Cooxidation of Isopropyl Alcohol and Oxalic Acid by Chromic Acid. A One-Step Three-Electron Oxidation

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Abstract: The chromic acid oxidation of a mixture of oxalic acid and isopropyl alcohol proceeds much faster than that of either of the two substrates alone. It is shown that both substrates undergo oxidation. In the presence of free-radical scavengers an exactly 1:1 ratio of acetone and carbon dioxide is formed, indicating that the alcohol undergoes a two-electron oxidation and oxalic acid a one-electron oxidation. The rate law governing the oxidation of the oxalic acid–isopropyl alcohol system over a wide range of conditions is rate $= 1.26 \times 10^{-2}[HCrO_4^-]\cdot[H^+]^2[ROH] + 8.78[HCrO_4^-][(COOH)_2][ROH] + 2.42 \times 10^{-1}[HCrO_4^-][(COOH)_2]^2$, where only undissociated oxalic acid is kinetically active. The second term of the rate law, which is the kinetically dominant term over a wide range of concentrations, corresponds to the cooxidation reaction in which one molecule of isopropyl alcohol and one molecule of oxalic acid are simultaneously oxidized to yield, in one three-electron oxidation step, a molecule of acetone, a molecule of CO_2, and a $\cdot CO_2^-$ or $\cdot CO_2H$ radical. The rate-limiting step of the cooxidation reaction involves the breaking of the C–H bond in the alcohol molecule and is preceded by the formation of an ester type intermediate. The intermediate is believed to be formed from the alcohol and a chromic acid–oxalic acid complex. Aluminum ions suppress the reaction by competing with chromic acid for the available oxalic acid in complex formation.

During a recent investigation of the formation of a chromium(V) intermediate in the oxidation of oxalic acid by chromic acid, Srinivasan and Roček[1] observed that under conditions in which the chromic acid oxidation of either oxalic acid or of isopropyl alcohol proceeds at only moderate rates, the oxidation of the mixture of the two substrates is practically instantaneous. Subsequent qualitative experiments showed that this unexpectedly rapid oxidation can be observed over a wide range of concentrations and is not restricted to isopropyl alcohol. The oxidation rate was found to be approximately first order in the alcohol, oxalic acid, and chromic acid.[2] No example of such rate acceleration in the chromic acid oxidation of a mixture of two substrates has ever been reported before.[3]

The observed rate acceleration could be due to catalysis, *e.g.*, by a higher reactivity of an oxalic acid–chromic acid complex toward the alcohol with only the alcohol undergoing oxidation.[6] Alternatively, both substrates could be oxidized simultaneously. The latter case would represent a new type of oxidation of considerable interest from the mechanistic point of view and furthermore offer the possibility of useful synthetic applications. We therefore undertook a detailed study of the reaction.

Experimental Section

Materials. Oxalic acid (Mallinckrodt AR) and isopropyl alcohol (Baker Instra-analyzed) were used without further purification. Perchloric acid solutions were prepared from 70% perchloric acid (B and A reagent).

Acrylonitrile (Practical Grade) was distilled before using and the fraction boiling between 77 and 79° collected.

2-Deuterio-2-propanol was prepared in 50% yield from acetone and lithium aluminum deuteride.[8] Vapor-phase chromatographic analysis using Carbowax column showed a single peak with the same retention time as isopropyl alcohol. The sample had, by nmr analysis, less than 0.2% proton at C-2.

Isopropyl ether ("Fisher Certified"), low in peroxide, was purified[9] according to the method suggested by Westheimer and coworkers.

Product Analysis. Acetone. In a typical experiment isopropyl alcohol (1.0 ml, 7.80 *M*), oxalic acid (10 ml, 0.22 *M*), perchloric acid (2.0 ml, 1.22 *M*), and distilled water (11.0 ml) were mixed at room temperature in a 125-ml erlenmeyer flask, and a solution of sodium dichromate (1.0 ml, 0.17 *M*) was added. Although visual observation indicated that the reaction was over in 15–20 min, the mixture was kept in a refrigerator at 5° for about 20 hr. A saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid was added. After about 12 hr in a refrigerator the precipitate was filtered, dried, and weighed both before and after recrystallization from 80% methanol. The difference in the crude yield and the yield determined after purification was about 1–2%. The product was identified as acetone 2,4-dinitrophenylhydrazone by comparison of the uv spectra with an authentic sample and by mixture melting point (mp 125° (lit.[10] 126°), mmp 124–126°).

In the presence of acrylonitrile, the yield of acetone was determined spectrophotometrically as the 2,4-dinitrophenylhydrazone in methanolic potassium hydroxide, using essentially Lappin and Clark's procedure.[11] However, we found that the solutions were unstable and the color disappeared after about 20 hr, contrary to the authors' claim of stability over the period of several days. In order to obtain reproducible results, the determinations were carried out within 5 min after the addition of potassium hydroxide. The determinations were carried out at two wavelengths (430 and 532 nm)[12] which generally agreed within 6%, and the average value of the two measurements was used.

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[1] V. Srinivasan and J. Roček, unpublished results.

[2] J. Roček and M. Roček, unpublished results.

[3] The highly accelerated oxidation of a two substrate system is of an entirely different nature than the well known effect of induced oxidations[4,5] which involves the oxidation of a relatively unreactive substrate in the presence of a more reactive compound. The oxidation rate in an induced oxidation is approximately equal to the rate of oxidation of the more reactive component, the inductor, and essentially independent of the concentration of the less reactive substance.

[4] W. A. Mosher and F. C. Whitmore, *J. Amer. Chem. Soc.*, 70, 2544 (1948).

