Three-Electron Oxidations. 11. Chromium(V) Oxidation of Alcohols[1,2]

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Abstract: The relative rates of chromium(V) oxidations of a series of primary and secondary alcohols have been determined. A very close similarity between the oxidative properties of chromium(V) and chromium(VI) is demonstrated. The mechanism of the reaction is discussed.

Chromium(V) plays an important role in chromic acid oxidations and is usually responsible for the formation of one-third of the reaction products regardless whether the reaction proceeds by an initial two-electron oxidation (Scheme I; S = substrate, P = products)[3-8] or the recently observed three-electron oxidation (Scheme II), which may take place if at least one of the two substrates is capable of acting as a bidentate ligand.[9,10] A good understanding of the oxidative properties of chromium(V) is therefore needed before one can have a full understanding of the reactions taking place during a "chromic acid oxidation".[13]

Scheme I

$$\mathrm{Cr(VI)} + \mathrm{S} \rightarrow \mathrm{Cr(IV)} + \mathrm{P} \qquad (1)$$
$$\mathrm{Cr(IV)} + \mathrm{S} \rightarrow \mathrm{Cr(III)} + \cdot\mathrm{R} \qquad (2)$$
$$\mathrm{Cr(VI)} + \cdot\mathrm{R} \rightarrow \mathrm{Cr(V)} + \mathrm{P} \qquad (3)$$
$$\mathrm{Cr(V)} + \mathrm{S} \rightarrow \mathrm{Cr(III)} + \mathrm{P} \qquad (4)$$

Scheme II

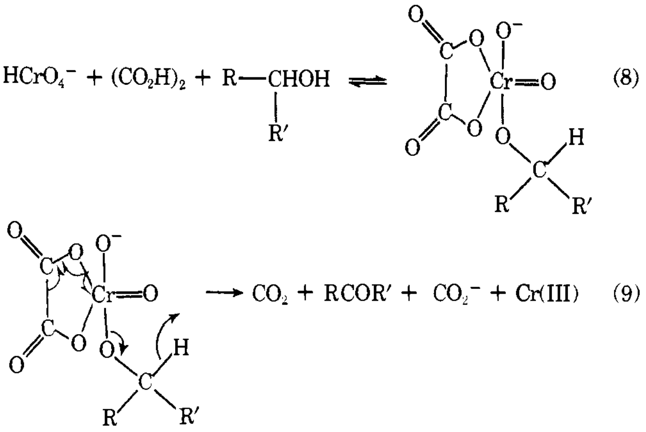
$$\mathrm{Cr(VI)} + \mathrm{S_1} + \mathrm{S_2} \rightarrow \mathrm{Cr(III)} + \mathrm{P} + \cdot\mathrm{R} \qquad (5)$$
$$\mathrm{Cr(VI)} + \cdot\mathrm{R} \rightarrow \mathrm{Cr(V)} + \mathrm{P} \qquad (3)$$
$$\mathrm{Cr(V)} + \mathrm{S_1} \rightarrow \mathrm{Cr(III)} + \mathrm{P} \qquad (6)$$
$$\mathrm{Cr(V)} + \mathrm{S_2} \rightarrow \mathrm{Cr(III)} + \mathrm{P} \qquad (7)$$

The study of chromium(V) oxidations has been hampered by its instability. Although chromium(V) forms a number of stable solid compounds[14-17] and also solutions of moderate stability in very strong potassium hydroxide and oleum,[17,18] it is very unstable in water and either undergoes rapid disproportionation into chromium(VI) and chromium(III) or, if an oxidizable substrate is present, rapid reduction to chromium(III). The first success in the investigation of chromium(V) oxidations was recorded by Wiberg and co-workers[19] when they observed that acetic acid accelerates chromium(VI) oxidations selectively and sufficiently to make their rate comparable to chromium(V) oxidations (or even faster). This permitted the investigation of the chromium(V) oxidation of isopropyl alcohol,[19] several aliphatic and aromatic aldehydes,[20] and cyclobutanol[21] by direct observation of the rate of formation and disappearance of the chromium(V) intermediate. The method could not be applied to aqueous solutions where chromium(V) is much more reactive than chromium(VI) and therefore does not accumulate in sufficient concentrations to permit its direct observation.

