_{i\text{-PrOH}}$ and k_{HMBA}). It is therefore inevitable that the rate constants for the cooxidation reaction

$$k_{coox} = k_{obsd} - (k_{i\text{-PrOH}} + k_{HMBA}) \quad (8)$$

are subject to larger errors than one would expect in more straightforward kinetic measurements. We would estimate that the errors range from ±3 to ±20% depending on the magnitude of the correction. The errors are particularly significant at low substrate concentrations where the correction ($k_{i\text{-PrOH}} + k_{HMBA}$) approaches the value of k_{obsd}.

Good straight lines were generally obtained for log A^{VI}_{350} vs. time plots (Figure 1). Table I shows that, while k_{obsd} decreases with increasing total concentration of chromium(VI), nearly constant values of k_{obsd}[Cr(VI)]/[$HCrO_4^-$] are obtained indicating that the reaction is first order in $HCrO_4^-$.

Table II shows that the cooxidation reaction is very approximately first order in 2-hydroxy-2-methylbutyric acid (HMBA) over a 500-fold concentration range and at several acidities. The slight trend toward lower values at very low concentrations of HMBA is not significant enough considering the larger experimental errors under these conditions.

Table III shows that the cooxidation reaction is first order in 2-propanol over a 500-fold concentration range of the alcohol.

Table IV shows that, at lower acidities, the cooxidation reaction is approximately first order in the concentration of hydrogen ions. As the concentration of perchloric acid is increased the magnitude of the fourth-order rate constant (last column) shows a noticeable decrease which is much more pronounced for 2-deuterio-2-propanol (Table V) than for the protio compound. At high acidities the rate constant begins increasing again, suggesting the operation of a new kinetic term.

The different acidity dependence for the protio and deuterio compound leads to a strong acidity dependence of the kinetic deuterium isotope effect: the value of k_H/k_D changes from one characteristic for secondary isotope effects to a large value typical of primary isotope effects. Although no similar acidity

Table IV. Dependence of Cooxidation Rates of 2-Hydroxy-2-methylbutyric Acid (HMBA) and 2-Propanol on Acidity[a]

[HMBA], M	[$HClO_4$], M	[*i*-PrOH], M	10^3k_{obsd}	10^3k_{coox}	$10^3k'_{coox}$[b]	$k'_{coox}/[HMBA]\cdot[i\text{-PrOH}][H^+]$
0.1	0.02	0.045	0.173	0.171	0.173	1.91
	0.005	0.049	0.501	0.497	0.508	2.07
	0.1	0.048	0.990	0.989	1.02	2.12
	0.2	0.046	1.78	1.75	1.84	2.00
	0.35	0.047	3.15	3.07	3.36	2.04
	0.5	0.048	3.72	3.59	4.02	1.78
	0.75	0.045	5.33	5.09	5.84	1.73
	1.26	0.046	9.90	9.12	10.8	1.89
	1.86	0.045	14.7	12.7	15.1	1.80
	2.25	0.045	31.5	27.7	32.9	3.29
	2.50	0.045	≈67	≈62	≈73	6.6
0.5	0.005	0.054	0.301	0.286	0.286	2.12
	0.02	0.048	0.990	0.973	0.983	2.05
	0.05	0.050	2.50	2.47	2.52	2.03
	0.1	0.045	4.42	4.39	4.56	2.03
	0.2	0.047	7.87	7.80	7.82	1.78
	0.35	0.048	13.0	12.9	14.1	1.67
	0.5	0.050	19.3	19.1	21.4	1.71
	0.75	0.052	25.2	24.7	28.2	1.45
	1.0	0.051	37.4	36.6	42.7	1.67
	1.26	0.045	40.0	39.0	46.0	1.62
	1.86	0.045	≈62	≈60	≈71	≈1.7

[a] $[Cr(VI)] = 5 \times 10^{-4}$ M; 25 °C. [b] $k'_{coox} = k_{coox}[Cr(VI)]/[HCrO_4^-] = k_{coox}(K_a + [H]^+)K_a$, where $K_a = [HCrO_4^-][H^+]/[H_2CrO_4^-]$ and was calculated for each acidity from the equation[21] $\log K_a = 0.175 + 0.19\sqrt{I} + 1.01\sqrt{I}/(1 + 1.45\sqrt{I})$, where I = ionic strength = [$HClO_4$].