[5] (a) J. Hampton, A. Leo, and F. H. Westheimer, *ibid.*, **78**, 306 (1956); (b) J. J. Cawley and F. H. Westheimer, *ibid.*, **85**, 1771 (1963); (c) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

[6] A similar explanation was proposed[7] to account for the greatly increased oxidation rates observed in acetic acid solutions. It was postulated that the increased reactivity of chromic acid under these conditions is due to the formation of acetochromic acid, $CH_3CO_2CrO_3H$.

[7] J. Roček, *Collect. Czech. Chem. Commun.*, **22**, 1509 (1957).

[8] A. Leo and F. H. Westheimer, *J. Amer. Chem. Soc.*, **74**, 4383 (1952).

[9] R. Brownell, A. Leo, Y. W. Chang, and F. H. Westheimer, *ibid.*, **82**, 406 (1960).

[10] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 51st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970–1971.

[11] G. R. Lappin and L. C. Clark, *Anal. Chem.*, **23**, 541 (1951).

[12] We noticed that the values for the absorption maximum for ace-

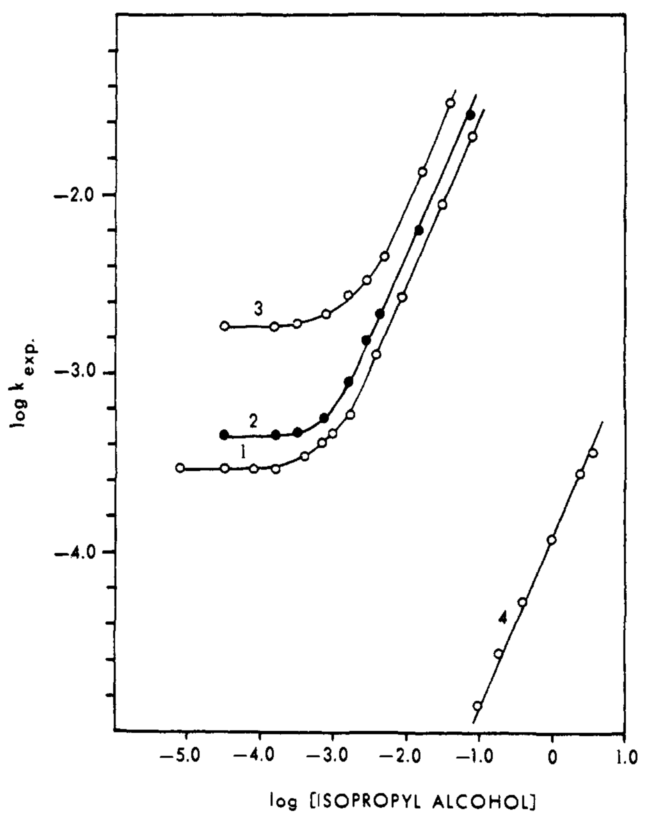

Figure 1. Effect of isopropyl alcohol on the rate of oxidation of oxalic acid at 25°, $HClO_4$ = 0.097 *M*. Concentration of oxalic acid: (1) 4.76×10^{-2} *M*; (2) 6.54×10^{-2} *M*; (3) 1.31×10^{-1} *M*; (4) 0.0.

Carbon Dioxide. The yield of carbon dioxide was determined manometrically in a Warburg apparatus[13] using Fast Green FCF dissolved in ethyl lactate as the manometric fluid. In a typical experiment, oxalic acid (1.0 ml, 0.22 *M*), isopropyl alcohol (0.1 ml, 7.80 *M*), perchloric acid (0.2 ml, 1.22 *M*), and 1.15 ml of water were mixed in a Warburg reaction flask; the mixture was saturated with carbon dioxide and a sodium dichromate solution (0.005 ml, 0.157 *M*) injected into the flask through a side arm with a serum cap from a microliter syringe. The reaction was carried out at room temperatue and was over in about 15 min. The result was corrected for the volume of liquid injected.

Test for Free-Radical Formation. When acrylamide (0.138 *M*) was present in the oxidation of isopropyl alcohol (0.62 *M*) and oxalic acid (0.106 *M*) by sodium dichromate (0.015 *M*), the formation of a polymer could be observed after diluting 25 ml of the reaction mixture with about 40 ml of methanol.

Kinetic Measurements. A large excess (10- to 500-fold) of both isopropyl alcohol and oxalic acid was used for all kinetic measurements. The reaction rates were determined spectrophotometrically using Cary 15 and Zeiss PMQ II spectrophotometers by following the decrease in the absorbance of chromium(VI) at 350 nm in thermostated cell holders. Pseudo-first-order rate constants were calculated from the slopes of the plots of the logarithm of the absorbance *vs.* time. The reactions obeyed good first-order kinetics and the rate constants obtained from multiple determinations were within ±4% of each other.

Results and Discussion

Rate Studies. Table I shows the effect of isopropyl alcohol on the experimental first-order rate constants for the chromic acid oxidation of the isopropyl alcohol–oxalic acid system at constant acidity and constant oxalic acid concentration. The rate increase is observable at a rather low isopropyl alcohol concentration and becomes approximately first order in alcohol at higher concentrations (*cf.* last column).

