Chromium(IV) Oxidation of Primary and Secondary Alcohols[1a,b]

Matiur Rahman and Jan Roček*

Contribution from the Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680. *Received December 9, 1970*

Abstract: The approach previously used to study the chromium(IV) oxidation of cyclobutanol has been developed into a general method for the investigation of the properties of chromium(IV) as an oxidant. The study of the reaction kinetics, product yield, and the effect of the presence of free-radical trapping agents supports the conclusion that chromium(IV) reacts rapidly with primary and secondary alcohols but is unreactive toward *tert*-butyl alcohol. The reaction is a one-electron oxidation leading to a free radical, probably $R_2\dot{C}OH$. The radical can be further oxidized by one of the oxidants present, but its rate of oxidation, particularly with chromium(VI), is slow enough to allow for sufficient accumulation permitting a bimolecular destruction of two radicals. The relative oxidation rates of a number of alcohols by chromium(IV) have been determined. The Taft ρ^* value of -0.85 found for primary alcohols indicates that the electronic requirements of the chromium(IV) oxidation are similar to those of chromium(VI) oxidations. The primary isotope effect for the oxidation of 2-deuterio-2-propanol is 1.9, a value of the same magnitude as found for some other one-electron oxidations of alcohols.

Both chromium(IV) and chromium(V), which appear as intermediates in the chromic acid oxidation of organic compounds,[2-4] are also formed during the reduction of chromium(VI) by vanadium(IV), a reaction the mechanism of which is, thanks to Espenson's work,[5] well understood (Scheme I). We have shown previously[6,7] that the chromium(VI)–vanadium(IV) system can be used as a source of chromium(IV). When cyclobutanol was introduced into this system under conditions in which its reaction with chromium(VI) is slow, the formation of an organic oxidation product, γ-hydroxybutyraldehyde, was observed. A mechanism (Scheme II) involving the formation of an organic free-radical intermediate in a one-electron oxidation was proposed.[6]

Scheme I

$$\mathrm{Cr^{VI} + V^{IV} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{V} + V^{V}} \qquad (1)$$

$$\mathrm{Cr^{V} + V^{IV} \xrightarrow[\text{rate limiting}]{k_2} Cr^{IV} + V^{V}} \qquad (2)$$

$$\mathrm{Cr^{IV} + V^{IV} \xrightarrow{k_3} Cr^{III} + V^{V}} \qquad (3)$$

Scheme II

$$\mathrm{Cr^{VI} + V^{IV} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{V} + V^{V}} \qquad (1)$$

$$\mathrm{Cr^{V} + V^{IV} \xrightarrow{k_2} Cr^{IV} + V^{V}} \qquad (2)$$

$$\mathrm{Cr^{IV} + \mathit{c}\text{-}C_4H_7OH \longrightarrow Cr^{III} + R\cdot} \qquad (4)$$

$$\mathrm{R\cdot + V^{V} \longrightarrow HO(CH_2)_3CHO + V^{IV}} \qquad (5)$$

The purpose of this paper is threefold: first, to examine whether the facile chromium(IV) oxidation in the chromium(VI)–vanadium(IV) system is restricted to alcohols with a particular tendency to undergo a cleavage reaction;[6,8] second, to obtain quantitative information about the reactivity of chromium(IV); third, to examine the mechanism of the chromium(IV) oxidation of a simple alcohol.

Experimental Section

Materials. Isopropyl alcohol, acetone, *tert*-butyl alcohol, diethyl ether, acrylonitrile, and acrylamide were Baker reagents. Gold Seal absolute ethyl alcohol was used without further purification. 2-Deuterio-2-propanol was prepared by lithium aluminum deuteride (Ventrom Corp.) reduction of acetone followed by isolation and purification through an F and M Prepmaster Junior gas chromatograph using a $^3/_4$ in. × 80 in. Carbowax 20M column. The nuclear magnetic resonance spectrum (Varian A-60A) of the neat liquid did not show any α-proton signal. Cyclobutanol was prepared from cyclopropylcarbinol[9] and purified by glpc as above. All the volatile compounds were checked for purity on an F and M 5750 Research Chromatograph.

Vanadyl sulfate and vanadium pentoxide were Fisher reagents, lithium and barium perchlorates were from G. F. Smith Co., and perchloric acid was Baker and Adamson's 72% reagent. A.R. grade potassium dichromate was used without further purification. Deionized water was used to prepare the solutions.

Stock Solutions. Vanadium(IV) perchlorate solutions were prepared from vanadyl sulfate and barium perchlorate according to Espenson's procedure.[5] Vanadium(V) perchlorate solutions were obtained by dissolving vanadium pentoxide in 0.2 *M* perchloric acid. A saturated aqueous solution of diethyl ether was prepared and its concentration established from available solubility data.[10] The concentrations of vanadium(IV), vanadium(V), and chromium(VI) solutions were determined spectrophotometrically.[5]

Reaction Products. Yield of Acetone in the Chromium(IV) Oxidation of Isopropyl Alcohol. Potassium dichromate (20 ml, 0.1 *M* in chromium(VI)) was introduced into 150 ml of a solution of vanadium(IV) perchlorate (6.9 mmol), vanadium(V) perchlorate (2.0 mmol), and isopropyl alcohol (140 mmol) in 0.1 *M* perchloric

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acid and allowed to react at room temperature (25 ± 1°) for 1 hr. A saturated solution of 2,4-dinitrophenylhydrazine (DNP) in 2 *M* hydrochloric acid (125 ml) was added to the reaction mixture, stirred at room temperature for 5 min, and kept overnight in a refrigerator.[11] The dinitrophenylhydrazone was collected, washed, and dried to give acetone 2,4-dinitrophenylhydrazone (350 mg, 1.47 mmol). A 38-mg portion of the crude product was recrystallized from 80% methanol to give 30 mg of acetone 2,4-dinitrophenylhydrazone, identified by mp and mmp 123–125°, lit.[12] 126°. Analysis of the crude product by tlc using a petroleum ether (bp 30–50°)–benzene–nitromethane (95:15:5) solvent system and a partially open tank[13] showed the absence of cleavage products (formaldehyde and acetaldehyde). Preparative scale tlc using[14] benzene–ethyl acetate (95:5) showed the crude product to be 85% acetone derivative with unreacted dinitrophenylhydrazine being the main impurity. This amount corresponds to a 40% yield of acetone based on the total chromium(VI) introduced.

The same procedure was used to determine the yield of acetone in the presence of acrylonitrile. Because of the low solubility of acrylonitrile in water, the reaction was carried out in 50% acetic acid.