A generally useful method for the investigation of reactive intermediates is based on the determination of reaction products formed under conditions where two different substrates compete for the same intermediate. Under usual conditions, when the chromic acid oxidation proceeds by the mechanism shown in Scheme I, this approach is complicated by the fact that there are two, rather than one, reactive intermediates (chromium(IV) and chromium(V)) and the approach using a competitive oxidation of two substrates, therefore, leads to ambiguous results.[22] Fortunately, this problem is removed when the reaction follows the three-electron mechanism (Scheme II) where no chromium(IV) is formed and chromium(V) becomes the only reactive intermediate capable of oxidizing either of the two substrates (S_1 or S_2).

In this paper we wish to report the results of a study in which a number of primary and secondary alcohols were oxidized in the presence of oxalic acid; under these conditions the reaction follows the cooxidation mechanism shown in Scheme III.[23]

Scheme III



$$\mathrm{Cr(VI)} + \mathrm{CO_2^-} \longrightarrow \mathrm{Cr(V)} + \mathrm{CO_2} \qquad (10)$$

$$\mathrm{Cr(V)} + \underset{\displaystyle\mathrm{R'}}{\mathrm{R{-}CHOH}} \xrightarrow{k_{\mathrm{ROH}}} \mathrm{Cr(III)} + \mathrm{RCOR'} \qquad (11)$$

$$\mathrm{Cr(V)} + \mathrm{(CO_2H)_2} \xrightarrow{k_{\mathrm{Ox}}} \mathrm{Cr(III)} + 2\mathrm{CO_2} \qquad (12)$$

Chromium(V) formed in reaction 10 can react either with the alcohol (reaction 11) or oxalic acid (reaction 12). The overall yield of RCOR′ and CO_2 will be a function of the reactivity of chromium(V) towards these two substrates and their concentrations. The limiting value of x = (mol CO_2)/(mol RCOR′) will be 1.0 if all chromium(V) reacted with the alcohol (reaction 11) and 4.0 if it oxidized oxalic acid only (reaction 12). If both reactions occur side by side, then the yields of CO_2 and of RCOR′ are given by eq 13 and 14, respectively.

$$\frac{\text{mol CO}_2}{2\text{ mol Cr(VI)}} = 2 + \frac{2k_{\mathrm{Ox}}[(\mathrm{CO_2H})_2]}{k_{\mathrm{Ox}}[(\mathrm{CO_2H})_2] + k_{\mathrm{ROH}}[\mathrm{ROH}]} \qquad (13)$$

$$\frac{\text{mol RCOR}'}{2\text{ mol Cr(VI)}} = 1 + \frac{k_{\mathrm{ROH}}[\mathrm{ROH}]}{k_{\mathrm{Ox}}[(\mathrm{CO_2H})_2] + k_{\mathrm{ROH}}[\mathrm{ROH}]} \qquad (14)$$

The ratio of CO_2 and RCOR′ formed in the oxidation is then

$$x = \frac{\text{mol CO}_2}{\text{mol RCOR}'} = \frac{4k_{\mathrm{Ox}}[(\mathrm{CO_2H})_2] + 2k_{\mathrm{ROH}}(\mathrm{ROH})}{k_{\mathrm{Ox}}[(\mathrm{CO_2H})_2] + 2k_{\mathrm{ROH}}[\mathrm{ROH}]} \qquad (15)$$

Table I. Products from Chromic Acid Cooxidation of Oxalic Acid and Primary and Secondary Alcohols