Table I. Chromic Acid Oxidation of Isopropyl Alcohol–Oxalic Acid System in 0.097 *M* Perchloric Acid at 25°[a]

Isopropyl alcohol, *M*	Chromium(VI), *M*	k_{exptl}, sec^{-1}	k_{exptl}/[*i*-PrOH]
0	4.24×10^{-5}	2.86×10^{-4}	
7.80×10^{-6}	4.24×10^{-5}	2.88×10^{-4}	
3.12×10^{-5}	4.24×10^{-5}	2.90×10^{-4}	
7.80×10^{-5}	4.24×10^{-5}	2.90×10^{-4}	
1.56×10^{-4}	4.24×10^{-5}	2.90×10^{-4}	
3.90×10^{-4}	4.24×10^{-5}	3.46×10^{-4}	
6.24×10^{-4}	4.24×10^{-5}	3.98×10^{-4}	
7.80×10^{-4}	4.24×10^{-5}	4.46×10^{-4}	
1.56×10^{-3}	4.24×10^{-5}	5.88×10^{-4}	
3.90×10^{-3}	4.24×10^{-4}	1.26×10^{-3}	0.32
7.80×10^{-3}	4.24×10^{-4}	2.56×10^{-3}	0.32
3.12×10^{-2}	4.24×10^{-4}	8.88×10^{-3}	0.28
7.80×10^{-2}	4.24×10^{-4}	2.20×10^{-2}	0.28

[a] Oxalic acid = 4.76×10^{-2} *M*.

The data from Table I are reproduced in Figure 1, together with oxidation rates at other oxalic acid concentrations. For comparison, the rate constants for the oxidation of isopropyl alcohol in the absence of oxalic acid (curve 4) are also included. Inspection of the graphs makes it particularly obvious that the rate-accelerating effect of isopropyl alcohol sets in long before the chromic acid oxidation of isopropyl alcohol itself could have been noticed. The first-order dependence on isopropyl alcohol is also clearly visible.

Table II shows the effect of oxalic acid on the experimental rate constant at constant acidity and isopropyl alcohol concentration.

Table II. Chromic Acid Oxidation of Isopropyl Alcohol–Oxalic Acid System in 0.097 *M* Perchloric Acid at 25°[a]

Oxalic acid, *M*	Chromium(VI), *M*	k_{exptl}, sec^{-1}	k_{exptl}/[oxalic acid]
0	4.24×10^{-5}	1.20×10^{-4}	
2.38×10^{-6}	4.24×10^{-5}	1.26×10^{-4}	
4.76×10^{-6}	4.24×10^{-5}	1.32×10^{-4}	
9.52×10^{-6}	4.24×10^{-5}	1.45×10^{-4}	
1.43×10^{-5}	4.24×10^{-5}	1.56×10^{-4}	
1.90×10^{-5}	4.24×10^{-5}	1.76×10^{-4}	
3.32×10^{-5}	4.24×10^{-5}	2.56×10^{-4}	
4.76×10^{-5}	4.24×10^{-5}	3.30×10^{-4}	6.93
4.76×10^{-4}	4.24×10^{-5}	2.90×10^{-3}	6.09
4.76×10^{-3}	4.24×10^{-4}	2.90×10^{-2}	6.09

[a] Isopropyl alcohol = 1.01 *M*.

Oxalic acid starts to influence the rate of the oxidation of isopropyl alcohol at the concentration of less than 10^{-4} *M* or under conditions when the isopropyl alcohol to oxalic acid concentration is more than 10,000 to 1. The reaction then becomes first order in oxalic acid, up to the highest concentrations which we were able to measure. At the concentration of 4.76×10^{-3} *M* of oxalic acid, the rate of oxidation was increased by a factor of almost 250 and under conditions in which the oxidation of oxalic acid is still far too slow to influence the results.

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tone 2,4-dinitrophenylhydrazone given in the original paper (λ_{max} 476 nm (ϵ 2.66×10^4)) are in error. Under the conditions specified by the authors, we observed a spectrum with two maxima (λ 430 nm (ϵ 1.00×10^4) and 532 (6.73×10^3)).

(13) W. W. Umbreit, "Manometric Techniques," 4th ed, Burgess Publishing Co., Minneapolis, Minn., 1964.

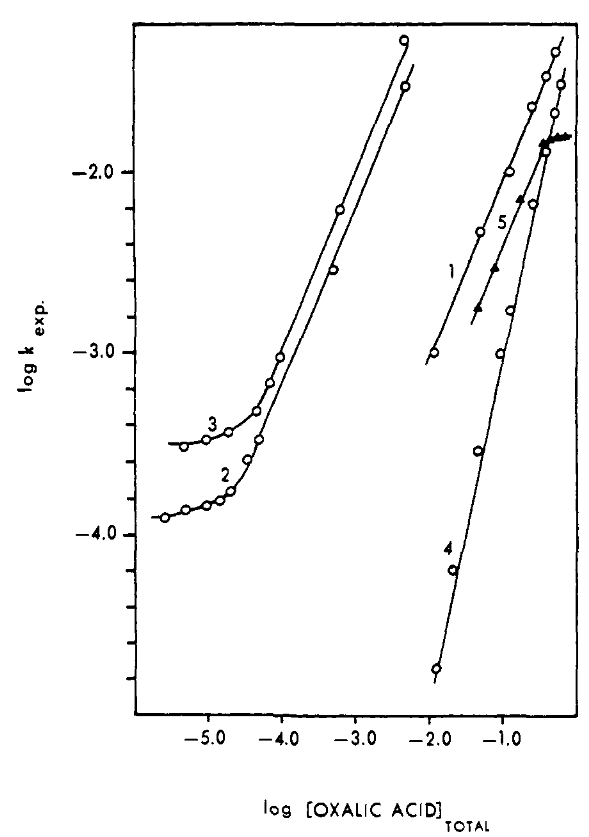

Figure 2. Effect of oxalic acid on the rate of oxidation of isopropyl alcohol: (1-4) 25°, $HClO_4$ = 0.097 *M*; (5) 5°, $HClO_4$ = 0.24 *M*. Isopropyl alcohol concentration: (1) 1.56×10^{-2} *M*; (2) 1.01 *M*; (3) 2.34 *M*; (4) 0.0; (5) 1.56×10^{-2} *M*.

