$$\left(\frac{d[CO_2]}{dt}\right)_{\text{from } CH_3\overset{O}{\overset{\|}{C}}OO\cdot} =$$

$$\left(\frac{d[^{46}CO_2]}{dt}\Big/a\right) = 11 \times 10^{-9}\ M\ \text{sec}^{-1} \quad (29)$$

then

$$\left(\frac{d[CO_2]}{dt}\right)_{\text{from DBPO}} = \left(\frac{d[CO_2]}{dt}\right)_{\text{total}} - \left(\frac{d[CO_2]}{dt}\right)_{CH_3\overset{O}{\overset{\|}{C}}OO\cdot} \quad (30)$$

From these rates, the number of CO_2 molecules per termination step is

$$CO_2/\text{term.} = (d[CO_2]/dt)_{CH_3\overset{O}{\overset{\|}{C}}OO\cdot}/0.87(d[CO_2]/dt)_{init} = 2.5/\text{chain} = 5.0/\text{pair}$$

or, based upon calculated initiation rates

$$CO_2/\text{term}\cdot = \frac{(d[CO_2]/dt)_{CH_3\overset{O}{\overset{\|}{C}}OO\cdot}}{2ek_i[\text{DBPO}]} \cong 3 \text{ per chain or } 6 \text{ per pair}$$

Therefore, the interaction of acetylperoxy radicals gives about 2.5 O_2 and 5 CO_2 in 2½ bimolecular interactions before termination, and about one more O_2 comes from *t*-BuOO· radicals, either through termination or self-reaction of *t*-BuOO· radicals. This would be explained by the reactions 31–34. These results corroborate the oxygen evolution

$$CH_3\overset{O}{\overset{\|}{C}}OO\cdot + CH_3\overset{O}{\overset{\|}{C}}OO\cdot \longrightarrow 2CH_3\cdot + 2CO_2 + O_2 \quad (31)$$

$$CH_3\cdot + O_2 \longrightarrow CH_3OO\cdot \quad (32)$$

$$CH_3OO\cdot + t\text{-BuOO}\cdot \longrightarrow CH_2O + O_2 + t\text{-BuOH} \quad (33)$$

$$2t\text{-BuOO}\cdot \longrightarrow 2t\text{-BuO}\cdot + O_2 \quad (34)$$

for acetylperoxy[7] and secondary alkylperoxy[8] radicals previously reported. In the absence of *t*-BuOOH, reaction 33 would be replaced by an interaction of methylperoxy radicals with themselves or with acetylperoxy radicals.

We conclude that all evidence presented in these three papers points to nonterminating interactions of acylperoxy radicals followed by termination involving the alkyl radicals from decarboxylation. This leaves the rapid termination of benzaldehyde[6] autoxidation, in which decarboxylation is very slow, a mystery to be investigated.

Acknowledgment. We are grateful to the Air Force Office of Scientific Research for support of this research.

References and Notes

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(9) If we had assumed that all the extra ^{16}O had come from self-reactions of *t*-BuOO· radicals resulting in an M_q, then $M_q' = \frac{1}{2}M_q$ and, in a plot like that in Figure 5, about 20% rather than 40% of evolved oxygen would arise from interactions of *t*-BuOO· radicals. This result would not change the conclusions of this paper.

Three-Electron Oxidations. X. Cooxidation of Isopropyl Alcohol and Glycolic Acid[1,2]

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Abstract: The chromic acid oxidation of a mixture of glycolic acid and isopropyl alcohol is a fast cooxidation process yielding acetone and gloxylic acid in an approximately 2:1 ratio. The mechanism consists in the formation of a termolecular complex of chromium(VI) with glycolic acid and isopropyl alcohol, which decomposes in a rate-limiting step in a three-electron oxidation-reduction process to a molecule of acetone, chromium(III), and a free radical intermediate $HO\dot{C}HCO_2H$ which is subsequently oxidized to glyoxylic acid. The substantial isotope effect observed for both substrates ($HOCH_2CO_2H$-$(CH_3)_2CDOH$, 6.0; $HOCD_2CO_2H$-$(CH_3)_2CHOH$, 5.8; $HOCD_2CO_2H$-$(CH_3)_2CDOH$, 34.4) provides clear evidence for the synchronous breaking of two different C-H bonds in the rate-limiting step. It also represents convincing proof for the proposed three-electron oxidation mechanism.