Acrylamide prevents complete precipitation of the acetone 2,4-dinitrophenylhydrazone. Therefore, yields in the presence of acrylamide were determined by spectrophotometric analysis of the dinitrophenylhydrazone in alkaline solution using Lappin and Clark's[15] procedure. However, solutions containing equal concentrations of the vanadium and chromium compounds had to be used as references. It was found that none of the metal salts nor the scavenger had any noticeable effect on the molar absorptivity of the dinitrophenylhydrazone. When acrylamide was used as the trapping agent, a polymer precipitated on dilution of the reaction mixtures with methanol. The precipitate was removed by filtration prior to the additon of DNP.

Yield of Vanadium(V). The yields of vanadium(V) were measured by the loss of vanadium(IV) determined spectrophotometrically at 764 nm where there is no interference from other species present in the solution.[5] We observed that alcohols slightly but measurably increased the molar absorptivity of vanadium(IV) (from 17.04 to 17.20). A small concentration of *tert*-butyl alcohol eliminated any further change in the molar absorptivity of vanadium(IV) on addition of other alcohols within the range used in our measurements. Therefore, all reactions in which vanadium(IV) was determined were carried out in a medium 0.04 *M* in *tert*-butyl alcohol.

In a typical experiment 0–30 mmol of isopropyl alcohol was added to a 10-ml volumetric flask containing 0.30 mmol of vanadium(IV), 0.1 mmol of vanadium(V), 1.2 mmol of perchloric acid, and 0.4 mmol of *tert*-butyl alcohol in about 9 ml of water. After mixing, 0.9 ml of 0.1 *M* chromium(VI) solution was added. The resulting solution was made up with water to 10.0 ml, allowed to react at room temperature for 30 min, and analyzed for vanadium(IV).[16] The yield of vanadium(V) was calculated from eq 6,

$$\mathrm{V^{V}}\ (\text{in mmol}) = ([\mathrm{V^{IV}}]_0 - A_{764}/17.20)10 \tag{6}$$

where $[\mathrm{V^{IV}}]_0$ is the initial vanadium(IV) concentration, and 17.20 is the molar absorptivity of vanadium(IV) (in the presence of *tert*-butyl alcohol) at 764 nm.

Kinetic Measurements. The rates of chromium(VI) oxidation of organic substrates at 25.0 ± 0.05° were determined by the procedure described by Roček and Riehl.[17]

Chromium(VI) Oxidation of Vanadium(IV). Mixtures of vanadium(IV) (4.0×10^{3} *M*), vanadium(V) (2.2×10^{-3} *M*), perchloric acid (0.04 *M*), lithium perchlorate (1.0 *M*), and 0–0.13 *M* in isopropyl alcohol were introduced into a glass-stoppered spectrophotometric cell (quartz, 1.0 cm) and thermally equilibrated. A weighed quantity of 0.05 *M* chromium(VI) solution was introduced and mixed, and absorbance at 350 nm (*A*) recorded as a function of time. The final absorbance (A_∞) was measured after at least 2–3 hr. The concentration of chromium(VI) was calculated from these absorbances and the stoichiometric relationship between the inorganic species.[5]

(a) **In the absence of the organic substrate** the stoichiometry of the reaction is given by eq 7. Since only chromium(VI), vanadium(V), and chromium(III) absorb[5] at 350 nm

$$\mathrm{Cr^{VI}} + 3\mathrm{V^{IV}} = \mathrm{Cr^{III}} + 3\mathrm{V^{V}} \tag{7}$$

$$A = \epsilon_{\mathrm{Cr^{VI}}}[\mathrm{Cr^{VI}}] + \epsilon_{\mathrm{V^{V}}}[\mathrm{V^{V}}] + \epsilon_{\mathrm{Cr^{III}}}[\mathrm{Cr^{III}}] \tag{8}$$

where ε's are the molar absortivities. Similarly at the end of the reaction

$$A_\infty = \epsilon_{\mathrm{Cr^{VI}}}[\mathrm{Cr^{VI}}]_\infty + \epsilon_{\mathrm{V^{V}}}[\mathrm{V^{V}}]_\infty + \epsilon_{\mathrm{Cr^{III}}}[\mathrm{Cr^{III}}]_\infty \tag{9}$$

From the stoichiometry of the reaction (eq 7) and assuming $[\mathrm{Cr^{VI}}]_\infty = 0$

$$[\mathrm{Cr^{VI}}] = \frac{A - A_\infty}{\epsilon_{\mathrm{Cr^{VI}}} - 3\epsilon_{\mathrm{V^{V}}} - \epsilon_{\mathrm{Cr^{III}}}} \tag{10}$$

The rate law for the chromium(VI)–vanadium(IV) reaction is[5]

$$-\frac{\mathrm{d}[\mathrm{Cr^{VI}}]}{\mathrm{d}t} = k\frac{[\mathrm{Cr^{VI}}][\mathrm{V^{IV}}]^2}{[\mathrm{V^{V}}]} \tag{11}$$

Expressing the concentrations of vanadium(IV) and vanadium(V) in terms of their initial concentrations and that of chromium(VI), one obtains eq 12. Substituting *a* for $[\mathrm{Cr^{VI}}]_0$, *b* for $[\mathrm{V^{IV}}]_0$, *c* for $[\mathrm{V^{V}}]_0$, and *x* for $[\mathrm{Cr^{VI}}]$, gives eq 13 which on integration[18] yields eq 14.

$$-\frac{\mathrm{d}[\mathrm{Cr^{VI}}]}{\mathrm{d}t} = k\frac{[\mathrm{Cr^{VI}}]([\mathrm{V^{IV}}]_0 - 3[\mathrm{Cr^{VI}}]_0 + 3[\mathrm{Cr^{VI}}])^2}{[\mathrm{V^{IV}}]_0 + 3[\mathrm{Cr^{VI}}]_0 - 3[\mathrm{Cr^{VI}}]} \tag{12}$$

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = k\frac{x(b - 3a + 3x)^2}{(c + 3a - 3x)} \tag{13}$$

$$\frac{3(b + c)(a - x)}{b(b - 3a)(b - 3a + 3x)} + \frac{(c + 3a)}{(b - 3a)^2}\ln\frac{bx}{a(b - 3a + 3x)} = -kt \tag{14}$$

(b) **In the Presence of Organic Substrates.** If an organic compound added to the vanadium(IV)–chromium(VI) system also undergoes oxidation, reaction 7 does not represent the stoichiometry and eq 10 is no longer valid. The stoichiometry of the reaction can be derived from Scheme III.