Table V. Dependence of Cooxidation Rates for 2-Hydroxy-2-methylbutyric Acid (HMBA) and 2-Deuterio-2-propanol (ROH) on Acidity and Deuterium Isotope Effects at 25 °C

[HMBA], M	[$HClO_4$], M	[ROH], M	10^3k_{obsd}	10^3k_{coox}	$10^3k'_{coox}$	$k'_{coox}/[HMBA]\cdot[ROH][H^+]$	k_H/k_D
0.1	0.02	0.043	0.131	0.130	0.131	1.52	1.26
	0.05	0.046	0.277	0.275	0.281	1.22	1.70
	0.1	0.045	0.385	0.376	0.389	0.864	2.46
	0.2	0.045	0.630	0.620	0.656	0.728	2.74
	0.35	0.045	0.787	0.765	0.831	0.527	3.87
	0.5	0.046	0.866	0.828	0.918	0.399	4.2
	0.75	0.0506	1.04	0.960	1.09	0.287	5.99
0.5	0.005	0.045	0.205	0.190	0.190	1.69	1.25
	0.02	0.05	0.920	0.903	0.912	1.82	1.13
	0.05	0.047	1.59	1.57	1.60	1.36	1.49
	0.1	0.045	2.26	2.23	2.32	1.03	1.97
	0.2	0.046	3.30	3.25	3.46	0.761	2.34
	0.35	0.046	4.01	3.93	4.32	0.532	3.14
	0.5	0.042	4.33	4.24	4.77	0.454	3.77
	0.75	0.051	6.13	5.95	6.78	0.355	4.08
	1.0	0.051	7.60	7.34	7.56	0.339	4.93
	1.26	0.045	8.40	8.09	9.51	0.236	4.82
	1.86	0.045	11.10	10.5	12.5	0.298	5.70

dependence was noticed in previously investigated cooxidation reactions of oxalic acid and 2-propanol[8] or cyclobutanol,[10] or of glycolic acid and 2-propanol,[11] it has been observed in the picolinic acid catalyzed chromic acid oxidation of alcohols.[22]

Thus, the principal reaction in the chromium(VI) cooxidation of 2-hydroxy-2-methylbutyric acid and 2-propanol is fourth order and obeys the rate law

$$-d[Cr(VI)]/dt = k[HCrO_4^-][HMBA][i\text{-PrOH}][H^+] \quad (9)$$

Tables VI and VII give the rate constants (k_{obsd}, s^{-1}) for the chromium(V) step. Except for the lowest concentrations, the values of the rate constants are generally at least an order of magnitude lower than those for the chromium(VI) step under comparable conditions (Tables II–IV).

The first-order dependency of the chromium(V) oxidation indicated by the linear log A vs. time plots (Figure 2) is confirmed by the approximately constant values of k_{obsd} over a 100-fold range of initial chromium(VI) (and thus chromium(V)) concentrations (Table VI). The modest influence of changes in the concentration of isopropyl alcohol (500-fold range) on the chromium(V) oxidation rates (Table VII) is in agreement with the finding that the alcohol is not oxidized by chromium(V) in the presence of HMBA (vide infra).

The reaction is first order in 2-hydroxy-2-methylbutyric acid at lower concentrations, but the order decreases at high concentrations and, particularly, at lower acidities. The dependence on acidity is more complex (Figure 5) and suggests the existence of a zero-order and a first-order term in hydrogen ions at lower acidities; at high acidities the reaction becomes essentially independent of acid concentration.

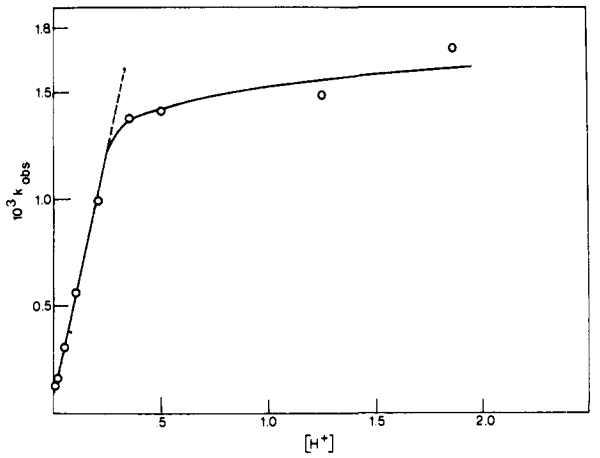


Figure 5. Dependence of chromium(V) oxidation rates (k_{obsd}, s^{-1}) on acidity. Data from Table VII.