Alcohol	Concn, M	Perchloric acid, M	Oxalic acid,[a] M	Chromium(VI), M	$[ROH]/[(CO_2H)_2]$[b]	Ketone[c] mmol	CO_2, mmol	CO_2/Ketone[c]
Methanol	1.01	0.120	0.085	0.00123	17.72	0.10	0.21[d]	1.91
	0.505				8.86	0.09	0.22[d]	2.46
	0.202				3.54	0.072	0.23[d]	3.19
	0.101				1.77	0.068	0.23[d]	3.42
	0.051				0.89	0.063	0.24[d]	3.81
	0.010				0.18	0.060	0.24[d]	4.0
Ethanol	2.72	0.120	0.043	0.00128	95.44	0.11	0.213[d]	1.94
	1.36				47.72	0.094	0.220[d]	2.34
	0.68				23.86	0.076	0.228[d]	3.00
	0.34				11.92	0.068	0.231[d]	3.40
	0.136				4.78	0.063	0.235[d]	3.73
	0.034				1.20	0.060	0.237[d]	3.95
2-Propanol	2.34	0.125	0.15	0.0140	22.94	0.280	0.290	1.04
	1.56				15.29	0.250	0.332	1.33
	1.17				11.47	0.250	0.350	1.40
	0.78				7.64	0.226	0.384	1.70
	0.39				3.82	0.198	0.450	2.27
	0.195				1.91	0.176	0.490	2.78
	0.098				0.95	0.156	0.536	3.44
	0.059				0.57	0.134	0.540	4.03
	0.039				0.38	0.140	0.540	3.86
2-Butanol	0.696	0.125	0.078	0.0157	13.13	0.160	0.162	1.01
	0.348				6.53	0.140	0.193	1.37
	0.174				3.28	0.125	0.211	1.77
	0.087				1.64	0.111	0.249	2.24
	0.044				0.83	0.102	0.267	2.62
	0.022				0.42	0.086	0.299	3.48
	0.011				0.21	0.078	0.315	4.03
3-Methyl-2-butanol	0.174	0.125	0.039	0.00314	6.44	0.028	0.038	1.34
	0.087				3.22	0.025	0.044	1.75
	0.044				1.63	0.022	0.050	2.30
	0.022				0.81	0.019	0.056	2.97
	0.011				0.41	0.018	0.058	3.15
	0.0044				0.16	0.016	0.063	4.08
sec-Phenylethanol	0.0603	0.125	0.00117	0.0033	75.8	0.0330	0.0329	1.00
	0.0563				65.7	0.0328	0.0336	1.02
	0.0402				50.6	0.0314	0.0363	1.15
	0.0268				33.8	0.0301	0.0390	1.29
	0.0134				16.9	0.0283	0.0426	1.50
	0.0067				8.4	0.0267	0.0456	1.70

[a] Total (analytical) concentration of oxalic acid. [b] Undissociated oxalic acid $[(CO_2H)_2] = [\text{Oxalic acid (total)}][H^+]/([H^+] + K_a)$; $K_a = 0.059$ M. [c] Or aldehyde. [d] Calculated from yield of aldehyde.

By rearrangement, eq 15 gives

$$\frac{4-x}{2(x-1)} = \frac{k_{ROH}}{k_{Ox}}\frac{[ROH]}{[(CO_2H)_2]} \tag{16}$$

which permits the determination of the rate of the chromium(V) oxidation of the alcohol relative to oxalic acid from a plot of $(4 - x)/2(x - 1)$ vs. $[ROH]/[(CO_2H)_2]$.

Experimental Section

Materials. Oxalic acid (Mallinckrodt AR), 2-butanol (Aldrich), 3-methyl-2-butanol (Aldrich), 1-phenylethanol (Aldrich), and 2-propanol (Baker Instra-Analyzed) were used without further purification.

Perchloric acid solutions were prepared from 60-62% perchloric acid (B&A Reagent). Chromium solutions were prepared from sodium dichromate (J. T. Baker, Reagent).

Product Analysis: Ketones. The ketones from the oxidation of alcohols were determined gravimetrically as their 2,4-dinitrophenylhydrazones. In a typical experiment, 2-butanol (1.0 ml, 1.74 M), oxalic acid (2.0 ml, 0.39 M), perchloric acid (1.0 ml, 1.26 M), distilled water (5.5 ml), and sodium dichromate (0.5 ml, 0.157 M) were allowed to react to completion, as indicated by the change in color. To the reaction mixture a saturated solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid was added until the precipitation was complete. The mixture was kept in the refrigerator overnight, after which the precipitate was filtered, washed, dried, and weighed. The crude product was crystallized from methanol and weighed. The difference between the two weights was less than 2%.

Carbon Dioxide. Carbon dioxide was determined manometrically using a Warburg apparatus.[23] For a typical experiment, 2-butanol (0.2 ml, 1.74 M), oxalic acid (0.40 ml, 0.39 M), perchloric acid (0.20 ml, 1.26 M), and distilled water (1.2 ml) were taken in the reaction flask of the Warburg apparatus at 25 °C. Sodium dichromate (10 μl, 1.57 M) was injected through the side arm. The yield of carbon dioxide was calculated from the reading of the manometer.

For methanol and ethanol the yields of carbon dioxide were not determined directly, but were calculated from the yields of the aldehydes or ketones.

Kinetic Measurements. Rates of chromium(VI) oxidation of the alcohols were determined spectrophotometrically using a Cary 14 spectrophotometer equipped with thermostated cell holders. Pseudo-first-order rate constants were calculated from the slopes of the log(absorbance) vs. time plots.[23] Rates of chromium(V) oxidations of alcohols relative to oxalic acid were determined graphically from the ratio of the products (Table I) using eq 16. A typical example of a plot of $(4 - x)/2(x - 1)$ vs. $[ROH]/[OxH_2]$ is shown in Figure 1.