Figure 2 shows the effect of oxalic acid concentration for three different isopropyl alcohol concentrations. We were able to cover an overall range of oxalic acid concentrations of almost five orders of magnitude and show that the oxidation is first order in oxalic acid over a range from approximately 10^{-4} *M* to at least 0.3 *M* in oxalic acid. The graph also contains data for the oxidation of oxalic acid alone (curve 4) which is second order in oxalic acid.

Curve 5 of Figure 2 is the result of measurements of the oxidation rates carried out at high oxalic acid concentrations. Because of the high rates involved, the measurements were carried out at a low temperature (5°). It can be seen that the rate increases initially with increasing oxalic acid concentration, but later levels off, and the reaction becomes essentially zero order in oxalic acid. This behavior is characteristic of the formation of an intermediate complex. We assume that chromic acid under the reaction conditions forms a complex with oxalic acid and that at high concentrations of oxalic acid virtually all chromium(VI) is converted to the complex. This assumption is expressed in eq 1 and 2 where C_1 is a 1:1 complex of oxalic acid and chromic acid. The concentration is given by 3 where $[Cr(VI)]_{total}$

$$(CO_2H)_2 + Cr(VI) \overset{K_1}{\rightleftarrows} C_1 \tag{1}$$

$$C_1 + ROH \xrightarrow{k} \text{products} \tag{2}$$

$$[C_1] = \frac{K_1[(CO_2H)_2][Cr(VI)]_{total}}{1 + K_1[(CO_2H)_2]} \tag{3}$$

$= [Cr(VI)] + [C_1]$. From the rate law (eq 4) corresponding to eq 2, eq 5 can be derived.

$$v = k[C_1][ROH] = k_{exptl}[Cr(VI)]_{total} \tag{4}$$

$$[ROH]/k_{exptl} = 1/k + 1/kK_1[(CO_2H)_2] \tag{5}$$

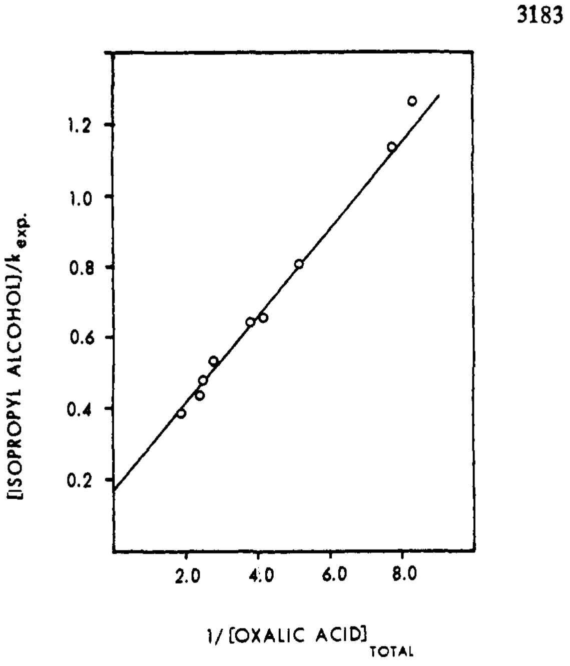

Figure 3. Determination of the equilibrium constant for the chromic acid–oxalic acid complex from rate data at 25°, $HClO_4$ = 0.097 *M*.

Expression 5 was tested quantitatively in Figure 3 by plotting $[ROH]/k_{exptl}$ *vs.* the reciprocal value of the oxalic acid concentration. A very good straight line plot was obtained, which supports the assumption of the complex formation and permits the calculation of the equilibrium constant K_1. The value of K_1 under these conditions (in 0.097 *M* perchloric acid) is 1.36, which is in excellent agreement with the value determined independently from the investigation of the kinetics of oxalic acid oxidations.[14]

The data so far obtained can be summarized by the following rate law

$$\text{rate} = k_1'[ROH][Cr(VI)]_{total} + k_2'[ROH][OxH_2]_{total}[Cr(VI)] + k_3'[OxH_2]_{total}^2[Cr(VI)] \tag{6}$$

which is approximately valid at constant mineral acid concentration and as long as only a small fraction of chromium(VI) is present in the form of the chromic–oxalic acid complex. At very high oxalic acid concentrations the corrections introduced in the preceding section would have to be incorporated.

In 0.097 *M* perchloric acid, which was used for most of our measurements, the values for these rate constants are $k_1' = 1.29 \times 10^{-4}$, $k_2' = 5.45$, and $k_3' = 2.42 \times 10^{-1}$.

It is thus obvious that over a wide range condition, the kinetic term containing both isopropyl alcohol and oxalic acid is by far greater than those relating to the oxidation of isopropyl alcohol or of oxalic acid alone. It was therefore possible to select conditions under which the cooxidation of isopropyl alcohol and oxalic

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(14) F. Hasan and J. Roček, to be submitted for publication.