Table VI. Chromium(V) Oxidation Rates. Dependence on Initial Chromium(V) Concentration[a]

10^4[Cr(V)], M[b]	0.5	1.25	2.5	12.5	25	50
$10^3 k_{obsd}$	0.34	0.32	0.31	0.25	0.24	0.24

[a] [$HClO_4$] = 0.1 M; [HMBA] = 0.1 M; [2-propanol] = 0.1 M; 25 °C. [b] The indicated concentration of chromium(V) is equal to one-half of the initial concentration of chromium(VI).

Table VII. Chromium(V) Oxidation Rates. Dependence on 2-Hydroxy-2-methylbutyric Acid, 2-Propanol, and Acidity[a]

[$HClO_4$], M	[HMBA], M	[*i*-PrOH], M	$10^3 k_{obsd}$	$10^3 k_{obsd}$/[HMBA]
0.02	0.1	0.045	0.075	0.75
	0.2		0.119	0.60
	0.5		0.157	0.31
0.1	0.05	0.045	0.16	3.2
	0.1		0.29	2.9
	0.2		0.42	2.1
	0.5		0.56	1.1
	1.0		0.74	0.74
0.5	0.05	0.045	0.163	3.3
	0.1		0.37	3.7
	0.2		0.75	3.8
	0.5		1.41	2.8
	1.0		1.73	1.7
	2.0		2.8	1.4
0.5	0.5	0.002	0.73	
		0.019	1.21	
		0.045	1.41	
		0.1	1.65	
		0.2	1.85	
		0.5	2.1	
		1.0	2.2	
0.005	0.5	0.045	0.131	
0.02			0.157	
0.05			0.32	
0.1			0.56	
0.2			0.99	
0.35			1.38	
0.5			1.41	
1.26			1.49	
1.86			1.71	

[a] [Cr(VI)] = 5×10^{-4} M; 25 °C.

Products. Acetone, 2-butanone, and carbon dioxide were the only reaction products and were formed in amounts which account for about 90% of the chromium(VI) introduced into the reaction; no other reaction products could be detected by LC.

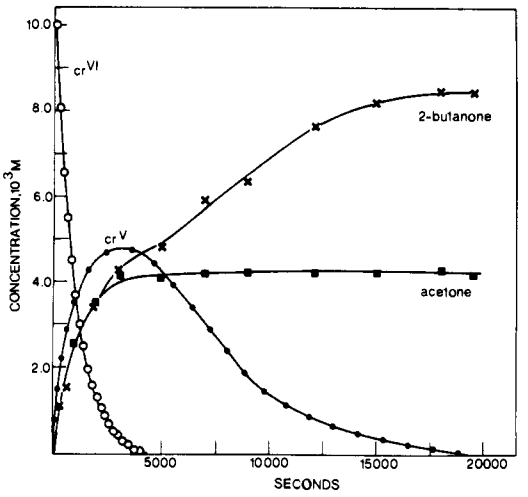


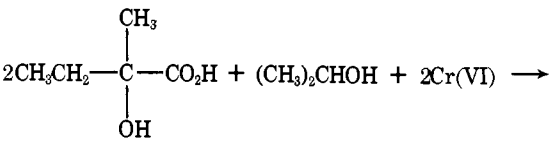
Figure 6. Concentrations of chromium(VI), chromium(V), 2-butanone, and acetone vs. time. [HMBA] = 0.1 M; [*i*-PrOH] = 0.1 M; [$HClO_4$] = 0.1 M; [Cr(VI)] = 0.01 M; 25 °C.

Table VIII. Reaction Products of the Cooxidation of 2-Hydroxy-2-methylbutyric Acid and 2-Propanol[a]

[$HClO_4$], M	[*i*-PrOH], M	2-butanone[b]	acetone[b]	CO_2[b]
0.1	0.01	0.85	0.42	0.90
	0.1	0.95	0.45	0.90
	2.0	0.93	0.45	0.93
0.5	0.1	0.95	0.45	0.90
	2.0	0.97	0.50	0.90
1.86	0.1	0.98	0.50	0.90

[a] Volume = 10 mL; [HMBA] = 0.1 M; [Cr(VI)] = 0.01 M. [b] Mol of product/mol of Cr(VI).