Results

Table II summarized the relative chromium(V) oxidation rates obtained for a selection of primary and secondary alco-

Table II. Chromium(V) and Chromium(VI) Oxidation Rates of Alcohols in 0.120 M $HClO_4$ at 25 °C

		Chromium(V)		Chromium(VI)		
Alcohol	σ^{*a}	$10^2 k_{ROH}/k_{(CO_2H)_2}$	k_{ROH}/k_{EtOH}	$10^5 k$, $M^{-1}s^{-1}$	k_{ROH}/k_{EtOH}	$k_{Cr(V)}/k_{Cr(VI)}$
Methanol	0.98	6.1	0.57	1.58	0.16	3.5
Ethanol	0.49	10.6	1.00	9.70	1.00	1.000
2-Propanol	0.0	27^b	2.5	18.0	1.86	1.3
2-Butanol	−0.10	45^b	4.2	22.0	2.27	1.9
3-Methyl-2-butanol	−0.19	59^b	5.6	26.0	2.68	2.1
1-Phenylethanol	0.61	14.0^b	1.32	8.0	0.82	1.6
Cyclobutanol^c		63	5.9	55.2	5.69	1.0
1-Deuteriocyclobutanol^c		12.7	1.20	9.3	0.96	1.3

$^a\sigma^* = \sigma_{R_1}^* + \sigma_{R_2}^*$ for alcohol R_1R_2CHOH; values from R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956. ^{b}0.126 M $HClO_4$. ^{c}Reference 31.

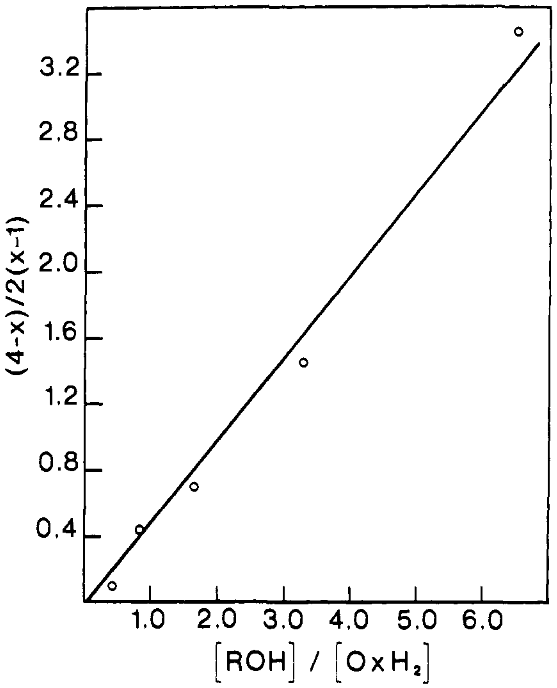


Figure 1. Determination of the relative rate of chromium(V) oxidation of 2-butanol and oxalic acid at 25 °C. Perchloric acid = 0.125 M.

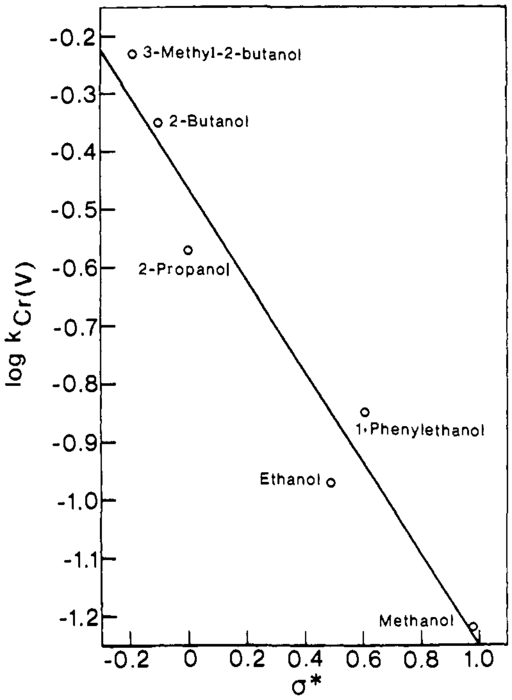


Figure 2. Taft plot of chromium(V) oxidation rates of alcohols relative to oxalic acid ($k_{ROH}/k_{(CO_2H)_2}$ from Table II) at 25 °C in 0.12 M $HClO_4$.