Scheme III

$$\mathrm{Cr^{VI}} + \mathrm{V^{IV}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cr^{V}} + \mathrm{V^{V}} \tag{1}$$

$$\mathrm{Cr^{V}} + \mathrm{V^{IV}} \xrightarrow{k_2} \mathrm{Cr^{IV}} + \mathrm{V^{V}} \tag{2}$$

$$\mathrm{Cr^{IV}} + \mathrm{V^{IV}} \xrightarrow{k_3} \mathrm{Cr^{III}} + \mathrm{V^{V}} \tag{3}$$

$$\mathrm{Cr^{IV}} + \mathrm{S} \xrightarrow{k_4} \mathrm{Cr^{III}} + \mathrm{R}\cdot \tag{4}$$

$$\mathrm{R}\cdot + \mathrm{V^{V}} \xrightarrow{k_5} \text{product} + \mathrm{V^{IV}} \tag{5}$$

The number of moles of vanadium(V) produced in the oxidation by 1 mol of chromium(VI) is equal to the yield in steps 1, 2, and 3, minus that in step 5. Each of steps 1 and 2 produces 1 mol of vanadium(V)/mole of chromium(VI) reduced. The yield in step

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[11] H. A. Iddles and C. E. Jackson, *Ind. Eng. Chem., Anal. Ed.*, 6, 454 (1934).

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[16] The chromium(VI)–vanadium(IV) reactions under these conditions were practically over within about 10 min. Therefore, yields of vanadium(V) were measured after about 30 min of reaction.

[17] J. Roček and A. Riehl, *J. Amer. Chem. Soc.*, **89**, 6691 (1967).

[18] J. H. Espenson and E. L. King, *ibid.*, **85**, 3328 (1963).

3 is m moles of vanadium(V), where m is defined by eq 15. Step 4

$$m = \frac{k_3[\mathrm{V^{IV}}]}{k_3[\mathrm{V^{IV}}] + k_4[\mathrm{S}]} \qquad (15)$$

yields $1 - m$ moles of an organic radical which in step 5 will consume $1 - m$ moles of vanadium(V). Hence the total yield of vanadium(V) per mole of chromium(VI) is

$$[\mathrm{V^V}] - [\mathrm{V^V}]_0 = (1 + 2m)([\mathrm{Cr^{VI}}]_0 - [\mathrm{Cr^{VI}}]) \qquad (16)$$

or

$$[\mathrm{V^V}] - [\mathrm{V^V}]_\infty = -(1 + 2m)([\mathrm{Cr^{VI}}] - [\mathrm{Cr^{VI}}]_\infty) \qquad (17)$$

In the absence of an organic substrate $m = 1$ and eq 16 becomes eq 18. Introducing the symbols V and $V_{\max}$ for the yields of vanadium(V), $[\mathrm{V^V}] - [\mathrm{V^V}]_0$, in the presence (eq 16) and absence (eq 18) of organic substrate, respectively, eq 19 is obtained

$$[\mathrm{V^V}] - [\mathrm{V^V}]_0 = 3([\mathrm{Cr^{VI}}]_0 - [\mathrm{Cr^{VI}}]) \qquad (18)$$

$$\frac{V}{V_{\max}} = \frac{1 + 2m}{3} \qquad (19)$$

or

$$m = \frac{3V - V_{\max}}{2V_{\max}} \qquad (20)$$

from which the value of m can be determined experimentally.

Following the above approach, it can be shown that in the presence of a substrate eq 10 will be modified to eq 21. Equation 21

$$[\mathrm{Cr}]^{\mathrm{VI}} = \frac{A - A_\infty}{\epsilon_{\mathrm{Cr^{VI}}} - (1 + 2\,m)\epsilon_{\mathrm{V}}{}^{\mathrm{V}} - \epsilon_{\mathrm{Cr^{III}}}} \qquad (21)$$

was therefore used to determine chromium(VI) concentrations in all kinetic measurements in the presence of organic substrates. The rate law (eq 11) in the presence of the substrate is unchanged.[6] However, introducing the changed stoichiometry in eq 11 gives

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = k\frac{x\{b - (1 + 2m)a + (1 + 2m)x\}^2}{c + (1 + 2m)a - (1 + 2m)x} \qquad (22)$$

which on integration becomes

$$\frac{(1 + 2m)(b + c)(a - x)}{b\{b - (1 + 2m)a\}\{b - (1 + 2m)a + (1 + 2m)x\}} + \frac{c + (1 + 2m)a}{b - (1 + 2m)a\}^2} \times \ln\frac{bx}{a\{b - (1 + 2m)a + (1 + 2m)x\}} = -kt \qquad (23)$$

Expressions 14 and 23 were calculated on a computer and the rate constant k (*cf.* eq 11) was determined graphically (*cf.* Figure 1).

Results and Discussion

The Induced Oxidation of Isopropyl Alcohol. The rate constant for the chromium(VI) oxidation of isopropyl alcohol in 0.1 M perchloric acid solution is $1.0 \times 10^{-4}\ M^{-1}\ \mathrm{sec}^{-1}$. Under the same conditions, the oxidation of isopropyl alcohol by vanadium(V) is too slow to measure. The oxidation of vanadium(IV) by chromium(VI) in 0.05 M perchloric acid is practically complete within about 25 min ($k \sim 0.6\ M^{-1}\ \mathrm{sec}^{-1}$). Therefore, if isopropyl alcohol is added to the vanadium(IV)–chromium(VI) reaction even in a 30-fold excess over vanadium(IV), less than 1% of acetone could be formed by chromium(VI) oxidation and considerably less by vanadium(V) oxidation. Nevertheless, it was found that when a mixture of 0.04 M vanadium(IV) and 0.8 M isopropyl alcohol was oxidized by 0.01 M chromium(VI), 0.007 M acetone was produced, corresponding to a 40% yield, based on the available amount of chromium(VI) and 60% based on Scheme II (with isopropyl alcohol and acetone as the substrate and product, respectively). It is thus obvious that an oxidation of isopropyl alcohol which cannot be attributed either to chromium(VI) or to vanadium(V) takes place.

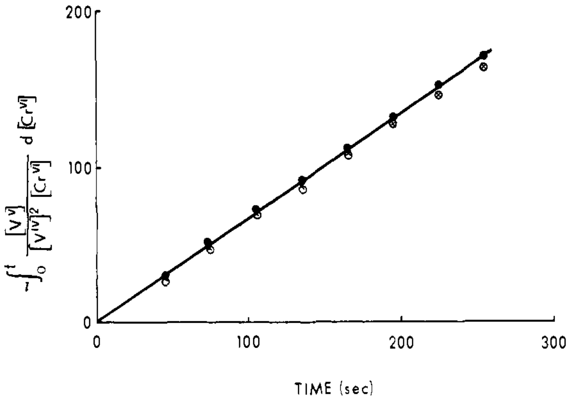

Figure 1. Linear plot of the integrated rate expression (eq 11) calculated from eq 23 of chromium(VI)–vanadium(IV) reaction in the presence of isopropyl alcohol. Concentration of alcohol: ○, 2.13 × 10^{-2} M; ×, 4.75 × 10^{-2} M; ●, 12.9 × 10^{-2} M.