Table VIII shows the amount of products obtained per mol of chromium(VI) after the completion of the entire reaction under several reaction conditions covering a fivefold range of hydrogen ion concentrations and a 200-fold range of 2-propanol concentrations. The yields of 2-butanone and of carbon dioxide are twice as high as that of acetone. The stoichiometry of the overall reaction thus corresponds to

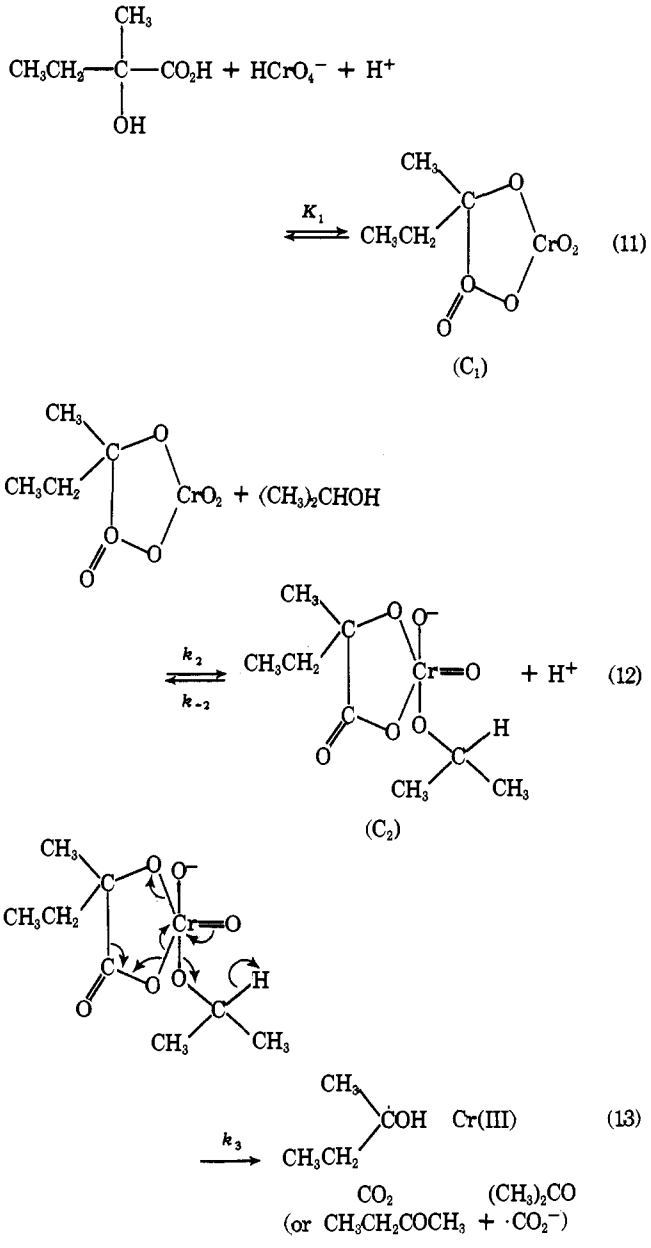


$$2CH_3CH_2COCH_3 + 2CO_2 + CH_3COCH_3 + 2Cr(III) \quad (10)$$

Figure 6 shows the results of a series of experiments in which the reaction was quenched at time intervals by the addition of chromium(II) and analyzed for 2-butanone and acetone by LC. The concentrations of chromium(VI) and chromium(V) were determined spectrophotometrically under identical reaction conditions (without quenching). *The results show quite unambiguously that the first phase of the reaction, the chromium(VI) oxidation, leads to equimolar quantities of 2-butanone and acetone, chromium(V), and chromium(III).*[23]

In the second phase of the reaction, the chromium(V) oxidation, additional 2-butanone is formed leading to a final 2-butanone:acetone ratio of 2:1 even in the presence of a 20-fold excess of 2-propanol, suggesting that the chromium(V) complex reacts with the hydroxy acid at least 200 times faster than with the alcohol. This is a surprising result which indicates a significant difference in the reactivity of chrom-