Chromic acid reacts with two-component systems containing oxalic acid together with a primary or secondary alcohol,[3,4] malachite green,[5] or indigo,[6] by several orders of magnitude faster than with either oxalic acid or the other component alone. A number of other bi- and polyfunctional compounds exhibit a similar effect as oxalic acid.[7,8]

In several cases it has been conclusively demonstrated that this rapid reaction is a cooxidation, in which both substrates are oxidized.[3-5,8] On the other hand, rapid oxidations of two-component systems in which only one of them is oxidized while the other acts as a catalyst have also been found: oxalic acid acts as an efficient catalyst in the oxidation of iodide[9] and of thiocyanate;[10] picolinic acid greatly accelerates the oxidation of alcohols.[11] At this point the amount of information on cooxidation and on catalysis in chromic acid oxidations is insufficient to permit the drawing of more general conclusions about the conditions necessary for either of these two processes to take place. Further study of both reaction types is therefore needed.

In this paper we wish to present the results of a detailed

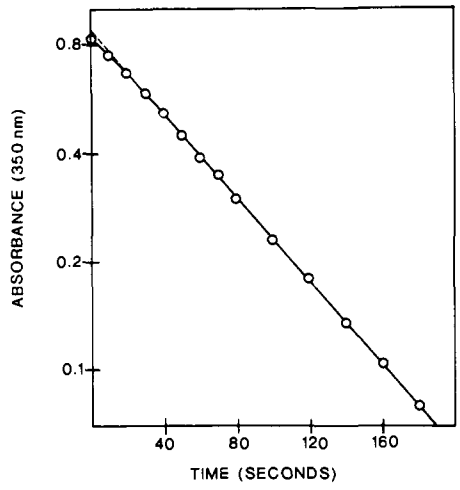


Figure 1. Rate plot for chromic acid cooxidation of isopropyl alcohol and glycolic acid at 25°. Concentrations: 0.78 *M* *i*-PrOH, 0.316 *M* $HOCH_2CO_2H$, 0.628 *M* $HClO_4$.

Table I. Chromic Acid Cooxidation of Isopropyl Alcohol and Glycolic Acid at 25°

[Glycolic acid], *M*	[Isopropyl alcohol], *M*	$[HClO_4]$ = 0.969 *M* 10^2k, sec^{-1}		$[HClO_4]$ = 0.628 *M* 10^2k, sec^{-1}		$[HClO_4]$ = 0.097 *M* 10^2k, sec^{-1}	
		Exptl	Calcd	Exptl	Calcd	Exptl	Calcd
1.8	3.12	17.9	17.5	8.25	8.08	1.16	1.40
1.8	2.34	13.7	13.15				
1.8	1.56	9.9	9.20	4.34	4.18	0.720	0.726
1.8	0.78	5.03	4.90	2.38	2.23	0.407	0.388
1.8	0.39	2.71	2.75	1.34	1.26	0.231	0.219
1.8	0.156	1.29	1.46	0.79	0.67	0.108	0.117
1.8	0.078	0.81	1.03	0.51	0.48	0.077	0.083
1.8	0.039	0.58	0.80	0.39	0.38	0.063	0.067
1.8	0.0156	0.56	0.66	0.28	0.32	0.053	0.057
0.36	3.12	11.6	10.3	6.02	5.63		
0.36	1.56	5.68	5.22	3.30	2.87		
0.36	0.78	3.01	2.70	1.72	1.49		
0.36	0.39	1.59	1.44	1.10	0.80		
0.36	0.156	0.69	0.69	0.45	0.39		
0.36	0.078	0.46	0.42	0.30	0.25		
0.36	0.039	0.29	0.31	0.22	0.18		
0.36	0.0156	0.22	0.23	0.17	0.14		
1.44	0.78	5.10	4.61				
0.72	0.78	3.40	3.61				
0.18	0.78	2.41	1.99				
0.072	0.78	1.89	1.42				
0.036	0.78	1.09	1.19				
0.018	0.78	1.00	1.08				
0.0072	0.78	1.02	1.00				

investigation of the chromic acid oxidation of glycolic acid–isopropyl alcohol mixtures. Glycolic acid was selected as the simplest α-hydroxy acid; its oxidation in the absence of other oxidizable substrates has been investigated separately.[1]