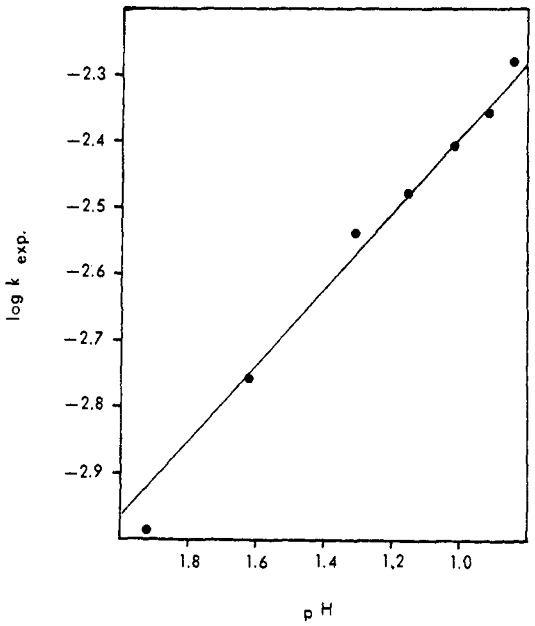

Figure 4. Effect of perchloric acid on the rate of cooxidation of isopropyl alcohol-oxalic acid system at 25°; isopropyl alcohol = 7.8 × 10^{-2} *M*; oxalic acid = 9.12 × 10^{-3} *M*.

acid can be studied without appreciable interference from the single substrate oxidations. Such conditions were used to study both reaction products and the acidity dependence of the reaction.

Under conditions under which only the kinetic term including both isopropyl alcohol and oxalic acid is significant, the reaction rate increases with acidity with an apparent 0.5 order in hydrogen ions (Figure 4).

As oxalic acid is a moderately strong acid, it is dissociated in solution to an appreciable amount and the concentration of the undissociated acid (eq 7, K_a =

$$[(CO_2H)_2] = [(CO_2H)_2]_{total}[H^+]/(K_a + [H^+]) \quad (7)$$

0.059[10]) will, therefore, increase with increasing concentration of hydrogen ions in the solution. Inserting this expression into the rate law, one obtains expression 8, which has been tested experimentally by plotting

$$k_{exptl} = k[ROH][OxH_2]_{total}[H^+]/(K_a + [H^+]) \quad (8)$$

log k_{exptl} *vs.* log $[H^+]/(K_a + [H^+])$ for a series of measurements where only the concentration of perchloric acid was varied while all other conditions were kept constant. A good straight line was obtained (Figure 5), indicating that only undissociated oxalic acid is kinetically active. This result parallels the findings of Bakore and Jain[15] for the chromic acid oxidation of oxalic acid.

Equation 9 gives the complete rate law of the reaction including the acidity dependence for all terms,[3c,15]

$$\begin{aligned}\text{rate} = {} & k_1[HCrO_4^-][ROH][H^+]^2 + \\ & k_2[HCrO_4^-][ROH][(COOH)_2]_{total}\frac{[H^+]}{K_a + [H^+]} + \\ & k_3[HCrO_4^-][(COOH)_2]_{total}^2\frac{[H^+]}{K_a + [H^+]} \quad (9) \\ = {} & k_1[HCrO_4^-][ROH][H^+]^2 + \\ & k_2[HCrO_4^-][ROH][(COOH)_2] + \\ & k_3[HCrO_4^-][(COOH)_2]^2\end{aligned}$$

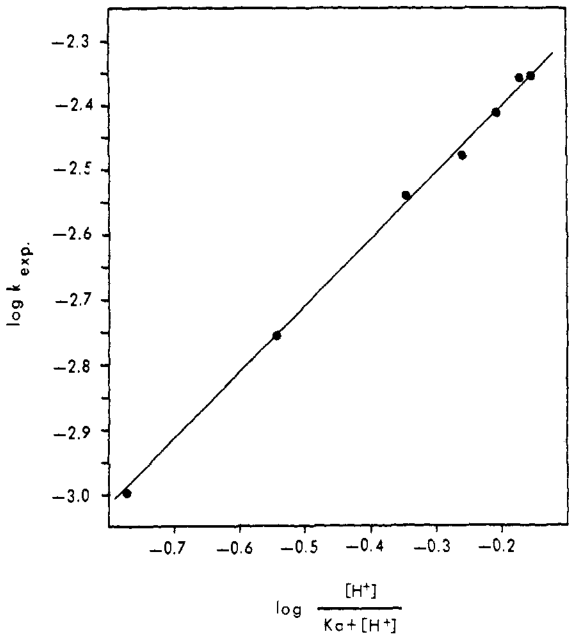

Figure 5. Acidity dependence of isopropyl alcohol-oxalic acid cooxidation: test of eq 8. Conditions: 25°; isopropyl alcohol = 7.8 × 10^{-2} *M*; oxalic acid = 9.12 × 10^{-3} *M*; perchloric acid = 0.012-0.196 *M*.

which is valid for the whole range investigated except for very high oxalic acid concentrations, where corrections taking into account the complexing of chromium(VI) have to be introduced. The values of the rate constants are $k_1 = 1.26 \times 10^{-2}$, $k_2 = 8.78$, and $k_3 = 2.42 \times 10^{-1}$. A comparison of experimental and calculated first-order rate constants over a large range of conditions is given in Table III.

Reaction Products. Reaction products were studied under conditions in which the kinetic term containing both oxalic acid and isopropyl alcohol vastly predominates over the direct oxidation of each of the components. Table IV summarizes the yields of acetone and carbon dioxide.

In all these experiments both oxalic acid and isopropyl alcohol were in large excess (10- to 100-fold) compared to chromic acid. The results are averages of several experiments; the reproducibility of the values was between 3 and 4%.

From these results it is obvious that the reaction does not represent a simple catalysis, but that both components are undergoing oxidation. The reaction is thus a *cooxidation* of two substrates, oxalic acid and isopropyl alcohol, by chromic acid.

