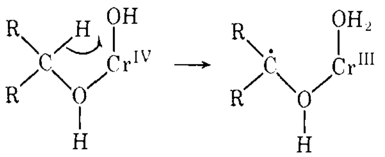
be that the oxidation takes place in a coordination complex in which the lower reactivity of the ether is more likely due to steric reasons than to the requirement of a readily replaceable hydroxyl hydrogen atom.

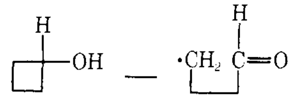
A mechanism which is consistent with all the observations discussed above could then contain a rapid reversible formation of a complex and its rate-limiting decomposition (eq 32). The radical then can undergo further oxidation or react with a second radical. It is possible that the existence of the radical in the form of a chromium(III) complex adds to its earlier discussed stability.



(32)

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 cyclobutanol (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]



(33)

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).

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

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

---

[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.

It is also generally agreed that a chromium(V) species will react as a two-electron oxidant[4] (reaction 8).

$$\mathrm{Cr^{V} + S \longrightarrow Cr^{III} + product} \qquad (8)$$

Therefore, the formation of free radicals is expected only if chromium(IV) reacts directly with the substrate in a one-electron oxidation (reaction 4).

The formation of free radicals has been observed in reactions in which carbon–carbon bond cleavage takes place,[5–7] and indirect evidence for free radical formation was also obtained for the oxidation of aromatic aldehydes.[8] However, attempts to observe free radical formation in the oxidation of simple aliphatic alcohols such as isopropyl alcohol were unsuccessful,[5,9] thus strengthening the belief that reaction 3 rather than reaction 4 takes place unless especially favorable conditions for a one-electron oxidation by chromium(IV) are created.

An investigation of the properties of chromium(IV) generated in a stepwise reduction of chromium(VI) by vanadium(IV) led us to conclude[10,11] that chromium(IV) is extremely reactive toward alcohols whereas chromium(V) seems to possess a rather low reactivity.

However, the uncertainty about the actual nature of the intermediate chromium species involved in the reactions makes the generalization of the findings to ordinary chromic acid oxidations open to questions. It is not inconceivable that the chromium(IV) and chromium(V) species produced in the chromium(VI)–vanadium(IV) reaction are sufficiently different in nature from those produced from chromium(VI) during the reduction by an alcohol to exhibit different properties in oxidation reactions. The purpose of this paper is to examine whether our findings based on the study of the chromium(VI)–vanadium(IV) system can indeed be extended to normal chromic acid oxidations.

Experimental Section

The sources of the materials and the preparation of stock solutions have been described in the preceding paper.[11]

Products. The yields of acetone from the chromic acid oxidation of isopropyl alcohol, in the presence and absence of acrylonitrile or acrylamide as trapping agents, were determined by spectrophotometric analysis of its 2,4-dinitrophenylhydrazone derivative in alcoholic alkali according to the procedure of Lappin and Clark.[12] Prior to the analysis, the polymers formed during the reaction were removed by centrifugation or filtration. Solutions containing chromium(III), isopropyl alcohol, the monomers, and the DNP reagent in concentrations equal to those in the analyzed samples were used as references for the spectrophotometric analysis. In the experiments with low perchloric acid concentrations the ionic strength was maintained at 1.0 *M* by lithium perchlorate.[13]

Kinetics. The rates of chromic acid oxidation of isopropyl alcohol in the presence of the olefinic monomers as well as their saturated analogs were measured by the procedure described previously.[14]

Results and Discussion

If the reaction proceeds according to Scheme I in

Scheme I

$$\mathrm{Cr^{VI} + S \longrightarrow Cr^{IV} + P} \qquad (9)$$

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

$$\mathrm{Cr^{VI} + R\cdot \longrightarrow Cr^{V} + P} \qquad (6)$$

$$\mathrm{Cr^{V} + S \longrightarrow Cr^{III} + P} \qquad (10)$$

which chromium(IV) reacts as a one-electron oxidant, then 33% of the product should be formed *via* a free radical, while 67% is formed by two-electron oxidations involving chromium(VI) and chromium(V). In the presence of a sufficiently reactive monomer, one can expect: (a) polymer formation induced by the free radical, and (b) reduction in the yield of the normal product.[6,15]

Table I shows that both acrylamide and acrylonitrile form polymers during the chromic acid oxidation of isopropyl alcohol in aqueous solutions. The yield of acetone decreases, approaching the limiting value of 67% as the concentration of acrylamide is increased. Acrylonitrile appears to be a less effective scavenger than acrylamide. In control experiments chromic acid did not induce polymerization of either acrylonitrile or acrylamide under the same conditions. As it was also demonstrated that chromium(IV), and chromium(V), formed in the chromium(VI)–vanadium(IV) system, do not induce polymerization of the free radical trapping agents,[11] the polymer formation constitutes strong evidence for free radical intermediates.[16]

Table I. Effect of Free Radical Scavengers on Yields of Acetone and PolymerFormation[a]