Kinetic Evidence for Chromium(IV) Oxidation. So far the oxidation of isopropyl alcohol in the chromium(VI)–vanadium(IV) system has been discussed as being due to chromium(IV) without actually presenting evidence ruling out chromium(V) as the reactive species.

According to Espenson's mechanism,[5] the rate-limiting step of the oxidation of vanadium(IV) by chromium(VI) is the reduction of chromium(V) to chromium(IV) (reaction 2). Therefore, if chromium(V) is capable of oxidizing another substrate under the reaction conditions, the overall reaction rate would be described by eq 24 instead of eq 11 and would thus

$$-\frac{\mathrm{d}[\mathrm{Cr^{VI}}]}{\mathrm{d}t} = k'\frac{[\mathrm{Cr^{VI}}][\mathrm{V^{IV}}]}{[\mathrm{V^V}]}(k_2[\mathrm{V^{IV}}] + k_2'[\mathrm{S}]) \qquad (24)$$

be a function of the substrate concentration. A situation like that is indeed encountered[5] in the induced oxidation of iodide ion. If iodide ions are added to the vanadium(IV)–chromium(VI) mixture, the reaction takes place at an immeasurably fast rate, yielding up to 67% of iodine as the oxidation product (Scheme IV).

Scheme IV

$$\mathrm{Cr^{VI} + V^{IV} \rightleftharpoons Cr^{V} + V^{V}} \qquad (1)$$

$$\mathrm{Cr^{V} + I^- + H_2O \longrightarrow Cr^{III} + HIO + H^+} \qquad (25)$$

$$\mathrm{I^- + HIO + H^+ \longrightarrow I_2 + H_2O} \qquad (26)$$

If the organic substrate is oxidized by chromium(IV), no change in the reaction rate should be observed as the reduction of chromium(IV) (reactions 3 and 4) occurs after the rate-limiting step. Table I shows the effect of the concentration of isopropyl alcohol and ethanol on the rate of reduction of chromium(VI) by vanadium(IV). No rate acceleration is observed. This observation is consistent only with chromium(IV) oxidation, and chromium(V) oxidation can thus be ruled out.

Table I. Effect of Isopropyl Alcohol and Ethanol on the Rate of the Chromium(VI)–Vanadium(IV) Reaction[a]

Initial concn, M					
$[V^{IV}] \times 10^3$	$[V^{V}] \times 10^3$	$[ROH] \times 10^3$	$[HClO_4] \times 10^2$	$[Cr^{VI}] \times 10^5$	k, M^{-1} sec^{-1}
2.7	0.54	0	6.4	46	0.75[b]
		Isopropyl alcohol			
4.1	2.3	21.3	3.7	7.6	0.65
3.9	2.2	47.5	3.7	9.1	0.68
4.1	2.3	71.5	3.7	10	0.64
4.1	2.3	129	3.7	9.6	0.66
		Ethanol			
4.7	2.4	39.2	3.8	5.1	0.57

[a] Temperature, 25 ± 0.05°; μ ($LiClO_4$), 1.0 M. [b] Determined by instantaneous slope measurement and separation of rates due to $HCrO_4^-$ and $Cr_2O_7^{2-}$ according to eq 8 of ref 5.

From the lack of rate acceleration shown in Table I we can also get an estimate of the upper limit of the reactivity of chromium(V) toward isopropyl alcohol. Making the conservative assumption that a 10% increase in reaction rate could be safely observed, one can estimate that the reactivity of chromium(V) toward vanadium(IV) must be at least 300 times greater than toward isopropyl alcohol. On the other hand, Espenson found that chromium(V) reacted 2.7 ± 10^3 times faster with iodide ion than with vanadium(IV).[5] Combining these two findings leads to the conclusion that the iodide ion is about 10^6 times more reactive than isopropyl alcohol, demonstrating thus a remarkably high selectivity of chromium(V).[19]

Evidence for the Formation of Free Radicals. The data presented so far demonstrate that the induced oxidation of isopropyl alcohol in the chromium(VI)–vanadium(IV) system is due to chromium(IV) rather than chromium(V). However, the product could, in principle, be formed either in one two-electron oxidation (reaction 27), or two successive one-electron oxidations (reactions 4 and 5)

$$(CH_3)_2CHOH + Cr^{IV} \longrightarrow (CH_3)_2CO + Cr^{II} \tag{27}$$

$$Cr^{II} + V^{V} \longrightarrow Cr^{III} + V^{IV} \tag{28}$$

$$(CH_3)_2CHOH + Cr^{IV} \longrightarrow (CH_3)_2\dot{C}OH + Cr^{III} \tag{4}$$

$$(CH_3)_2\dot{C}OH + V^{V} \longrightarrow (CH_3)_2CO + V^{IV} \tag{5}$$

The overall result of these sequences would lead to the same kinetics and products. Each of the sequences involves the formation of an unstable intermediate (chromium(II) and a free radical, respectively).

In order to test for free-radical formation the reaction was carried out in the presence of acrylonitrile and acrylamide.[20,21] The observation of polymer formation and the reduction in the yield of acetone (Tables II and III) strongly support a mechanism involving a free-radical intermediate and thus make a two-electron oxidation by chromium(IV) appear improbable.[22]

Table II. Effect of Acrylonitrile on the Yield of Acetone[a]

Concn, M			
$[i\text{-PrOH}] \times 10^{-1}$	[Acrylonitrile] $\times 10^{-2}$	Acetone, %[b,c]	Polymer formation
2	0	49	
2	2	6.1	Yes
0	2		No

[a] Solvent, 50% aqueous acetic acid; $[HClO_4]$, 0.1 M; $[Cr^{VI}]_0$, 1.2×10^{-2} M; $[V^{IV}]_0$, 5.0×10^{-2} M; no V^V added; reaction time, 40 min; dark, room temperature, under nitrogen. [b] Determined by gravimetric analysis of 2,4-dinitrophenylhydrazone. [c] Based on total chromium(VI) introduced.

Table III. Effect of Acrylamide on the Yield of Acetone[a,b]

[Acrylamide], M	A at 476 nm	Acetone rel yield, %	Polymer formation[c]
0.0	0.74	100	
0.1	0.65	88	Yes
0.5	0.45	61	Yes
1.0	0.13	17	Yes

[a] Analyzed by spectrophotometry of 2,4-dinitrophenylhydrazone.[14] [b] Initial concentrations, $[HClO_4]$, 0.10 M; $[i\text{-PrOH}]$, 0.78 M; reaction mixtures, $[V^{IV}]_0$, 0.033 M; $[Cr^{VI}]_0$, 0.07 M; reference solutions, $[V^{IV}]$, 0.009 M; $[V^{V}]$, 0.018 M; $[Cr^{III}]$, 0.007 M. [c] Polymers precipitated out on dilution with methanol.