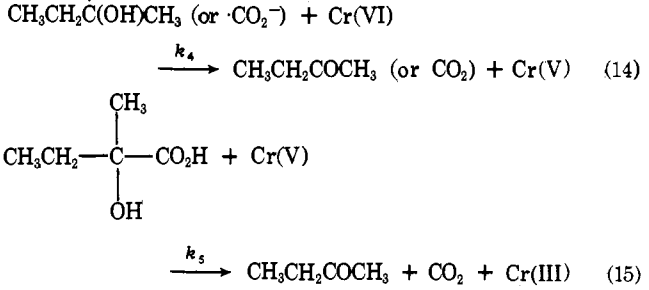
Scheme II



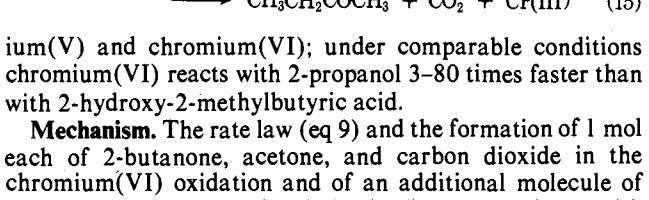
(11)

(12)

(13)



(14)



(15)

ium(V) and chromium(VI); under comparable conditions chromium(VI) reacts with 2-propanol 3–80 times faster than with 2-hydroxy-2-methylbutyric acid.

Mechanism. The rate law (eq 9) and the formation of 1 mol each of 2-butanone, acetone, and carbon dioxide in the chromium(VI) oxidation and of an additional molecule of 2-butanone in the chromium(V) oxidation are consistent with the mechanism shown in Scheme II.

The Chromium(VI) Step. The first step of the mechanism (eq 11) represents the formation of a bimolecular cyclic complex C_1 of chromic acid and 2-hydroxy-2-methylbutyric acid. This complex reacts with 2-propanol to give a termolecular complex C_2 (eq 12) which in the succeeding (eq 13) undergoes oxidative decomposition. As drawn in Scheme II the decomposition indicates a synchronous oxidation of both the alcohol and the hydroxy acid resulting thus in a direct reduction of Cr(VI) to Cr(III). The deuterium isotope effect provides evidence that the alcohol is oxidized in the rate-limiting step at higher acidities. Whether the oxidation of the carbon–carbon bond in the hydroxy acid is indeed simultaneous or whether it occurs in rapid succession following the alcohol oxidation cannot be decided on the basis of the currently available data. So far, we have been unable to determine the identity of the free radical product formed in reaction 13. Although some polymer formation was observed in the presence of acrylamide and acrylonitrile and provided qualitative support for the formation of free-radical intermediates, all attempts at quantitative or semiquantitative free-radical trapping were unsuccessful. However, results obtained in the oxidation of dihydroxy acids[3] suggest that the formation of a $R_2\dot{C}OH$ radical from the hydroxy acid may be favored.

The next step is the reduction of a molecule of Cr(VI) to Cr(V) by the free radical formed in reaction 13.

Scheme II leads to the following rate law for the chromium(VI) phase of the oxidation:

$$-\frac{d[Cr(VI)]}{dt} = \frac{2d[Cr(V)]}{dt} = k_{coox}[Cr(VI)] = k'_{coox}[HCrO_4^-] = \frac{2K_1k_2k_3[HMBA][i\text{-PrOH}][HCrO_4^-][H^+]}{k_{-2}[H^+] + k_3} \quad (16)$$

In deriving the rate law we assumed that intermediate C_1 is in rapid equilibrium with 2-hydroxy-2-methylbutyric acid and $HCrO_4^-$ and that reaction 14 is always fast; we applied the steady-state approximation to intermediate C_2. At high acidities, particularly for the less reactive 2-deuterio-2-propanol, $k_{-2}[H^+] > k_3$ and eq 16 will be simplified further to

$$-d[Cr(VI)]/dt = 2K_1K_2k_3[HMBA][i\text{-PrOH}][HCrO_4^-] \quad (17)$$

where $K_2 = k_2/k_{-2}$. Under these conditions the cooxidation reaction should be independent of acidity and exhibit a primary kinetic deuterium isotope effect determined by the ratio k_3^H/k_3^D, which is in agreement with experimental data (Tables IV and V). However, the change from first to zero order in hydrogen ions is not complete, probably because of the operation of an additional kinetic term at very high acidities, reflecting the oxidative decomposition of the conjugate acid of C_2.