In the absence of acrylonitrile, the yields of acetone and carbon dioxide obtained were not compatible with a simple mechanism. As chromium(VI) undergoes a three-electron reduction to chromium(III), one would expect that acetone and carbon dioxide would be formed in a 1:1 ratio (corresponding to a two-electron oxidation of isopropyl alcohol and a one-electron oxidation of oxalic acid to one molecule of CO_2 and a free radical $\cdot CO_2^-$ or $\cdot CO_2H$) or in a 1:4 ratio (corresponding to a one-electron oxidation of isopropyl alcohol to a free radical and a two-electron oxidation of oxalic acid to two molecules of CO_2).[16]

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[15] J. V. Bakore and C. L. Jain, *J. Inorg. Nucl. Chem.*, 31, 805 (1969).

[16] These ratios would be correct only if the free radicals did not undergo further oxidation, but reacted by bimolecular reaction, *i.e.*,

Table III. Observed and Calculated (Eq 9) First-Order Rate Constants (Sec^{-1}) for the Chromic Acid Oxidation of the Isopropyl Alcohol–Oxalic Acid System at 25°

		[H$^+$], *M*											
		0.012		0.072		0.097		0.122		0.146		0.486	
Oxalic acid, *M*	Isopropyl alcohol, *M*	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
0.282	0.00016					0.0078	0.0080						
0.282	0.001					0.0091	0.0083						
0.131	0.00016					0.0017	0.0018						
0.131	0.001					0.0023	0.0021						
0.0456	0.039	0.0046	0.0040	0.0096	0.0086	0.0097	0.0101	0.0113	0.0106	0.0120	0.0116	0.0178	0.0203
0.0228	0.0312			0.0040	0.0035	0.0384	0.0390	0.0055	0.0046	0.0060	0.0048	0.0110	0.0090
0.0182	0.156	0.0053	0.0055	0.0130	0.0138	0.0158	0.0155	0.0173	0.0168	0.0186	0.0178	0.0340	0.0351
0.0091	0.156	0.0023	0.0026	0.0070	0.0068	0.0079	0.0077	0.0096	0.0090	0.0106	0.0096		
0.0091	0.078	0.0010	0.0013	0.0033	0.0033	0.0042	0.0039	0.0044	0.0045	0.0053	0.0048	0.0110	0.0091
0.0023	1.56			0.0155	0.0171	0.0192	0.0195	0.0220	0.0223	0.0231	0.0245	0.0428	0.0478
0.000048	1.56					0.00060	0.00050						
0.000019	1.01					0.00023	0.00017						

Table IV. Chromic Acid Oxidation of Oxalic Acid–Isopropyl Alcohol System in 0.097 *M* Perchloric Acid

Isopropyl alcohol, *M*	Oxalic acid, *M*	Acrylonitrile, *M*	Mol of acetone/mol of Cr(VI)	Mol of CO_2/mol of Cr(VI)
0.312	0.088		0.80	1.56
0.312	0.088		0.74	1.60
0.312	0.088	0.017	0.99	1.02
0.155	0.018		0.86	1.32
0.155	0.018	0.017	1.01	0.94
0.155	0.018	0.170	0.98	0.99

Table V. Isotope Effect in the Oxidation of 2-Deuterio-2-propanol

Isopropyl alcohol, *M*	Oxalic acid, *M*	k_H/k_D
1.56×10^{-1}	1.82×10^{-1}	5.95
1.56×10^{-1}	9.12×10^{-2}	5.99
7.80×10^{-2}	9.12×10^{-2}	5.81

In the absence of a free-radical scavenger, the yield ratio of CO_2 to acetone is between 1.5 and 2.2, thus clearly higher than predicted for the two-electron oxidation of the alcohol, but considerably lower than would correspond to a two-electron oxidation of oxalic acid. No clear decision could thus be drawn from these results.

However, the problem can be answered very easily from experiments in the presence of acrylonitrile acting as a free-radical scavenger. First, the yield of acetone is increased rather than decreased. It thus becomes clear that acetone must be formed directly and not *via* a free radical. Second, the two products are formed in an almost exactly 1:1 ratio. It thus becomes clear that the reaction involves a two-electron oxidation of the alcohol and a one-electron oxidation of oxalic acid. In the presence of acrylonitrile, a bimolecular, nonoxidative destruction of the free radicals formed from acrylonitrile and from the primary radical generated in the oxidation reaction must take place.

Isotope Effect. It is, of course, entirely conceivable that the cooxidation of oxalic acid and isopropyl alcohol would proceed from the point of view of the alcohol substrate by an entirely different mechanism than in the well-investigated chromium(VI) oxidation of alcohols. We therefore determined the isotope effect and found that, under conditions under which the cooxidation is the only kinetically significant term, the magnitude of the isotope effect (Table V) is very close to that observed in simple chromium(VI) oxidations. The average value of 5.92 compares well with the value 6 obtained by Westheimer.[18]

It can thus be concluded that the breaking of the C–H bond in the alcohol is still part of the rate-limiting step of the oxidation.

The Reactivity of Isopropyl Ether. The chromium(VI) oxidation of alcohols involves the formation of an ester intermediate. Therefore, the presence of a free hydroxyl group is essential and ethers show a considerably lower reactivity than alcohols.[9] In order to test whether the presence of a free hydroxyl group in the molecule is an equally important requirement in the cooxidation reaction, we measured the oxidation of isopropyl ether under conditions used in the investigation of the cooxidation of isopropyl alcohol (*cf.* Table I and Figure 1, curve 1). The results show that up to the limit of its solubility (4.9×10^{-2} *M*) isopropyl ether has no effect on the rate of oxidation of oxalic acid.

The presence of the free hydroxyl group is thus essential in the chromic acid cooxidation of isopropyl alcohol, and we conclude that an ester type intermediate is involved.

Free-Radical Formation. The observation that acrylonitrile has a pronounced effect on the reaction products (Table IV) makes it obvious that free radicals capable of reacting with this monomer are formed in appreciable amounts. The reaction of the radicals with acrylonitrile leads only to low molecular weight products as polymer formation cannot be observed visually. If the reaction is, however, carried out in the presence of acrylamide, polymerization can be observed.