Quantitative Relationship between Substrate Concentrations and Oxidation Products. From Scheme III and eq 15 and 20, the yield of vanadium(V) can be expressed as a function of the substrate and vanadium(IV) concentrations (eq 29). The concentration of the

$$\frac{V_{max} - V}{V - 0.33V_{max}} = \frac{k_4}{k_3}\frac{[S]}{[V^{IV}]_{av}} \tag{29}$$

substrate, [S], can be considered approximately constant. An average of the initial and final concentration of vanadium(IV) was used in eq 29 (*cf.* the use of $[V^{IV}]_{av}$ in eq 29 in place of $[V^{IV}]$ in eq 15).

According to eq 29, the yield of vanadium(V) at large substrate concentrations ($m \rightarrow 0$) should drop to only 33% of the yield obtained in its absence. Also, a linear relationship between the expression $(V_{max} - V)/(V - 0.33V_{max})$ and the concentration ratio $[S]/[V^{IV}]_{av}$ should be obtained, with the slope equal to the relative reactivity of chromium(IV) toward the organic substrate with respect to vanadium(IV), k_4/k_3.

Table IV (first and second columns) and curve 1, Figure 2, show that while the yield of vanadium(V)

Table IV. Effect of Isopropyl Alcohol Concentration on the Yield of Vanadium(V)[a]

At $[V^V]_0 = 1.0 \times 10^{-3}$ M		At $[V^V]_0 = 1.0 \times 10^{-2}$ M	
$[i\text{-PrOH}]$, M	V^V yield,[b] %	$[i\text{-PrOH}]$, M	V^V yield,[b] %
0.00	100	0.00	100
0.060	88.1	0.050	87.9
0.15	81.0	0.10	81.1
0.30	72.2	0.18	74.5
0.45	69.0	0.50	61.1
0.60	65.6	0.75	55.8
0.90	59.4	1.0	51.5
1.2	58.1	1.3	48.7
1.7	55.3	1.5	44.7
2.0	53.5	2.0	43.9

[a] $[V^{IV}]_0$, 0.030 M; $[Cr^{VI}]_0$, 0.009 M; $[HClO_4]$, 0.10 M. [b] Measured spectrophotometrically using eq 6.

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(19) We found that iodide ions react about 5 × 10^3 times faster than isopropyl alcohol with chromium(VI).

(20) (a) G. Mino, S. Kaiserman, and E. Rasmussen, *J. Amer. Chem. Soc.*, **81**, 1494 (1959); (b) W. A. Mosher and G. L. Driscoll, *ibid.*, **90**, 4189 (1968).

(21) Acrylamide was used with particular success in the detection of free-radical intermediates in oxidation reactions by Trahanovsky.[8a]

(22) No polymer formation was observed in the absence of the alcohol. Hence, neither chromium(IV) nor chromium(V) could be held responsible for the polymerization reaction.

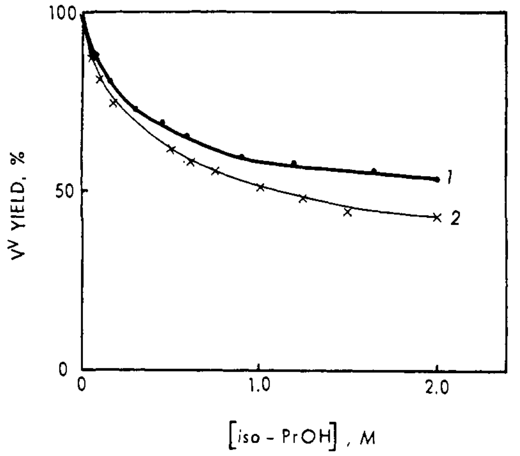

Figure 2. Effect of isopropyl alcohol concentration on the yield of vanadium(V): 1, $[V^V]_0 = 1 \times 10^{-3}\ M$; 2, $[V^V]_0 = 1 \times 10^{-2}\ M$.

is indeed decreasing with increasing isopropyl alcohol concentration, the predicted reduction to 33% is not observed. This may, of course, be due to a relatively low reactivity of isopropyl alcohol as compared with vanadium(IV). However, a plot of the data according to eq 29 shows a curve (curve 1, Figure 3) rather than the expected straight line. The induced oxidation of the organic substrate thus increases more slowly with its concentration than required by eq 29. It is therefore obvious that Scheme III from which eq 29 was derived does not describe completely the reactions taking place in the system.

In Scheme III it was assumed that each free radical formed in the oxidation of the substrate by chromium(IV) reduces one vanadium(V) to vanadium(IV) (reaction 5). It appears that this assumption becomes less satisfactory with increasing concentration of the substrate.

Scheme III predicts an increase in the steady-state concentration of free radicals with increasing substrate concentration. This in turn could lead to a bimolecular reaction between two free radicals, disproportionation, or dimerization. The increasing importance of this nonoxidative free-radical destruction with increasing substrate concentration can then be used to explain the observed deviation from eq 29. The free radicals may therefore react either with the oxidant, vanadium(V), or in a bimolecular reaction.[23] The

$$(C_3H_7O)\cdot + V^V \longrightarrow C_3H_6O + V^{IV} \qquad (5)$$

$$2(C_3H_7O)\cdot \longrightarrow C_3H_6O + C_3H_7OH \qquad (30)$$

$$2(C_3H_7O)\cdot \longrightarrow C_6H_{14}O_2 \qquad (31)$$

relative importance of the two reactions is determined by both the concentration of the radical and of vanadium(V). Increasing the concentration of vanadium(V) should favor reaction 5.

If reactions 30 and 31 could be suppressed completely Scheme III would become valid. Table V and Figure 4 show the effect of vanadium(V) introduced at the beginning of the reaction on the yield of vanadium(V) in the presence of cyclobutanol.[25] Though the amount of vanadium(V) which actually could be introduced was rather limited due to the low solubility of vanadium pentoxide in 0.2 M perchloric acid, a rather striking effect can be observed. The vanadium(V) yield[26] is considerably reduced even though the limiting value of 33% is not reached.[27] The effect of the addition

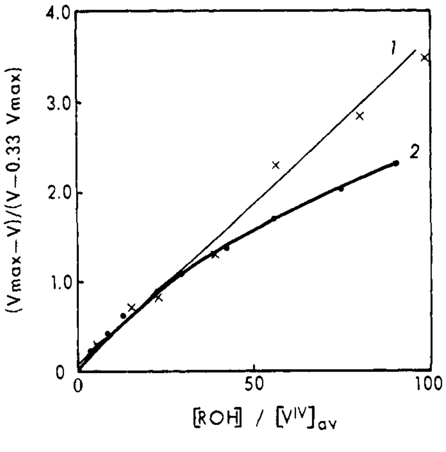

Figure 3. Plots of the function of vanadium(V) yield against substrate to average vanadium(IV) ratio: 1, $[V^V]_0 = 1.0 \times 10^{-3}\ M$; 2, $[V^V]_0 = 1.0 \times 10^{-2}\ M$.