At lower acidities, $k_3 > k_{-2}[H^+]$ and the rate law becomes

$$-d[Cr(VI)]/dt = 2K_1k_2[HMBA][i\text{-PrOH}][HCrO_4^-][H^+] \quad (18)$$

which corresponds to the experimental rate law (eq 9) and which is valid over a large range of concentrations. Under these conditions the rate-limiting step is the formation of complex C_2 (eq 12) and, consequently, no kinetic isotope effect should be expected as long as eq 18 is strictly valid. This is true only at quite low acidities, while at higher acidities, where $k_{-2}[H^+]$ becomes comparable in magnitude to k_3, an isotope effect of intermediate magnitude is observed (Table V).

The rate laws derived from Scheme II are thus in satisfactory qualitative agreement with our results. The significant deviation from first-order dependence on hydrogen ions observed in the cooxidation of 2-deuterio-2-propanol between 0.005 and 0.5 M $HClO_4$ permits a semiquantitative comparison of rate law 16 with experimental data. From eq 16 one obtains

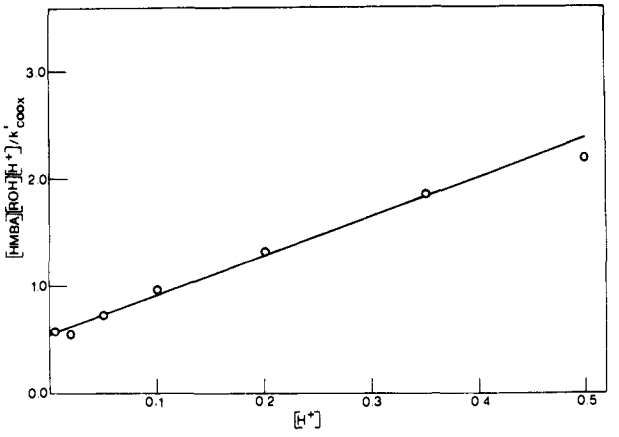


Figure 7. Plot of $[HMBA][i\text{-PrOH-}d][H^+]/k'_{coox}$ vs. $[H^+]$. Data from Table V.

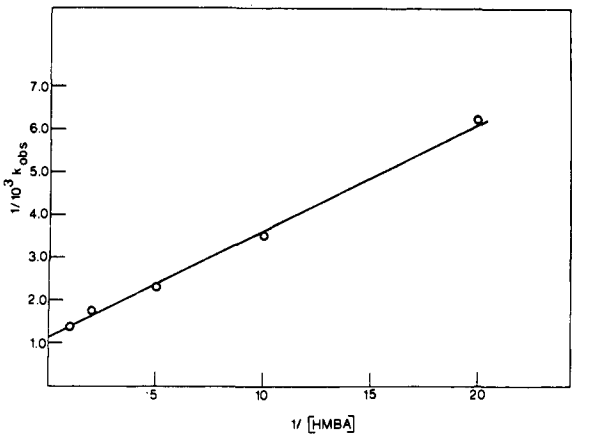


Figure 8. Plot of $1/k_{obsd}$ vs. $1/[HMBA]$ for the chromium(V) oxidation. Data from Table VII.

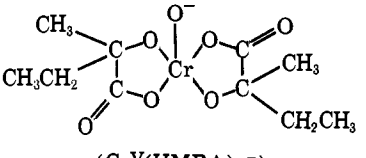
$$\frac{[HMBA][i\text{-PrOH}][H^+]}{k'_{coox}} = \frac{k_{-2}}{2K_1k_2k_3}[H^+] + \frac{1}{2K_1k_2} \quad (19)$$

A plot of $[HMBA][i\text{-PrOH-}d][H^+]/k_{coox}$ vs. $[H^+]$ gives a reasonably straight line (Figure 7) from which the values of $K_1k_2 = 0.83$ and 0.91 and $k_3^D/k_{-2} = 0.16$ and 0.14 can be obtained for 0.1 and 0.5 M HMBA, respectively, using a least-squares treatment.