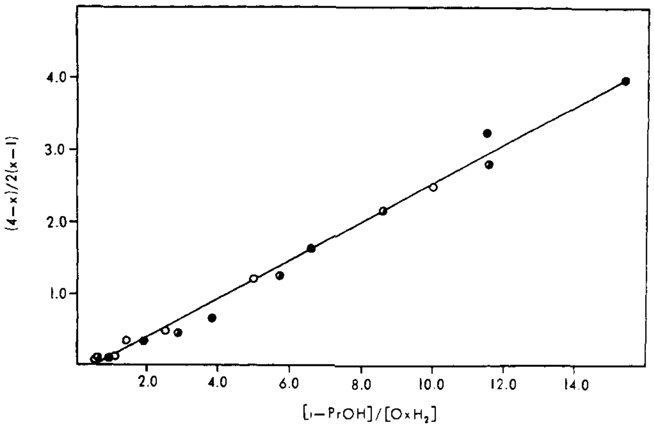


Figure 3. Determination of the relative rate of chromium(V) oxidation of isopropyl alcohol and oxalic acid at different acidities at 25 °C. Perchloric acid (○) 0.063, (●) 0.125, (◑) 0.63 M.

hols. Chromium (VI) oxidation rates determined under identical conditions are included for comparison. In order to make the comparison more meaningful, the last column gives the relative Cr(V)/Cr(VI) rates using ethanol as standard. The values are almost constant and close to 1.0. The results show that structural factors have a very similar effect on the two reactions. The largest deviation is found for methanol, which is known to exhibit an anomalously low reactivity in chromium(VI) oxidations.[24] The somewhat higher value for 3-methyl-2-butanol may suggest that chromium(V) oxidations differ from chromium(VI) oxidation more in their response to steric than to polar effects.

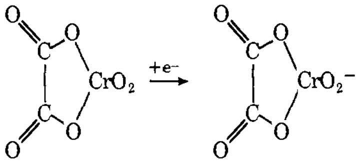
Figure 2 gives the Taft plots for the chromium(V) oxidation. The value of the reaction constants ($\rho^* = -0.80 \pm 0.17$) for chromium(V) has the same sign and magnitude, but is somewhat lower than the value $\rho^* = -1.06 \pm 0.06$ obtained earlier for the chromium(VI) oxidation of a large set of primary alcohols.[24] It is worth noting that the points for primary and secondary alcohols fall on a single line.

Figure 3 gives a plot of $(4 - x)/2(x - 1)$ vs. $[ROH]/[(CO_2H)_2]$ at three different acidities: all points lie on a single line, where $[(CO_2H)_2] = [(CO_2H)_2]_{total}[H^+]/([H^+] + K_a)$ is the undissociated oxalic acid and $K_a = 0.059$ M is the first dissociation constant of oxalic acid.[25]

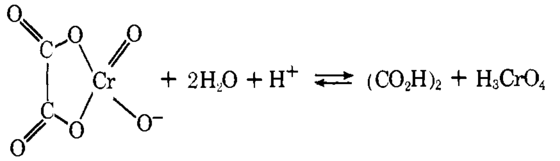
As the rate of the chromium(VI) oxidation of oxalic acid as well as the relative rate of chromium(V) and chromium(VI) oxidation of oxalic acid are independent of acidity, we conclude that the chromium(V) oxidation of alcohols *in the presence of oxalic acid* is zero order in hydrogen ions.

The chromium(VI) oxidation of alcohols is known to be strongly acid catalyzed: the rate is first order in hydrogen ions at very low acidities,[26] second order at medium acidities,[26] and proportional to the acidity function (H_0) at high acidities.[27] However, before one can reach the conclusion that the chromium(V) and the chromium(VI) differ in this respect, one needs to examine the reaction in more detail.

As chromic acid in the presence of oxalic acid is present to a large extent in the form of the oxalato complex, it can be assumed that the chromium(V) species formed in reaction will also be an oxalato complex. Whether this complex will be present in its anionic or neutral form depends on its dissociation constant, which is hard to estimate. H_3CrO_4 itself is probably only a medium strong acid, comparable to arsenic acid (K_1 = 5.62 × 10^{-3} M)[25] or ortho-phosphoric acid (K_1 = 7.52 × 10^{-3} M).[25] However, the presence of the oxalato group in the molecule may make the complex $(CO_2)_2CRO_2H$ a considerably stronger acid and may thus make the anion $(CO_2)_2CrO_2^-$ the predominant species.