Results

Kinetics. Figure 1 gives a typical example of a pseudo-first-order rate plot for the chromic acid oxidation of a mixture of isopropyl alcohol with glycolic acid.[12]

Table I and Figures 2 and 3 give the dependence of the rate of reduction of chromic acid on the concentration of the two substrates and on acidity. Figure 2 shows clearly that the rate of reduction of chromic acid by glycolic acid is greatly increased by isopropyl alcohol, although the reduction between chromic acid and this alcohol in the absence of glycolic acid (curve A) would be too slow to increase the reaction rate measurably. At higher concentrations the

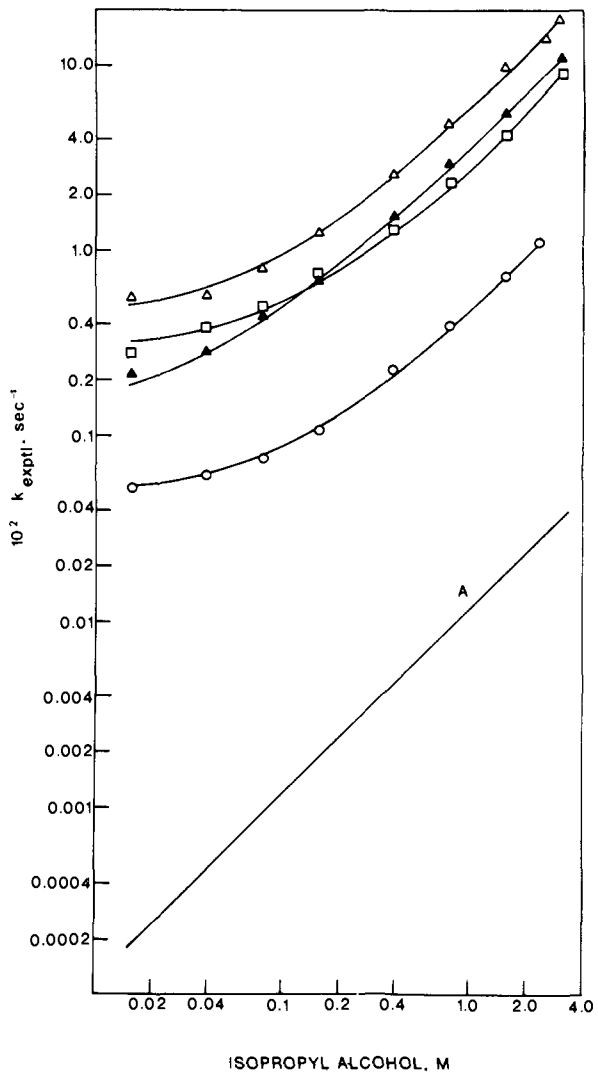


Figure 2. Effect of isopropyl alcohol concentration on the rate of cooxidation of isopropyl alcohol and glycolic acid at 25°: (△) 1.8 *M* $HOCH_2CO_2H$, 0.969 *M* $HClO_4$; (□) 1.8 *M* $HOCH_2CO_2H$, 0.628 *M* $HClO_4$; (○) 1.8 *M* $HOCH_2CO_2H$, 0.097 *M* $HClO_4$; (▲) 0.36 *M*, $HOCH_2CO_2H$, 0.969 *M* $HClO_4$; (curve A) no $HOCH_2CO_2H$, 0.097 *M* $HClO_4$.

reaction becomes approximately first order in the alcohol. The effect of glycolic acid on the rate of reduction of chromic acid by isopropyl alcohol is similar, although less obvious from visual inspection of the plot (Figure 3) due to the high oxidation rate of glycolic acid alone (curve B). The results therefore suggest that the observed rate acceleration is due to a reaction with a transition state containing chromium(VI), glycolic acid, and isopropyl alcohol.