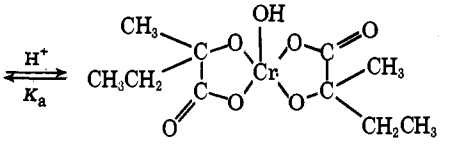
The Chromium(V) Step. In the last step of Scheme II (eq 15) chromium(V) oxidizes 2-hydroxy-2-methylbutyric acid to 2-butanone and carbon dioxide.

The observation that the reduction of chromium(V) is first order in 2-hydroxy-2-methylbutyric acid (Table VII) is surprising. It indicates that the second step of the reaction is not simply a unimolecular decomposition of the chromium(V) complex, but that the chromium(V) oxidation of 2-hydroxy-2-methylbutyric acid occurs in a complex or transition state containing one more molecule of the hydroxy acid then does the chromium(V) species prevalent in the solution. Chromium(V) forms stable solid complexes with two molecules of hydroxy acids;[13] it is therefore reasonable to assume that a complex of this type is the predominant chromium(V) species in solution. In order to account for the first-order observed dependence in 2-hydroxy-2-methylbutyric acid, the activated complex for the oxidation reaction therefore must contain three molecules of hydroxy acid. The observed acidity dependence

Scheme III



$(Cr^V(HMBA)_2^-)$



$(Cr^V(HMBA)_2H)$ (20)

$$Cr^V(HMBA)_2^- + HMBA \underset{}{\overset{K_4}{\rightleftharpoons}} Cr^V(HMBA)_3^- \quad (21)$$

$$Cr^V(HMBA)_3^- \xrightarrow{k_5} CH_3CH_2COCH_3 + CO_2 + Cr^{III} \quad (22)$$

$$Cr^V(HMBA)_3^- + H^+ \underset{K_a'}{\rightleftharpoons} Cr^V(HMBA)_3H \quad (23)$$

$$Cr^V(HMBA)_3H \xrightarrow{k_6} CH_3CH_2COCH_3 + CO_2 + Cr^{III} \quad (24)$$

suggests that the reaction can take place through two activated complexes differing by the presence of one proton.

A reaction mechanism which takes account of the observed dependence of reaction rates on acidity and on the concentration of 2-hydroxy-2-methylbutyric acid is given in Scheme III.

This scheme shows not only the formation of the 3:1 complex of 2-hydroxy-2-methylbutyric acid with chromium(V) ($Cr^V(HMBA)_3^-$), but also the protonation of both the 2:1 and the 3:1 complexes. The mechanism leads to the rate law

$$-d[Cr(V)]/dt = k_{obsd}[Cr^V] \quad (25)$$

$$= k_5[Cr^V(HMBA)_3^-] + k_6[Cr^V(HMBA)_3H]$$

$$= \frac{(k_5 + k_6[H^+]/K_a')K_4[HMBA][Cr^V]}{K_4[HMBA] + 1 + [H^+]/K_a + K_4[HMBA][H^+]/K_a'}$$

Thus

$$\frac{1}{k_{obsd}} = \frac{[H^+] + K_a'}{k_5K_a' + k_6[H^+]} + \frac{1 + [H^+]/K_a}{K_4(k_5 + k_6[H^+]/K_a')}\frac{1}{[HMBA]} \quad (26)$$

In agreement with the requirements of eq 26, good straight-line plots for $1/k_{obsd}$ vs. $1/[HMBA]$ are obtained (Figure 8). At lower acidities, when $(1 + K_4[HMBA]) > [H^+]\cdot(K_4[HMBA]/K_a' + 1/K_a)$, eq 25 is reduced to

$$k_{obsd} = \frac{K_4[HMBA]}{1 + K_4[HMBA]}(k_5 + k_6[H^+]/K_a') \quad (27)$$

At higher acidities, when k_5 becomes small in comparison with $k_6[H^+]/K_a'$, eq 25 may be rearranged to

$$\frac{[HMBA]}{k_{obsd}} = \frac{K_4[HMBA] + K_a'/K_a}{k_6K_4} + \frac{1 + K_4[HMBA]}{k_6K_4/K_a'}\frac{1}{[H^+]} \quad (28)$$

At constant [HMBA] plots of k_{obsd} vs. $[H^+]$ and of $[HMBA]/k_{obsd}$ vs. $1/[H^+]$ (Figures 5 and 9) give reasonably good straight lines in the initial parts of the curves where the assumptions underlying eq 27 and 28, respectively, are valid. Unfortunately, the complexity of the rate law and particularly the presence of two acid dissociation equilibria (K_a and K_a') preclude the numerical determination of the individual rate and equilibrium constants.