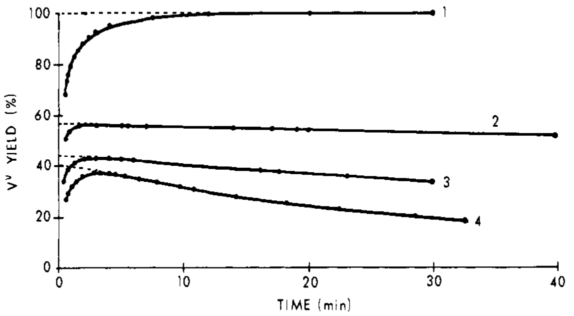

Figure 4. Effect of initial vanadium(V) concentration on the yield of vanadium(V) from the chromium(VI) oxidation of vanadium(IV) in the presence of cyclobutanol. Concentrations (M) of [ROH] $[V^V]_0$: 1, 0.00, 0.015; 2, 0.33, 0.00; 3, 0.33, 0.010; 4, 0.33, 0.025.

Table V. Effect of Initial Vanadium(V) Concentration on the Yield of Vanadium(V) in the Presence of Cyclobutanol[a]

$[V^V]_0 \times 10^2$, M	$[c\text{-}C_4H_7OH]$, M	V^V yield,[b] %
1.5	0.0	100
0.0	0.33	57
1.0	0.33	45
2.5	0.33	41

[a] Other concentrations: $[V^{IV}]_0$, $1.9 \times 10^{-2}\ M$; $[Cr^{VI}]_0$, $5.0 \times 10^{-3}\ M$; $[HClO_4]$, 0.12 M. [b] Cyclobutanol (unlike isopropyl alcohol) is sufficiently reactive toward vanadium(V) that the yield of vanadium(V) had to be determined by extrapolating to zero time (Figure 4).

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(23) No attempt was made to isolate the products of the bimolecular reactions 30 and 31. However, results obtained in a recent study of cerium(IV) oxidations of cyclobutanol have shown that dimerization and disproportionation of a free-radical intermediate may under certain conditions become the dominant reaction.[24]

(24) K. Meyer and J. Roček, *J. Amer. Chem. Soc.*, in press.

(25) Cyclobutanol was used instead of isopropyl alcohol for the higher reactivity of the former with chromium(IV).

(26) As the yield of vanadium(V) was determined indirectly from the decrease in vanadium(IV) concentration, the addition of vanadium(V) did not affect the accuracy of the analysis.

(27) The concentration of cyclobutanol used in the experiment was not sufficient to eliminate the competing oxidation of vanadium(IV) by chromium(IV) (reaction 3, Scheme III) completely. From relative rate measurements (Table VIII) it can be estimated that the yield of vanadium(V) under these conditions should be reduced to 37%. The value of 41% actually obtained is rather close to this limit.

of vanadium(V) is also clearly visible in the oxidation of isopropyl alcohol. Curve 2 on Figure 2 shows that the yield of vanadium(V) is significantly lowered if the initial concentration of vanadium(V) is increased. Moreover, the plot of $(V_{\max} - V)/(V - 0.33V_{\max})$ against $[S]/[V^{IV}]_{av}$ becomes linear as required by eq 29 (curve 2 of Figure 3). The results obtained in the presence of vanadium(V) thus support the assumption that a bimolecular free-radical reaction does take place and that Scheme III should be expanded into the more complete Scheme V.

Scheme V

$$Cr^{VI} + V^{IV} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{V} + V^{V} \qquad (1)$$

$$Cr^{V} + V^{IV} \xrightarrow{k_2} Cr^{IV} + V^{V} \qquad (2)$$

$$Cr^{IV} + V^{IV} \xrightarrow{k_3} Cr^{III} + V^{V} \qquad (3)$$

$$Cr^{IV} + S \xrightarrow{k_4} Cr^{III} + R\cdot \qquad (4)$$

$$R\cdot + V^{V} \longrightarrow V^{IV} + \text{product} \qquad (5)$$

$$2R\cdot \longrightarrow \text{products} \qquad (30, 31)$$

The fact that the deviation from Scheme III could be corrected or minimized by the addition of vanadium(V) indicates that vanadium(V) is probably a better oxidant for the free-radical intermediate than chromium(VI), since the latter is present in a concentration of the same order of magnitude. As vanadium(V) is a one-electron oxidant,[28] whereas chromium(VI) acts preferentially as a two-electron oxidizing agent,[29] the higher reactivity of vanadium(V) toward the free radical seems reasonable.

The above assumption that chromic acid is a relatively poor oxidant for free radicals violates the commonly held view[29] that free radicals are generally far too easily oxidized to build up, in the presence of a large excess of an oxidant, a concentration sufficiently high to permit a bimolecular reaction. However, we find encouragement for our proposal in the recent works of Kochi and coworkers[30] who have established that while free radicals react at rates approaching duffusion control with some oxidants (copper (II)), their reactivities toward other oxidants (lead(IV)) are considerably lower.

Determination of Relative Rates in Chromium(IV) Oxidations. As pointed out in the previous section the introduction of larger amounts of vanadium(V) at the beginning of the reaction results in the suppression of the bimolecular free radical reaction. The simpler Scheme III can then be used instead of the more complex Scheme V and eq 29 is then obeyed. Therefore, quantitative data on the reactivity of various substrates toward chromium(IV) can be obtained from $(V_{\max} - V)/(V - 0.33V_{\max})$ *vs.* $[S]/[V^{IV}]_{av}$ plots. Curve 2, Figure 3, provides an example for the determination of the relative reactivity of isopropyl alcohol with respect to vanadium(IV). In five series of experiments, values for k_4/k_3 ranging from 0.037 to 0.051 with an average of 0.042 and a probable error of 0.005 were obtained.[31] The same approach was used in the determination of the relative reactivities of a number of alcohols and related compounds.

Oxidation of Primary Alcohols. Both to test the generality of our approach and to obtain information needed for the understanding of the mechanism of chromium(IV) oxidations, a series of primary alcohols was investigated. The results are summarized together with chromium(VI) oxidation rates[32] in Table VI. The values of k_4/k_3 are obtained driectly from the slopes of the plots of $(V_{\max} - V)/(V - 0.33V_{\max})$ *vs.* $[S]/[V^{IV}]_{av}$ and give the reactivities of alcohols relative to vanadium(IV). The relative reactivities with respect to ethanol as standard are obtained from the k_4/k_3 values.[33]

Table VI. Reactivities of Primary Alcohols

Compd	k_4/k_3	k/k_{EtOH} Cr^{IV}	k/k_{EtOH} $Cr^{VI\,a}$
c-$C_3H_5CH_2OH$	0.46	2.1	1.9
CH_2CHCH_2OH	0.44	2.0	5.7
$(CH_3)_2CHCH_2OH$	0.30	1.4	0.9
CH_3CH_2OH	0.22	1.0	1.0
CH_3OH	0.16	0.73	0.042
$CH_3OCH_2CH_2OH$	0.076	0.35	0.12
$ClCH_2CH_2OH$	0.026	0.13	0.064
$NCCH_2CH_2OH$	0.018	0.080	0.020
Cl_2CHCH_2OH	0.0081	0.037	0.0086
Cl_3CCH_2OH	0.0087	0.0040	0.0021

[a] From data in ref 32.