The simplest reaction scheme which can account for the experimental observation is Scheme I (GA = glycolic acid;

Scheme I

$$Cr(VI) + GA \overset{K_1'}{\rightleftharpoons} C_1 \quad (1)$$

$$C_1 \xrightarrow{k_2'} \text{products} \quad (2)$$

$$C_1 + GA \xrightarrow{k_3'} \text{products} \quad (3)$$

$$Cr(VI) + ROH \xrightarrow{k_4'} \text{products} \quad (4)$$

$$C_1 + ROH \xrightarrow{k_5'} \text{products} \quad (5)$$

ROH = isopropyl alcohol; Cr(VI) = $HCrO_4^- + H_2CrO_4$).

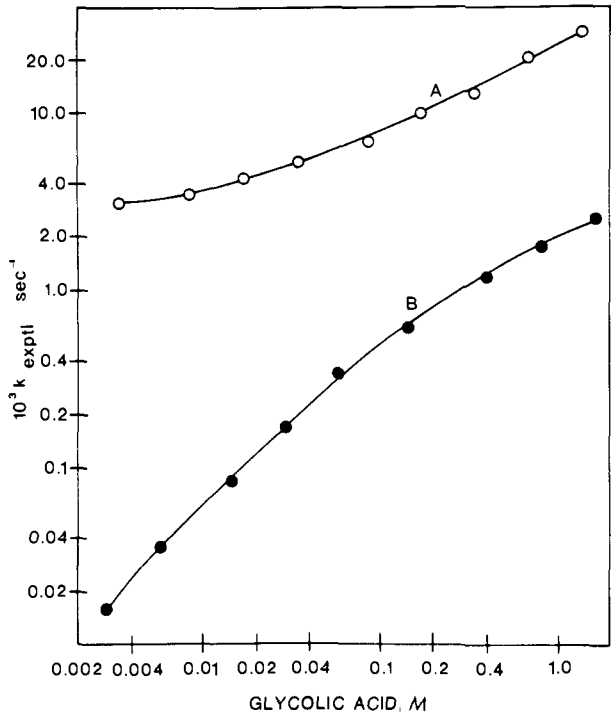


Figure 3. Dependence of oxidation rates on the concentration of glycolic acid in the presence of isopropyl alcohol (curve A; 0.78 *M* *i*-PrOH) and in its absence (curve B); 0.628 *M* $HClO_4$, 25°.

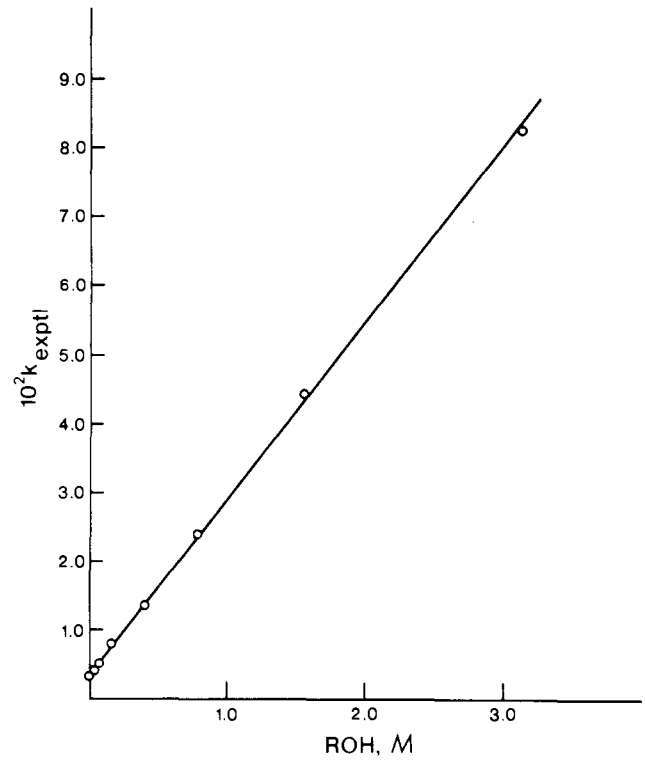


Figure 4. Determination of k_5' from eq 7; [glycolic acid] = 1.8 *M*; 25°.