Why the oxidation of 2-hydroxy-2-methylbutyric acid requires the formation of 3:1 complex is not clear. It could be that this complex is octahedral and that this facilitates the reduction of chromium(V) to chromium(III). Another factor could be

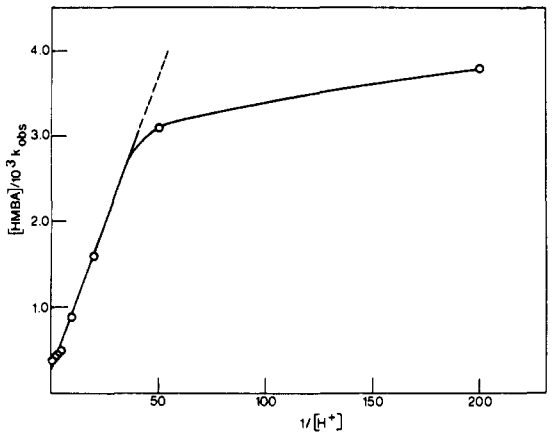


Figure 9. Plot of $[HMBA]/k_{obsd}$ vs. $1/[H^+]$ for the chromium(V) oxidation. Data from Table VII.

the stability of the reaction product, most likely $[Cr^{III}(HMBA)_2(H_2O)_2]^+$. It is interesting to note that at low concentrations HMBA stabilizes Cr(V).[13] This suggests that chromium(V) achieves maximum stability in a complex with two molecules of HMBA; both the loss of an HMBA ligand as well as the addition of a third HMBA molecule result in destabilization.

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References and Notes

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Determination of the Lifetimes of Unstable Ion Radicals by Homogeneous Redox Catalysis of Electrochemical Reactions. Application to the Reduction of Aromatic Halides

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Abstract: Application of the usual electrochemical techniques to the detection and characterization of short-lived ion radicals fails as soon as the lifetimes are shorter than about 0.1 ms. Homogeneous redox catalysis of the electrochemical reaction yielding the ion radical as an intermediate permits the characterization of much more unstable species allowing the determination of lifetimes down to the nanosecond time range. Instead of occurring at the electrode surface the initial electron transfer is carried out by the active form of the catalyst couple. This is produced electrochemically in the context of a standard electrochemical method such as cyclic voltammetry. The kinetics of the overall reaction is derived from the increase of the catalyst wave in the presence of the substrate. According to the relative magnitude of the rate constants of the backward homogeneous electron transfer and of the follow-up decomposition of the initial anion radical, the kinetic control of the catalytic process is either by the latter reaction or by the forward electron transfer step. Mixed kinetic control is obtained for intermediate values of the rate constant ratio. The determination of the lifetime of the ion radical is based upon the shift of the system from one limiting control to mixed kinetic control with a change in the catalyst concentration. Another approach involves the concomitant use of the data featuring the electrode reaction when it is under the kinetic control of the decomposition reaction. The reduction of five aromatic halides (2-chloroquinoline, 9-chloro- and bromoanthracene, and 1-chloro- and bromonaphthalene) in aprotic medium is analyzed to illustrate the practical application of the redox catalytic method to the determination of the lifetimes of frangible ion radicals. The relationships between the lifetimes of the anion radicals, the standard potentials for their formation, and the structure of the parent compound are briefly discussed.

The electrochemical reduction of aromatic halides generally involves the cleavage of the carbon–halogen bond of the initial anion radical followed by further reduction of the resulting neutral aryl radical:

$$ArX + 1e \rightleftarrows ArX^{-}\cdot \quad (1el)$$

$$ArX^{-}\cdot \xrightarrow{k} Ar\cdot + X^{-} \quad (2)$$

$$Ar\cdot + 1e \rightarrow Ar^{-} \quad (3)$$

$$Ar\cdot + ArX^{-}\cdot \xrightarrow{k_4} Ar^{-} + ArX \quad (4)$$

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