It is also not clear whether an equilibrium between the complex and free chromium(V) will be established or whether the rate of reduction of the chromium(V) complex is faster than its hydrolysis. However, even if such an equilibrium (reaction 17) is established, it is likely to lie quite far to the left, as suggested by the large difference in stability of chromium(V) in the presence and absence of oxalic acid.[28] It therefore appears more likely that the chromium(V) species responsible for the oxidation of the alcohol is the oxalato complex $(CO_2)_2CrO_2^-$, rather than free hypochromic acid H_3CrO_4. The observation that a large fraction of chromium(III) formed in the reaction is found in the form of the oxalato complex $(CO_2)_2Cr(OH_2)_4^+$ adds further support for this assumption.[29]

 (17)

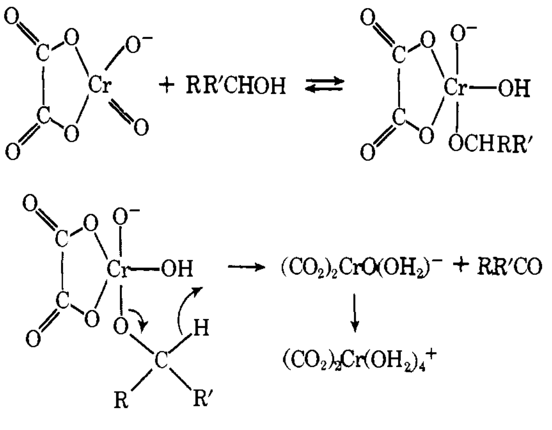
The chromium(V) oxidation of alcohols, or more correctly, the oxidation of alcohols with chromium(V) oxalate thus should be compared with the oxidation of alcohols with the chromium(VI) oxalate rather than with free chromic acid. Oxidation of an alcohol by a chromium(VI) oxalato complex takes place in the course of the three-electron oxidation of the alcohol in the presence of oxalic acid (reactions 8 and 9, Scheme III). The rate law for this reaction is[23]

$$\text{Rate} = k[HCrO_4^-][ROH][(CO_2H)_2]$$

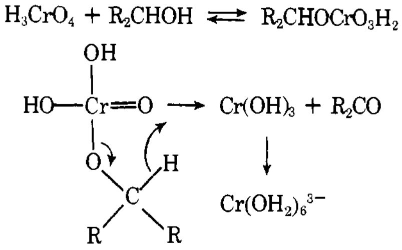
where $[(CO_2H)_2]$ is the concentration of undissociated oxalic acid. The oxidation of alcohols by the chromium(VI) oxalate thus shows no acidity dependence and chromium(V) and chromium(VI) hence exhibit entirely similar behavior even in this respect.[30]

The results show that chromium(VI) and chromium(V) oxidations of secondary alcohols respond to changes in the substrate in a parallel way, although chromium(VI) oxidations are somewhat more sensitive to polar effects than chromium(V) oxidations, as indicated by the difference in the magnitude of the ρ^* constants (−1.05 for chromium(VI) and −0.80 for chromium(V)). The chromium(VI) oxidation is also somewhat more sensitive to isotopic substitution than chromium(V) oxidations; the kinetic isotope effect in the oxidation of 1-deuteriocyclobutanol is k_H/k_D = 5.9 for chromium(VI) and 5.0 for chromium (V).[31] Both differences suggest a lower extent of the breaking of the C–H bond in the transition state of the reaction. The most probable mechanism of the chromium(V) oxidation is the presence of oxalic acid, as given in Scheme IV. No direct conclusion about the mechanism of chromium(V) oxidation in the absence of oxalic acid can be drawn from this study. However, the close similarity between the chromium(VI) and chromium(V) oxidations permits us to suggest that Scheme V may provide a likely sequence of reactions in aqueous chromium(V) oxidations. The extent of hydration of the chromium in the rate-limiting step in Schemes IV and V cannot be estimated; however, the observation that up to three bidentate ligands can be incorporated into the chromium(III) species formed in the reduction of chromium(VI)[32,33] suggest that the first chromium(III) compound formed is not a stable octahedral species.

Scheme IV



Scheme V



References and Notes

(1) (a) Part 10: F. Hasan and J. Roček, *J. Am. Chem. Soc.*, **97**, 3762 (1975); (b) Preliminary communication: *ibid.*, **94**, 8946 (1972).

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

(3) J. Roček and A. E. Radkowsky, *J. Am. Chem. Soc.*, **90**, 2986 (1968); **95**, 7123 (1973).