Equations 1, 2, and 3 represent reactions taking place in the chromic acid oxidation of glycolic acid;[1] eq 4 represents the chromic acid oxidation of isopropyl alcohol.[14] Reaction 5 is represented as involving chromic acid and glycolic acid in the form of the complex C_1 as well as isopropyl alcohol; it is this reaction which is responsible for the observed rate acceleration. The rate law corresponding to Scheme I is given in eq 6, where $[Cr_T] = [Cr(VI)] + [C_1]$ represents the total

$$v = k_{exptl}[Cr_T] = [C_1](k_2' + k_3'[GA] + k_5'[ROH]) + k_4'[Cr(VI)][ROH] \quad (6)$$

concentration of chromium(VI). Equation 6 corresponds to a linear relationship between k_{exptl} and [ROH] (eq 7),

$$k_{exptl} = \frac{K_1'[GA]k_5' + k_4'}{1 + K_1'[GA]}[ROH] + \frac{K_1'[GA](k_2' + k_3'[GA])}{1 + K_1'[GA]} \quad (7)$$

where the values of all constants with the exception of k_5' are known from previous work.[1,3] Figure 4 gives an example of a plot of k_{exptl} vs. [ROH] used to determine the value of k_5'; Table II summarizes the results and shows that the values of k_5' are proportional to acidity and that an acidity independent rate constant can be obtained. As the acidity dependency of all other constants in eq 6 and 7 is known, a complete rate law for the chromic acid oxidation of glycolic acid–isopropyl alcohol mixture can be written (eq 8), where

$$k_{expt} = \frac{K_1[GA](k_2 + k_3[GA] + k_5[ROH]) + k_4[ROH][H^+]^2}{1 + K_1[GA]/[H^+] + [H^+]/K_a} \quad (8)$$

$K_1 = 2.2$, $k_2 = 3.0 \times 10^{-3}\ M^{-1}$ sec^{-1}, $k_3 = 1.3 \times 10^{-3}\ M^{-2}$ sec^{-1}, $k_4 = 1.26 \times 10^{-2}\ M^{-1}$, $k_5 = 4.55 \times 10^{-2}\ M^{-2}$ sec^{-1}, and $K_a = [H^+][HCrO_4^-]/[H_2CrO_4] = 4.2\ M$. The last term in the denominator reflects the protonation of $HCrO_4^-$ and becomes important only at high acidities in which h_0 is substituted for $[H^+]$.

Table II. Determination of k_5 from Eq 7 ([Glycolic Acid] = 1.8 *M*, 25°)

$[HClO_4]$, *M*	10^2 slope	K_1'	$10^3 k_4'$	$10^2 k_5'$	$10^2 k_5'/[H^+] = 10^2 k_5$
0.969[a]	5.80	1.37	12.2	7.7	4.81
0.628	2.53	3.22	4.97	2.9	4.62
0.097	0.40	22.57	0.12	0.41	4.23

Average $k_5 = 0.0455\ M^{-2}$

[a] h_0 used instead of $[H^+]$; the value of $h_0 = 1.6$ was taken from M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957).

The validity of the equation was tested by calculating rate constants for each of the concentrations under which experimental rate constants were determined and comparing them with the experimentally observed values. As can be seen from Table I, a very good agreement between experimental and calculated values could be obtained over the full range of conditions employed in this study. The calculated values were further used to construct the curves given in Figures 2 and 3.