Scavenger	Concn, *M*	Acetone, %	Polymer formation
Acrylamide	0.0	100	No
	0.1	93	Yes[b]
	0.5	86	Yes[b]
	1.0	72	Yes[b]
Acrylonitrile	0.0	100	No
	1.5	94	Yes[c]

[a] $[\mathrm{Cr^{VI}}]_0 = 5 \times 10^{-3}$ *M*, [*i*-PrOH] = 0.5 *M*, $[\mathrm{HClO_4}]$ = 0.3 *M* (for acrylamide), 0.5 *M* (for acrylonitrile); reaction time, 24 hr at room temp (25± 1°) in the dark under nitrogen atmosphere. [b] The polymers remained in aqueous solutions but precipitated on dilution with methanol. [c] The polymer precipitated from the reaction mixture within a few minutes.

The effectiveness of the free radical scavengers decreases with increasing acidity of the medium (Table II). This may be well understood if one assumes that the oxidation of the free radical to acetone by chromium(VI) (reaction 6), like all other chromium(VI) oxidations, is an acid-catalyzed reaction, whereas the addition of the free radical to the monomer molecule

---

(4) A one-electron oxidation of chromium(V) would lead to a "chain branching" (autocatalytic) reaction.[2c]

(5) W. A. Mosher, W. H. Clement, and R. L. Hillard, *Advan. Chem. Ser.*, **51**, 81 (1965).

(6) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **92**, 1120 (1970).

(7) J. Hampton, A. Leo, and F. H. Westheimer, *ibid.*, **78**, 306 (1956).

(8) K. B. Wiberg and W. H. Richardson, *ibid.*, **84**, 2800 (1962).

(9) W. A. Mosher and G. L. Driscoll, *ibid.*, **90**, 4189 (1968).

(10) J. Roček and A. E. Radkowsky, *ibid.*, **90**, 2986 (1968).

(11) M. Rahman and J. Roček, *ibid.*, **93**, 5455 (1971).

(12) G. R. Lappin and L. C. Clark, *Anal. Chem.*, **23**, 541 (1951); S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," Wiley, New York, N. Y., 1963, pp 124–128.

(13) The solubility of acrylonitrile in the aqueous medium increased appreciably with increased ionic strength.

(14) J. Roček and Sr. A. Riehl, *J. Amer. Chem. Soc.*, **89**, 6691 (1967).

(15) G. Mino, S. Kaiserman, and E. Rasmussen, *ibid.*, **81**, 1494 (1959).

(16) Implied in this argument is the assumption that the intermediate chromium species formed during the reduction of chromic acid by either an organic alcohol or by vanadium(IV) would react with acrylonitrile or acrylamide in a similar manner. This assumption seems to be reasonable and justified by the absence of any noticeable difference in the reaction of chromium(IV) with organic alcohols regardless of its origin.[10,11]

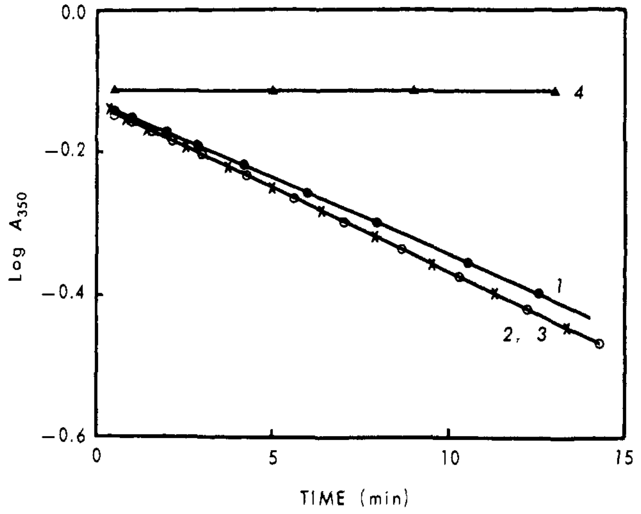


Figure 1. Rates of chromic acid oxidation: **1**, *i*-PrOH (●); **2**, *i*-PrOH and acrylonitrile (⊙); **3**, *i*-PrOH and acetonitrile (×); **4**, acrylonitrile (▲).

is not.[17] This acid dependence may explain earlier failures to observe free radical formations in chromic acid oxidation of simple alcohols.[18]

Table II. Effect of Acidity on Scavenging[a]

Scavenger (concn, *M*)	[HClO$_4$], *M*	Acetone, %[b]	Polymer formation
Acrylamide	0.2[c]	88	Yes[d]
(1.0)	0.5[c]	87	Yes[d]
	1.0	91	Yes[d]
	2.5	92	Yes[d]
Acrylonitrile	0.2[c]	88	Yes (*ca.* 3 g)
(1.5)	0.5[c]	94	Yes (*ca.* 2 g)
	1.0	96	Yes (*ca.* 1.3 g)
	2.5	100	Trace

[a] $[Cr^{VI}]_0 = 5 \times 10^{-3}$ *M*, [*i*-PrOH] = 0.5 *M*, room temp, dark, under nitrogen, time varied from 20 to 32 hr (lowest acidity given longest time). [b] Based on 100% yield without the scavengers. [c] $\mu = 1.0$ *M* (LiClO$_4$). [d] The polymers remained in aqueous solutions.