(4) M. Rahman and J. Roček, *J. Am. Chem. Soc.*, **93**, 5455 (1971).

(5) F. Hasan and J. Roček, *Tetrahedron*, **30**, 21 (1974).

(6) J. Roček and C.-S. Ng, *J. Am. Chem. Soc.*, **96**, 1522, 2840 (1974).

(7) P. M. Nave and W. S. Trahanovsky, *J. Am. Chem. Soc.*, **92**, 1120 (1970); **93**, 4536 (1971).

(8) K. B. Wiberg and S. K. Mukherjee, *J. Am. Chem. Soc.*, **93**, 2543 (1971); **96**, 1884 (1974).

(9) Cf. ref 1a and other preceding papers in this series.

(10) The participation of chromium(V) in the oxidation is reduced only if a bimolecular dimerization or disproportionation of the free radicals ·R competes effectively with reaction 3 and thus inhibits the formation of chromium(V), or if the chromium(V) already formed undergoes a bimolecular disproportionation (2Cr(V) → Cr(IV) + Cr(VI)) instead of reacting with the substrate. Both cases have been observed,[3,7,11,12] but are only of limited importance under usual oxidation conditions.

(11) F. Hasan and J. Roček, *J. Org. Chem.*, **39**, 2612 (1974).

(12) J. C. Drozd, Ph.D. Thesis, University of Illinois at Chicago Circle, Chicago, Illinois, 1971.

(13) Although chromic acid oxidations in which the first step is a one-electron oxidation are common and well known in inorganic chemistry,[14] their ex-

istence in the oxidation of stable organic substrates has not been conclusively demonstrated; however, if such a mechanism exists, then chromium(V) will, of course, be formed and may again be expected to appear as an oxidant in the overall reaction scheme.

(14) J. K. Beattie and G. P. Haight, Jr. in "Inorganic Reaction Mechanisms", Part II, J. O. Edwards, Ed., Interscience, New York, N.Y., 1972, p 93.
(15) R. Scholder and H. Schwarz, *Z. Anorg. Allg. Chem.*, **326**, 1,11 (1963).
(16) R. Scholder and H. Suchy, *Z Anorg. Allg. Chem.*, **308**, 295 (1961) and numerous references given therein.
(17) Cf. also K. B. Wiberg in "Oxidation in Organic Chemistry", Part A, K. B. Wiberg, Ed., Academic Press, New York, N.Y., 1965, p 69, and references given therein.
(18) H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 4490 (1963).
(19) K. B. Wiberg and H. Schafer, *J. Am. Chem. Soc.*, **89**, 455 (1967); **91**, 933 (1969).
(20) K. B. Wiberg and G. Szeimies, *J. Am. Chem. Soc.*, **96**, 1889 (1974).
(21) K. B. Wiberg and S. K. Mukherjee, *J. Am. Chem. Soc.*, **96**, 6647 (1974).
(22) K. B. Wiberg and W. H. Richardson, *J. Am. Chem. Soc.*, **84**, 2800 (1962).
(23) F. Hasan and J. Roček, *J. Am. Chem. Soc.*, **94**, 3181 (1972).
(24) J. Roček, *Collect. Czech. Chem. Commun.*, **25**, 1052 (1960).
(25) R. C. Weast, Ed., "Handbook of Chemistry and Physics", 51st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970.
(26) F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943).
(27) J. Roček and J. Krupička, *Collect. Czech. Chem. Commun.*, **23**, 2068 (1958).
(28) V. Srinivasan and J. Roček, *J. Am. Chem. Soc.*, **96**, 127 (1974).
(29) In the cooxidation, a solution of 1.0 M isopropyl alcohol, 0.10 M in oxalic acid, 0.10 M in perchloric acid, and 9.85 × 10^{-3} M in chromium(VI) and chromium(III) formed, composed of 31% $Cr(OH_2)_6^{3+}$, 42% Cr(oxalate) $(OH_2)_4^{+}$, and 26% dioxalate and trioxalate complexes. The separation was carried out with Dowex 50W-X8 resin. The anionic complexes were eluted with 0.01 M perchloric acid, the monooxalate with 1.0 M perchloric acid, and $Cr(OH_2)_6^{3+}$ with 3.0 M perchloric acid. We are indebted to Dr. Ray E. Hintze for carrying out this experiment.
(30) The close similarity between chromium(V) and chromium(VI), which we found in this study, is consistent with our earlier finding that both chromium(V) and chromium(VI) act as two-electron oxidants.[3,31]
(31) F. Hasan and J. Roček, *J. Am. Chem. Soc.*, **96**, 534 (1974).
(32) G. P. Haight, Jr., T. J. Huang, and B. Z. Shakhashiri, *J. Inorg. Nucl. Chem.*, **33**, 2169 (1971).
(33) F. Hasan and J. Roček, *J. Am. Chem. Soc.*, **94**, 9073 (1972).