Reaction Products. Oxidation products were determined under conditions where the kinetic term containing k_5 in eq 8 was sufficiently dominant to ensure that reaction 5 was responsible for 95% of the chromic acid reduced; results are shown in Table III. At low chromic acid concentrations acetone and glyoxylic acid, formed in an approximately 2:1 ratio, are the only reaction products. At higher chromic acid concentrations glyoxylic acid is oxidized further to carbon dioxide. The results thus show clearly that a cooxidation rather than a catalyzed oxidation is taking place.

Free radical scavengers, acrylonitrile or acrylamide, drastically reduce the yield of glyoxylic acid (and of carbon dioxide at high chromic acid concentrations), whereas the yield of acetone either remains essentially uneffected or is increased. Obviously, of the two products, only glyoxylic acid is formed via a free radical intermediate.

Table III. Chromic Acid Cooxidation of Glycolic Acid and Isopropyl Alcohol[a]

[Isopropyl alcohol], M	[Glycolic acid], M	[Perchloric acid], M	Chromium(VI)		Acetone		Glyoxylic acid		Carbon dioxide		Total
			M	mmol	mmol	% yield	mmol	% yield	mmol	% yield	
1.56	0.36	0.485	0.007	0.35	0.328	62.8	0.196	37.5	0.0	0.0[d]	100.3
1.56	0.36	0.0	0.007	0.35	0.330	62.9	0.203	38.7	0.0	0.0[d]	101.6
1.56	0.36	0.0	0.007	0.35	0.340[b]	65.0[b]	0.011[b]	2.1[b]	0.0	0.0[d]	67.1[b]
1.56	0.36	0.485	0.07	0.70	0.17	16.2	0.12	11.4	0.50	71.4	99.0
1.56	0.18	0.485	0.07	0.70	0.36	34.3	0.06	5.7	0.44	62.9	102.9
1.56	0.18	0.0	0.07	0.70	0.70[c]	68.0[c]	0.02[c]	1.9[c]	0.04[c]	6.3[c]	76.2[c]
0.78	0.36	0.485	0.07	0.70	0.33	31.1	0.09	8.9	0.40	57.1	97.1

[a] Yields calculated as in ref 1. [b] [Acrylonitrile] = 0.277 M. [c] [Acrylamide] = 0.61 M. [d] A yield of 5% or more would have been detected.

Mechanism. The rapid oxidation of glycolic acid–isopropyl alcohol mixtures and the corresponding appearance of the kinetic term $k_5K_1[HCrO_4^-][GA][ROH]$ in the rate law indicates that the reduction of chromium(VI) through a termolecular complex must be much more favorable, and hence faster, than through either of the two bimolecular complexes (with either glycolic acid or alcohol), which certainly are present in the solution and of which the glycolic acid–chromic acid complex is formed in large concentrations. We are convinced that the reason for this preference stems from the opportunity offered by the termolecular complex to avoid the formation of unstable (and therefore high energy) intermediates, particularly of chromium(IV); this is accomplished by a one-step three-electron reduction of chromium(VI) to chromium(III). The effect of acrylonitrile and acrylamide on the product composition (Table III) indicates that two of the required electrons are provided by the alcohol and the third by glycolic acid.

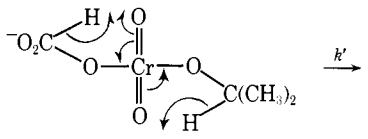
A mechanism consistent with these conclusions is shown in Scheme II. Omitted are the equations showing the

Scheme II

$$HCrO_4^- + H^+ \underset{K_8}{\rightleftharpoons} H_2CrO_4 \quad (9)$$

$$HOCH_2CO_2H + HCrO_4^- \overset{K_1}{\rightleftharpoons} {}^-O_2CCH_2OCrO_3^- + H^+ \quad (10)$$

$$^-O_2CCH_2OCrO_3^- + (CH_3)_2CHOH + H^+ \overset{K_2}{\rightleftharpoons} {}^-O_2CCH_2O\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}OCH(CH_3)_2 \quad (11)$$