There is a rough general agreement between the chromium(IV) and chromium(VI) relative reactivities with notable exceptions found in the cases of methanol and allyl alcohol. Methanol is known to behave in an anomalous manner in the chromium(VI) oxidation.[32] Allyl alcohol is oxidized at a relatively slower rate by chromium(IV) than by chromium(VI). This may point to a higher stabilization offered by the conjugated double bond to the incipient carbonyl group from chromium(VI) oxidation than the free radical formed in the chromium(IV) oxidation.

Figure 5 shows a plot of the logarithm of the relative rates against the Taft's substituent constant σ^*. The plot gives a good straight line with a correlation coefficient of 0.99, standard deviation 0.12.[34] This is a much better fit than previously obtained for chromium(VI) oxidation[32] despite the experimental difficulties and indirect nature in which the chromium(IV) rate constants have been obtained. Whereas in the chromium(VI) oxidation, methanol is oxidized unusually slowly, the value obtained for the chromium(IV) reaction lies (after applying the statistical correction of $^3/_2$) very close to the line. From Figure 5, the ρ^* value has been found to be -0.85. The ρ^* constant

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(28) W. A. Waters and J. S. Little in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965 pp 198–199.

(29) W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949).

(30) (a) J. K. Kochi and R. V. Subramanian, *J. Amer. Chem. Soc.*, **87**, 4855 (1965); (b) J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, **33**, 83 (1968).

(31) It should be pointed out that the method of determining the reactivity of chromium(IV) toward an organic substrate relative to vanadium(IV) using eq 29 depends on the use of differences between large values and is therefore very sensitive to the precise determination of $V_{\max}$.

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

(33) To check whether the investigation of primary alcohols might be complicated by a further rapid reaction of the products, the oxidation rate of acetaldehyde was determined. Acetaldehyde was found to react more slowly ($k_4/k_3 = 0.12$; $k/k_{EtOH} = 0.52$) than ethanol. Therefore, chromium(IV) oxidation in the presence of an excess of alcohol does not proceed beyond the aldehyde stage.

(34) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

for the chromium(IV) oxidation thus has the same sign but a somewhat lower numerical value than determined previously for chromium(VI) oxidation ($\rho^* = -1.06$).[32]

Effect of Acidity. Table VII gives the effect of acidity on the relative rate of the isopropyl alcohol oxidation by chromium(IV). The rates show relatively little variation with large changes in the concentration of perchloric acid. While this result does not allow us to determine whether or not the chromium(IV) oxidation of isopropyl alcohol is an acid-catalyzed reaction, it is obvious that the acid dependence for the oxidation of the alcohol and vanadium(IV) is the same. In this respect chromium(IV) oxidation differs noticeably from the chromium(VI) oxidation. The oxidation of alcohols by chromium(VI) is an acid-catalyzed reaction over a wide range of acidities;[35] on the other hand, chromium(VI) oxidation of vanadium(IV) is acid independent as long as the concentration of chromium(VI) is low enough to make the dichromate ion concentration negligible.[5] One might thus suspect that the chromium(IV) oxidation of alcohols may also be an acidity-independent reaction. However, no definite conclusion about the acidity deference of chromium(IV) oxidation can be drawn at the present time.[36]

Table VII. Effect of Acidity[a]

Perchloric acid concn, M	$10^2 \times k_4/k_3$
0.1	4.7
0.4	5.0
0.5	4.1
1.0	4.7
1.8	5.8

[a] These results were obtained by Mr. Chiu Ng, Chemistry Department, University of Illinois at Chicago Circle.

Mechanism of the Chromium(IV) Oxidation of Alcohols. Table VIII summarizes the relative reactivities of a number of compounds which were investigated in order to achieve a better insight into the mechanism of chromium(IV) oxidations. The oxidation of isopropyl alcohol exhibits a primary isotope effect of 1.9. This value is considerably smaller than those observed in the chromium(VI)[37] and chromium(V)[3] oxidation, but is of comparable value to those of other one-electron oxidants[38] (Table IX). Despite the relatively low value of the isotope effect, one still can conclude that the rate-limiting step involves a breaking of the carbon–hydrogen bond. This point is further strengthened by the observation that *tert*-butyl alcohol is very unreactive (Table VIII) toward chromium(IV) oxidation.

Table VIII. Reactivities of Organic Substrates with Chromium(IV)

Compd	k_4/k_3
$(CH_3)_2CHOH$	0.042[a]
$(CH_3)_2CDOH$	0.022
$c\text{-}C_4H_7OH$	0.89
CH_3CH_2OH	0.21[a]
$(C_2H_5)_2O$	0.007
$(CH_3)_3COH$	0.0007

[a] Average of five measurements, relative deviation ~10%.

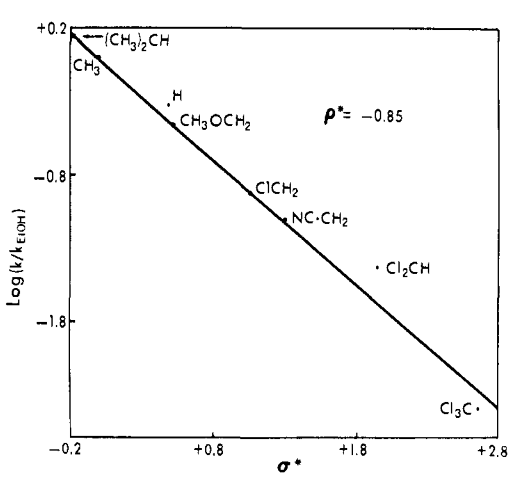
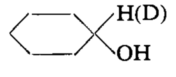
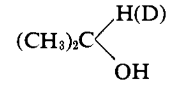


Figure 5. Dependence of the relative rate of chromium(IV) oxidation of the primary alcohols, RCH_2OH, on the σ^* value of the group R.