Reaction in the Presence of Aluminum Salt. Chatterjee and coworkers[19] recently reported that the

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if $\cdot CO_2H$ would dimerize to oxalic acid and if the $(CH_3)_2\dot{C}OH$ radicals would disproportionate to acetone and isopropyl alcohol. The assumption that a bimolecular reaction between two radicals takes place is quite reasonable in light of our recent work.[17] If further oxidation of the free radicals is taken into account, the results become much more complex and any prediction would have to involve an assumption whether the chromium(V) species formed from chromium(VI) and the free radical would be more likely to react with oxalic acid or with the alcohol.

(17) M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5455 (1971).

(18) F. H. Westheimer and N. Nicolaides, *ibid.*, 71, 25 (1949).

(19) S. Chandra, S. N. Shukla, and A. C. Chatterjee, *Z. Phys. Chem. (Leipzig)*, 237, 137 (1968).

chromic acid oxidation of oxalic acid can be effectively prevented by the presence of aluminum nitrate. This effect is obviously due to the ability to complex rather firmly with oxalic acid and thus prevent the formation of the oxalic acid–chromic acid complex which is an intermediate in the oxidation reaction.

As we believed that the formation of an oxalic acid–chromic acid complex plays a crucial role in the cooxidation of isopropyl alcohol, we were interested in testing whether the presence of aluminum salt would prevent the cooxidation reaction from occurring. The results are shown in Table VI. The result (Table VI), that the rate-accelerating effect of oxalic acid is almost completely canceled by the presence of aluminum nitrate, is in agreement with the assumption that the chromic acid–oxalic acid complex is an intermediate in the cooxidation reaction.

Table VI. Effect of Aluminum Nitrate on the Cooxidation Reaction at 25°[a]

Oxalic acid, 10^3 *M*	Aluminum nitrate, *M*	10^3k_{exptl}, sec^{-1}
0.0		2.8
2.66		270.0
2.66	0.178	3.2

[a] Perchloric acid = 0.097 *M*, isopropyl alcohol = 2.34 *M*.

Mechanism. The mechanism of the cooxidation must account for the following facts.

(a) The transition state contains one molecule of isopropyl alcohol, one molecule of oxalic acid, and one acid chromate ion.

(b) Both acetone and carbon dioxide are formed.

(c) Polymer formation is observed when the cooxidation reaction is carried out in the presence of acrylamide.

(d) In the presence of a free-radical scavenger, acrylonitrile, the yield of acetone increases to exactly one molecule acetone per each molecule of chromium(VI) reduced to chromium(III).

(e) The yield of carbon dioxide in the presence of acrylonitrile is decreased to exactly one molecule of CO_2 formed per each molecule of chromium(VI) reduced to chromium(III).

(f) The 1:1 ratio of acetone to CO_2 obtained in the presence of acrylonitrile does not depend on the isopropyl alcohol:oxalic acid concentration ratio.

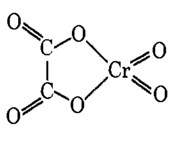
(g) A sizable deuterium isotope effect is observed, indicating that the carbon–hydrogen bond of the alcohol is broken in the rate-limiting step.

(h) Isopropyl ether is unreactive, indicating that the free hydroxyl group of the alcohol plays an important part in the reaction mechanism.

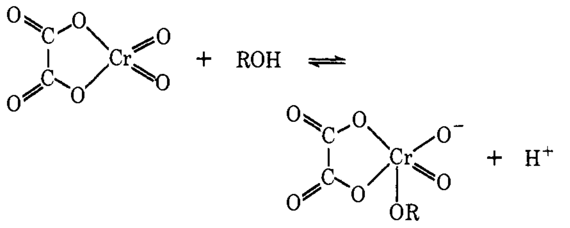
(i) The reaction is fast compared with both the oxidation of isopropyl alcohol and of oxalic acid.

As we were able to demonstrate[14] that chromic acid and oxalic acid form a neutral 1:1 complex, probably of a cyclic nature (eq 10), the reaction intermediate decomposing in the rate-limiting step is either formed with a loss of a proton or loses a proton in the rate-limiting step. The former alternative can be represented, for example, by eq 11. The intermediate undergoing decomposition could have retained the cyclic structure (as shown above) of the chromium–oxalic acid complex, or could be acyclic.

$(CO_2H)_2 + HCrO_4^- + H^+ \rightleftharpoons$



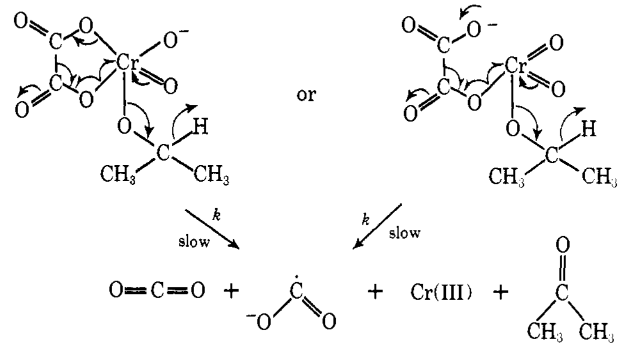
(10)



(11)