$(k = k'K_2)$

$$^-O_2C\dot{C}HOH + Cr(III) + (CH_3)_2CO \quad (12)$$

$$HO_2C\dot{C}HOH + Cr(VI) \longrightarrow HO_2CCHO + Cr(V) \quad (13)$$

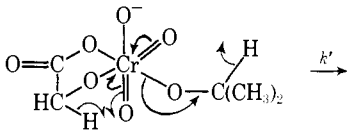
$$Cr(V) + (CH_3)_2CHOH \longrightarrow Cr(III) + (CH_3)_2CO \quad (14)$$

$$Cr(V) + HOCH_2CO_2H \longrightarrow Cr(III) + OCHCO_2H \quad (15)$$

chromium(VI) oxidation of isopropyl alcohol (reaction 4) and of glycolic acid (reactions 2 and 3), although these reactions are important enough to contribute substantially to the overall rate of reduction of chromium(VI) and are therefore reflected in the rate law (eq 8). In this scheme we propose that the termolecular complex C_2 forms reversibly and decomposes in the rate-limiting step. It is assumed that the free radical $HO\dot{C}HCO_2H$, formed in this step, reduces a molecule of chromium(VI) to chromium(V). The formation of a chromium(V) intermediate has been clearly demonstrated in the chromic acid oxidation of glycolic acid.[11]

Chromium(V) can react further in a two-electron oxidation either with isopropyl alcohol (reaction 14) or with glycolic acid (reaction 15); the formation of acetone and glyoxylic acid in an almost 2:1 ratio suggests that the oxidation of isopropyl alcohol by chromium(V) is preferred to that of glycolic acid at least under the conditions employed in the products study (alcohol in 4.6-fold excess over glycolic acid).

It should be pointed out that the amount of information at hand does not suffice to draw more definite conclusions about the structure of the termolecular complex C_2 or of the activated complex of the rate-limiting step (reaction 12). We represented both in Scheme II as acyclic and tetracoordinated with respect to the chromium atom. However, the fact that cooxidation reactions seem to be restricted to compounds which can act as effective bidentate ligands may suggest that a cyclic form with a penta- or hexacoordinated chromium atom (e.g., eq 16) may be preferable.



$$HO\dot{C}HCO_2^- + Cr(III) + (CH_3)_2CO \quad (16)$$

Isotope Effects. The mechanism shown in Scheme II parallels to a large degree that proposed earlier for the cooxidation of isopropyl alcohol and oxalic acid.[3] The two mechanisms differ, however, in one important aspect; while the one-electron oxidation of oxalic acid involved a carbon–carbon bond cleavage reaction, the corresponding oxidation of glycolic acid consists of a breaking of a carbon–hydrogen bond. The transition state shown in eq 12 or 16 suggests that two carbon–hydrogen bonds are broken simultaneously. The fact that each of them is in a different substrate offers a unique opportunity of obtaining a much more detailed insight into the nature of the transition state and the sequence and degree of bond breaking during the rate-limiting step.

If the two oxidation steps, the two-electron oxidation of the alcohol and the one-electron oxidation of glycolic acid occurred in sequence, then only one of the two substrates would exhibit an isotope effect. The same would be true even if the second oxidation step followed essentially immediately, i.e., if the intermediate chromium(IV) complex of glycolic acid or chromium(V) complex of isopropyl alcohol were too short lived to permit ligand exchange with other molecules present in the solution. If the process were synchronous, but the extent of bond breaking substantially different with one bond being broken to a considerably larger degree than the other, then isotope effects for both substrates, albeit with a substantial difference in magnitude, should be observed.

The results of the study of isotope effects given in Table IV show that the effects are of equal magnitude for both

Table IV. Chromic Acid Cooxidation of Isopropyl Alcohol and Glycolic Acid at 25° ([$HClO_4$] = 0.628 M)

[Isopropyl alcohol], M	[Isopropyl alcohol-d], M	[Glycolic acid], M	[Glycolic acid-d_2], M	$10^2 k_{exptl}$, sec^{-1}	k_H/k_D
1.56		0.36		3.30[a]	
	1.56	0.36		0.55	6.0
1.56			0.36	0.57	5.8
	1.56		0.36	0.092	34.4
				0.099	

[a] Average of three measurements: 3.26, 3.30, and 3.33.

substrates. These results are consistent only with a mechanism in which breaking of the bonds in both substrates is fully synchronous and the extent of bond breaking in the transition state has reached about the same level. The results also provide the most convincing support for the correctness of the three-electron oxidation mechanism.