The presence of free radical scavengers has no pronounced effect on the rate of consumption of chromium(VI) by isopropyl alcohol (Table III, Figure 1).[19]

In the absence of a scavenger, a second molecule of chromium(VI) is reduced in a rapid step (reaction 6), thus making the overall reaction rate twice that of the rate-limiting step. The polymeric free radical $RM_x\cdot$ could either terminate in a bimolecular combination or disproportionation reaction (reaction 11) or reduce a

$$2RM_x\cdot \longrightarrow \text{products} \tag{11}$$

molecule of chromium(VI) (reaction 12). The bimolecular termination step should result in a reduction of the reaction rate to one-half of the value in the absence of scavengers. As no such reduction was observed, we conclude that the termination step of the polymerization reaction involves an oxidation of the polymer radical by chromium(VI) and the formation of chromium(V) (reaction 12).

$$RM_x\cdot + Cr^{VI} \longrightarrow \text{product} + Cr^{V} \tag{12}$$

Table III. Effect of Scavengers and Nonolefinic Additives on Rates[a]

Additive	Concn, *M*	[HClO$_4$], *M*	[*i*-PrOH], *M*	$k_{obsd} \times 10^2$ M^{-1} sec^{-1}
None		1.0	0.08	1.0
Acrylonitrile	0.80	1.0	0.08	1.1
Acetonitrile	0.080	1.0	0.08	1.1
None		0.5	0.32	0.24
Acrylamide	3.2	0.5	0.32	0.27

[a] $[Cr^{IV}]_0 = 5.0 \times 10^{-4}$ *M*, temp 25.0 ± 0.05°.

All the data obtained in this study thus support the mechanism given in Scheme I. Therefore the chromium(IV) species formed by vanadium(IV) and by alcohol reduction of chromium(VI) either do not differ dramatically or the equilibrium between the various chromium(IV) species and the solvent must be rapidly established. We thus feel that reaction 3, the formation of chromium(V) from chromium(IV) and chromium(VI), does not play any major role in chromic acid oxidations.

The reactions taking place in the presence of a monomer acting as a free radical scavenger can be summarized by Scheme II in which M, $RM_x\cdot$, and RM_xOH represent a monomer, a polymeric radical, and its oxidation product, respectively.

Scheme II

$$Cr^{VI} + (CH_3)_2CHOH \longrightarrow Cr^{IV} + (CH_3)_2CO$$

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

$$R\cdot + M \longrightarrow RM\cdot$$

$$RM\cdot + (x-1)M \longrightarrow RM_x\cdot$$

$$RM_x\cdot + Cr^{VI} \longrightarrow RM_xOH + Cr^{V}$$

$$Cr^{V} + (CH_3)_2CHOH \longrightarrow Cr^{III} + (CH_3)_2CO$$

Our conclusion that chromium(IV) *does not reduce* a molecule of chromium(VI) but rather *oxidizes* a molecule of the organic substrate is in agreement with the oxidation potentials of the unstable chromium species in aqueous acidic medium.[2a,20] The estimated reduction potential of the chromium(IV)–chromium(III) and chromium(V)–chromium(IV) couples are +2.10 and +1.34 V, respectively.[20] From the potential diagram

$$\overbrace{Cr^{VI} \xrightarrow{+0.55\ V} Cr^{V} \xrightarrow{+1.34\ V} Cr^{IV} \xrightarrow{+2.10\ V} Cr^{III}}^{+1.33\ V}$$

in acid solution one can therefore estimate[21] the equilibrium constant for reaction 3 to have a value of about 4 ± 10^{-14}. The equilibrium is thus entirely on the side of chromium(IV) and chromium(VI) making any oxidation mechanism involving reaction 3 most unlikely, particularly considering the relatively low reactivity[2d,10,11] of chromium(V).[22]

---

[17] As pointed out by Professor W. S. Trahanovsky, Iowa State University, an additional factor may be that a greater part of the oxidations may be due to chromium(IV) at lower acidities, leading thus to more free radical formation. The additional chromium(IV) could be formed by the disproportionation[5,10] of chromium(V): $2Cr^{V} \rightarrow Cr^{VI} + Cr^{IV}$.

[18] Mosher and coworkers observed some polymerization of acrylonitrile in the oxidation of phenyl-*tert*-butylcarbinol[5] and the isopropyl alcohol induced oxidation of benzaldehyde.[9]

[19] The rates of chromic acid consumption by acrylonitrile (plot 4 in Figure 1) or acrylamide are immeasurably slow under the conditions of alcohol oxidations.

[20] L. J. Csanyi, *Magy. Kem. Foly.*, **65**, 415 (1959).

[21] W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice Hall, New York, N. Y., 1952, Chapter 1.

[22] In fact, under certain conditions chromium(V) is about 14 times less reactive[2d] than even chromium(VI).