Alkene Epoxidation by Intermediates Formed during the Ozonation of Alkynes[1]

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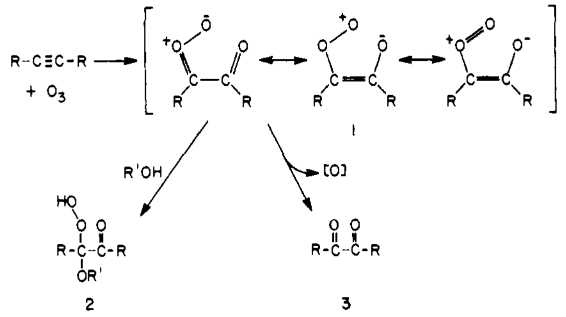
Abstract: The ozonation of various alkynes at −70 °C produces low levels of at least one species capable of epoxidizing cyclohexene and other added alkenes. More detailed studies using 0.02 M 2-butyne in dichloromethane solution, ca. 0.8 equiv of ozone, and subsequent addition of excess alkene indicated the following: (1) up to a 30% yield (based on the amount of alkyne which reacts) of epoxide is formed; (2) three different epoxidizing species are involved, one (X) which is stable only at −70 to −50 °C and which epoxidizes alkenes within 1 min at −70 °C, the second (Y) which is stable to −15 °C and epoxidizes alkenes within minutes at −25 °C, and the third (Z) which was shown to be a peroxy acid; (3) the epoxidation of cis and trans alkenes by X is almost completely stereospecific, while that by Y is essentially nonstereospecific; (4) epoxidations by both X and Y show electrophilic character and a large steric effect (in competition experiments cis alkenes react more than an order of magnitude more rapidly than trans alkenes). The evidence is consistent with X being a five-membered ring trioxide (trioxolene). A definitive structure for Y could not be assigned, but it may be a three-membered ring peroxide. The relevance of this work to some enzymic oxygenations is considered.

Since many oxygenase-catalyzed reactions are believed to occur by an oxygen atom transfer or oxenoid mechanism,[3-9] various studies in this laboratory have been aimed at investigating potential oxenoid agents and establishing the characteristics of each.[6,7,10-12] For some of the enzyme-catalyzed reactions, one of us has suggested[5,7] that the oxenoid reagent is an α-carbonyl carbonyl oxide, sometimes referred to as "vinylogous ozone" because it is a homologue of ozone having a carbon-carbon double bond between two of the oxygens. As shown in eq 1, vinylogous ozone (**1**) is believed to be an intermediate in the ozonation of alkynes;[13] if the reaction is carried out in the presence of protic solvents, compounds such as **2** are frequently isolated.[14] In the absence of the protic solvent traps a major product of the alkyne ozonation reaction is the α-diketone **3**. The formation of **3** indicates that **1**, or some species similar to it, can act as an oxygen atom transfer reagent, but the characteristics of such a transfer had not been investigated. The original goal of the present research was to determine these characteristics. During the study it was found that the alkyne ozonation reaction leads to a complex mixture of intermediates and products, at least three of which are capable of converting alkenes to epoxides. One of these intermediates appears to be the cyclized trioxide tautomer of **1**.[2] In this paper we report the experimental evidence for these oxidants and the characteristics of alkene epoxidation by each species.[15]



(1)

Experimental Section

Materials. All materials, including the alkynes, were of the highest purity possible and were shown by GC to be free of interfering impurities. Except for preliminary experiments, the dichloromethane used throughout this study was purified by extracting with concentrated sulfuric acid and 20% sodium hydroxide, washing with water, drying, and distilling from calcium hydride. Peroxyacetic acid and the epoxides of the various alkenes were prepared according to the procedures of Lewis.[16] Ozone was prepared using a Welsbach Model T-408 laboratory ozonator with an oxygen feed.

Analyses. Perkin-Elmer Series 881 gas chromatographs equipped with flame-ionization detectors were used for quantitative determinations. The following columns gave convenient separations of the reaction products as indicated: (1) 20% polypropylene glycol on Chromosorb W (12 ft × ⅛ in.); (2) 20% Carbowax 20 M on Chro-