Experimental Section

Materials. Glycolic acid (Eastman Kodak) was crystallized from petroleum ether (mp 74–76°). Isopropyl alcohol (Baker Instra-Analyzed) and sodium dichromate (J.T. Baker, Reagent) were used without further purification. Acrylonitrile (Practical) was distilled and the fraction boiling between 77 and 79° was collected. Perchloric acid solutions were prepared from 60% perchloric acid (B & A reagent).

Isopropyl alcohol-d and glycolic acid-d_2 were prepared by the method described earlier.[1,3]

Kinetic Measurements. Reaction rates were determined spectrophotometrically at 350 nm using Cary 14, Cary 15, and Zeiss PMQII spectrophotometers equipped with thermostated cell holders. Pseudo-first-order rate constants were calculated from the slopes of the linear parts of the log (absorbance) vs. time plots (Figure 1). Rate constants obtained from multiple determinations were within ±5% of each other.

Product Analysis. In a typical experiment isopropyl alcohol (20.0 ml, 7.8 M), glycolic acid (10.0 ml, 3.6 M), perchloric acid (5.0 ml, 9.69 M), and sodium dichromate (0.2 ml, 1.745 M) were allowed to react in a 100 ml volumetric flask, the total volume made up to the mark with distilled water. The reaction products were isolated and identified by previously described methods.[1,3]

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Effect of Cationic Micelles on the Acidity of Carbon Acids and Phenols. Electronic and ^1H Nuclear Magnetic Resonance Spectral Studies of Nitro Carbanions in Micelles[1]

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Abstract: The acid dissociation constants (K_a values) for five α-substituted 4-nitrophenylacetonitriles [4-$NO_2C_6H_4CH(R)CN$ where R = H, C_6H_5, p-ClC_6H_4, p-$NO_2C_6H_4$, and CN] and for 1-nitroindene, 4-nitrophenol, and 2,6-di-*tert*-butyl-4-nitrophenol were determined in aqueous buffer solutions both with and without micelle forming concentrations of the cationic surfactant, cetyltrimethylammonium bromide (CTABr). For all compounds, the presence of 10^{-2} M CTABr causes an increase in K_a values, but the effect is most pronounced for the nitro carbanion forming ionizations of the 4-nitrophenylacetonitriles; e.g., the K_a of bis(4-nitrophenyl)acetonitrile is increased 10^4-fold. The nature of the interaction between nitro carbanions and CTABr molecules was investigated by visible and ^1H NMR spectroscopy. CTABr micelles cause an unprecedented red shift in the visible spectra of several nitro carbanions; identical red shifts are observed when water is replaced by a wide variety of organic solvents, suggesting that the interaction between water and a nitro carbanion increases the energy of its $\pi \rightarrow \pi^*$ transition, possibly because of hydrogen bonding between water and the nitro group. The association between aromatic carbanions and CTABr molecules causes upfield shifts in the ^1H NMR signals for the aromatic protons of the carbanion and for the $N^+(CH_3)_3$ protons of the surfactant, indicating that the carbanion interacts tightly with the cationic head groups of neighboring surfactant molecules. Line broadening studies show that the ionization of aromatic acid molecules solubilized in a cationic micelle increases the rigidity of the micelle-solubilisate aggregate.

Cationic micelles[3] enhance the acid dissociations of phenolic pH indicators,[4] phenols,[5] carboxylic acids,[6] and the N-conjugate acids of methyl orange[7] and p-chlorobenzylidene-1,1-dimethylamine.[8] The effect of cationic micelles on carbanion formation by carbon acids has not been reported but is interesting, because the reaction involves proton loss from carbon rather than a hydrophilic oxygen or nitrogen atom, and the negative charge in carbanions is more delo-