Table IX. Isotope Effects in the Oxidation of Secondary Alcohols by One-Electron Oxidants

Alcohol	Oxidant	k_H/k_D	Ref
	Cerium(IV) Cobalt(III) Manganese(III)	1.9 1.7 1.6	38a 38b 38c
 $(CH_3)_2C{<}^{H(D)}_{OH}$	Chromium(IV)	1.9	

The role of the hydroxyl group can be judged from the relative rates of ethanol as compared with diethyl ether.[39] The alcohol is oxidized 31 times faster than the ether. The chromium(VI) oxidation rates for the two compounds were determined for comparison and the alcohol was found to be 2400 times more reactive than the ether (ethanol, $k = 8.2 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$; diethyl ether, $k = 3.4 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$ at 25° in 1.0 M $HClO_4$).[40]

The high reactivity of the alcohol compared with the corresponding ether in the chromium(VI) oxidation results from the need for the formation of a chromium(VI) ester intermediate in the oxidation. The much lower value of the alcohol–ether reactivity observed in the chromium(IV) oxidation does not justify postulating a similar mechanism. While ester formation cannot be ruled out, a more likely interpretation would

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(35) F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943).

(36) One of the referees pointed out the interesting possibility that the mechanics of alcohol oxidation might change with the acidity of the solution if the oxidation of alcohols by chromium(IV) is acid independent and the oxidation of chromium(V) is acid catalyzed.

(37) F. H. Westheimer and N. Nicholaides, *J. Amer. Chem. Soc.*, **71**, 25 (1949).

(38) (a) J. S. Littler, *J. Chem. Soc.*, 4135 (1959); (b) D. G. Hoare and W. A. Waters, *ibid.*, 965 (1962); (c) J. S. Littler, *ibid.*, 2190 (1962); (d) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

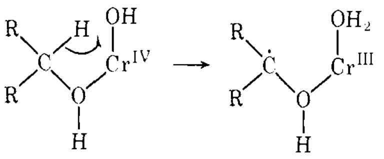
(39) Diethyl ether was used because of the low solubility of diisopropyl ether in water.[10]

(40) This value is even higher than the value of 750 found by Westheimer, *et al.*,[41] for the pair isopropyl alcohol–diisopropyl ether.

(41) R. Brownell, A. Leo, Y. W. Chang, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **82**, 406 (1960).

be that the oxidation takes place in a coordination complex in which the lower reactivity of the ether is more likely due to steric reasons than to the requirement of a readily replaceable hydroxyl hydrogen atom.

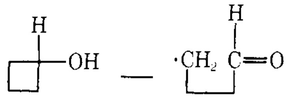
A mechanism which is consistent with all the observations discussed above could then contain a rapid reversible formation of a complex and its rate-limiting decomposition (eq 32). The radical then can undergo


(32)

further oxidation or react with a second radical. It is possible that the existence of the radical in the form of a chromium(III) complex adds to its earlier discussed stability.

The value of the reaction constant ρ^* is also in agreement with the proposed mechanism; hydrogen abstraction reactions generally exhibit[34,42] ρ values in the range from -0.5 to -1.5.

It should be emphasized that this mechanism is proposed only for alcohols not undergoing cleavage. For example, in cyclobutanol carbon–carbon rather than carbon–hydrogen bond cleavage is observed, and the rate-limiting step of the chromium(IV) oxidation probably involves step 33. The high reactivity of cyclo-


(33)

butanol (it reacts 21 times faster than isopropyl alcohol with chromium(IV), but ~3 times faster[43] with chromium(VI)) is in accord with the assumption of a different mechanism.[6,7]

Acknowledgment. We wish to thank Mr. Chiu Ng for measuring the effect of acidity and Mr. David Aylward for his help in the preparation of cyclobutanol. The use of computer time through a University of Illinois Research Board grant is also acknowledged.

[42] (a) C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, **82**, 6113 (1960); G. A. Russel and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964); (c) E. S. Huyser, *ibid.*, **82**, 394 (1960); (d) R. D. Gilliom and B. F. Ward, Jr., *ibid.*, **87**, 3944 (1965).

[43] H. G. Kuivila and W. J. Becker, III, *ibid.*, **74**, 5329 (1952).

Mechanism of Chromic Acid Oxidation of Isopropyl Alcohol. Evidence for Oxidation by Chromium(IV)[1]

Matiur Rahman and Jan Roček*

Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680.
Received December 9, 1970

Abstract: The presence of acrylonitrile or acrylamide in the oxidation of isopropyl alcohol by chromic acid leads to the formation of polymers and a considerable reduction in the yield of acetone. The observations are consistent with a mechanism involving a rapid one-electron oxidation of the alcohol by chromium(IV). The mechanism often preferred involving the reaction $Cr^{VI} + Cr^{IV} \rightarrow 2Cr^{V}$ is shown to be inconsistent both with the findings of this work and with electrochemical data which lead for this reaction to an estimated equilibrium constant of 4×10^{-14}. The results thus support conclusions drawn earlier from the investigation of chromium(IV) generated from chromium(VI) and vanadium(IV).

Although the mechanism of chromic acid oxidation of alcohols has been the subject of numerous studies during the past 25 years, only the rate-limiting step (which is responsible for only 33% of the total products) is well understood. It is generally agreed that it involves a direct two-electron oxidation to a carbonyl compound with the concomitant formation of a chromium(IV) species[2] (reactions 1 and 2). There

$$R_2CHOH + H_2CrO_4 + H^+ \rightleftharpoons R_2CHOCrO_3H_2^+ + H_2O \quad (1)$$

$$R_2CHOCrO_3H_2^+ \longrightarrow R_2CO + Cr^{IV} \quad (2)$$

is much less agreement on the next step of the reaction.

The unstable chromium(IV) compound may either *reduce* a molecule of chromic acid (reaction 3) or

$$Cr^{IV} + Cr^{VI} \longrightarrow 2Cr^{V} \quad (3)$$

oxidize an organic substrate in a one- or two-electron oxidation (reaction 4 or 5) where S and R· represent

$$Cr^{IV} + S \longrightarrow Cr^{III} + R\cdot \quad (4)$$

$$Cr^{IV} + S \longrightarrow Cr^{II} + \text{product} \quad (5)$$

the organic substrate and a free radical intermediate, respectively. The expected step following either reaction 4 or 5 is the formation of a chromium(V) compound[3] (reaction 6 or 7).

$$Cr^{VI} + R\cdot \longrightarrow Cr^{V} + \text{product} \quad (6)$$

$$Cr^{VI} + Cr^{II} \longrightarrow Cr^{V} + Cr^{III} \quad (7)$$

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[1] This investigation was supported by the Petroleum Research Fund (Grant No. 1529-4A), administered by the American Chemical Society, and by the National Science Foundation (Grant No. 9441).

[2] (a) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949); (b) K. B. Wiberg in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 159–170; (c) W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949); (d) K. B. Wiberg and H. Schäfer, *J. Amer. Chem. Soc.*, **91**, 927, 933 (1969); **89**, 455 (1967).

[3] Since chromium(V) may be formed from either of the above reactions, the direct observation of this species[2d] offers unfortunately no clue to the understanding of the role of chromium(IV) in chromic acid oxidations.