To account for the observed ratio of reaction products, we assume that the intermediate will decompose to yield one molecule of acetone, one molecule of carbon dioxide, one $\cdot CO_2^-$ or $\cdot CO_2H$ radical (Scheme I), and a chromium(III) species. The free radical can then undergo further oxidation with either free or complexed chromium(VI), producing carbon dioxide and chromium(V). Chromium(V) can then react with the free oxalic acid or with the free alcohol, or could disproportionate into a chromium(VI) and a chromium(IV) species.[20] Under these conditions, the exact stoichiometry is difficult to predict. Further, the radical can dimerize and regenerate oxalic acid. The dimerization reaction is obviously not complete. If it were, an exact 1:1 ratio of acetone and carbon dioxide would be formed, which is not the case. The yield of carbon dioxide is considerably higher, indicating thus that a substantial part of the radical undergoes further oxidation to yield additional carbon dioxide. However, if the reaction is carried out in the presence of a free-radical scavenger, acrylonitrile, then all the free-radical products seem to react with the scavenger to form a relatively unreactive radical which is eventually destroyed by a bimolecular free-radical dimerization or disproportionation. Under these conditions, the theoretical yield of one molecule of acetone and one molecule of carbon dioxide is produced for each molecule of chromium (VI).

Scheme I



The most interesting question is the reason for the unusually high reactivity of the complex composed of a molecule of chromic acid and oxalic acid, and a molecule of the substrate. This high reactivity suggests that a complex containing both components offers the reac-

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(20) (a) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2986 (1968); (b) P. M. Nave and W. S. Trahanovsky, *ibid.*, **92**, 1120 (1970).

tion a more favorable pathway than the oxidation of a single substrate.

The oxidation of a single molecule of a substrate, *e.g.*, isopropyl alcohol, leads to an unstable and very reactive chromium(IV) species.[21] One can certainly expect that the reaction would be greatly facilitated if chromium(VI) could be reduced directly to chromium(III), thus avoiding the formation of the energetically unfavorable chromium(IV). The presence of the molecule of oxalic acid within the complex offers such a possibility. We thus propose that the unusual reactivity is due to the fact that the reaction represents a direct three-electron reduction of chromium(VI) to chromium(III) coupled with the formation of a very stable molecule of carbon dioxide and of a relatively stable free radical, $\cdot CO_2H^-$ or $\cdot CO_2H$.

This mechanism is strongly supported by the observation that the two products, acetone and carbon dioxide, are formed in exactly equimolar ratios in the presence of a free-radical trap. The ratio does not depend on the relative concentration of isopropyl alcohol and oxalic acid in the solution. Thus no intermediate chromium species is produced in the reaction which would have a long enough lifetime to react with a molecule in its surrounding. Instead, one would have to assume that it reacts entirely with the oxalic acid molecule present in the complex. Thus, one would have to postulate the formation of a very short-lived chromium(IV)-oxalic acid intermediate for which no evidence of kinetic independence could be obtained. The proposed mechanism, in which such an intermediate is never formed but chromium(VI) is reduced directly to chromium(III) in the rate-limiting step, not only correctly predicts the product ratio and its independence of the composition of the solution, but also offers a very attractive interpretation of the unusual two-substrate activated complex and of the high rate of the cooxidation reaction. To the best of our knowledge, the cooxidation of oxalic acid and isopropyl alcohol by chromic acid presents the first case where there is valid ground to believe that a one-step three-electron oxidation is taking place.

Some data can be quoted to support the assumption of the stability of the $\cdot CO_2^-$ or $\cdot CO_2H$ radicals. The C–H bond dissociation energy for formic acid is 90 kcal/mol, which is 14 kcal/mol lower than that of the C–H bond in methane and 1 kcal/mol lower than for the tertiary C–H bond in isobutane. This indicates that the $\cdot CO_2H$ radical should be more stable than the *tert*-butyl radical.[22] A similar value can be derived from the bond dissociation energies for the C–C bonds of ethylbenzene and phenylacetic acid. The energies for breaking of the bonds which would lead to a benzyl radical as one fragment and to a methyl or carboxyl radical as the other fragment are 70 and 55 kcal/mol, respectively, indicating that the $\cdot CO_2H$ radical is 15 kcal/mol more stable than the methyl radical.[23] The $\cdot CO_2^-$ radical ion is stable enough to permit its formation and direct observation in the gas phase,[24] as well as the use of CO_2 as scavenger for solvated electrons in radiation chemistry.[25]

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[21] M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5462 (1971).

[22] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[23] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

[24] J. F. Paulson, *J. Chem. Phys.*, **52**, 963 (1970).

[25] M. Shirom, R. F. C. Claridge, and J. E. Willard, *ibid.*, **47**, 286 (1967).

Mechanism for the Reaction of Lead Tetraacetate and Hydrogen Fluoride with Olefins

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Abstract: A mechanism for the reaction of the lead tetraacetate–hydrogen fluoride reagent with olefins has been proposed. From a mechanistic analysis of the possible paths leading to the formation of the products from the reactions of 1,1-diphenylethylene and norbornene with this reagent, it is proposed that a transient intermediate lead–ligand addition product is first formed in these reactions. Breaking of the lead–carbon bond yields cationic intermediates which result in the observed products. The nature of the rearrangement products in both reactions necessitates the formation of carbonium ion species, and the stereochemistry of the products formed in the norbornene reaction is best explained by a cis-exo-2,3-metal–ligand addition to this olefin as the first step in the reaction sequence.

The fluorination of an olefin by lead tetraacetate and hydrogen fluoride was first reported by Dimroth and Bockemüller.[1] They observed that when 1,1-diphenylethylene was treated with a 4:1 mixture of anhydrous hydrogen fluoride and lead tetraacetate a difluorinated hydrocarbon was obtained in 28% yield. Accompanying the fluorinated material, deoxybenzoin was obtained in a 15% yield. These authors proposed that lead tetrafluoride was the active halogenating reagent and assigned the structure 1,2-difluoro-1,1-di-

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