to reaction with olefin are in agreement with published spectra.[21] Photolysis of Fe(CO)$_5$–olefin mixtures produces two new bands, a pair of absorptions with maxima at 1980 and 1983 cm^{-1}, and a sharp band at 2083 cm^{-1}. Saturating Fe(CO)$_5$ solutions with carbon monoxide prior to photolysis does not produce any changes in these spectra.

The metal carbonyl region of the infrared spectra recorded during the photolysis of Fe(CO)$_5$–benzonorbornadiene solutions in n-octane are shown in Figure 2. Figures 2B–E show the changes occurring in the iron carbonyl region of the spectrum during photolysis under one atmosphere of CO. Two distinct sharp bands appear at 2065 and 2100 cm^{-1} while a band at 1972 cm^{-1} appears and masks the original 1970-cm^{-1} band. The intensity of these bands increases with time until 45 min when a steady-state condition is attained. No further increase in intensity is noted, although ketonic product continues to form. Once steady state was obtained, the solution was purged with nitrogen in the dark. As shown (Figures 2F–G), the bands at 1972 and 2065 cm^{-1} decrease and after 60 min of nitrogen purging the 2100-cm^{-1} band reaches a maximum intensity.

Similar results are found for compound 10 as the reactive olefin (Figure 3). However, in this case ketone formation is initiated after a longer photolysis time than with benzonorbornadiene as the reactive olefin. This is in accord with the relative reactivities found for these two olefins in competition experiments. One observation of particular importance is that the band at 2100 cm^{-1} does not appear until the onset of ketone formation; the band at 2065 cm^{-1} begins to decrease at this time (Figure 3).

The spectra recorded during photolysis of Fe(CO)$_5$ in the presence of monoene 14 are shown in Figure 4. Photolysis of the solution for 30 min produces a spectrum identical with that in Figure 3B. Purging the solution with nitrogen in the dark causes a steady de-

crease in the 2065-cm^{-1} band; however, no band at 2100 cm^{-1} appears. In addition, the solution changes from homogeneous yellow to green during this time, indicating the presence of Fe$_3$(CO)$_{12}$. Continued purging with nitrogen steadily decreases the bands at 2065, 1965, and 1987 cm^{-1}; the band corresponding to Fe$_3$(CO)$_{12}$ (2055 cm^{-1}) increases.

These observations are consistent with the mechanism proposed as steps 1–9. The infrared bands appearing during photolysis in the presence of a carbon monoxide atmosphere (2065, 1987, and 1965 cm^{-1}) correspond to the monoolefintetracarbonyliron(0) complex (3). The presence of additional bands may be masked by the absorption bands of Fe(CO)$_5$ (ca. 2030 and 2000 cm^{-1}). The carbonyl stretching frequencies reported[16] for C$_2$H$_4$Fe(CO)$_4$ are 2088, 2007, 2013, and 1986 cm^{-1}. In the absence of a reactive olefin, intermediate 4 proceeds to Fe$_3$(CO)$_{12}$. The band which appears at 2100 cm^{-1} may correspond to the bisolefin complex 5, the metallocycle 7, the acyl complex 8, or the final iron carbonyl following elimination. Careful inspection of the infrared spectra indicate the appearance of other absorpton bands in addition to the 2100-cm^{-1} band, viz., 2018 and 2040 cm^{-1}.

Further similar experiments have shown that cyclohexene behaves as monoene 14; however, the absorption intensity associated with the cyclohexenetetracarbonyliron(0) complex was much lower after equal photolysis times. These results are also consistent with those found in the competition experiments. Photolysis of Fe(CO)$_5$ in the presence of monoene 14 in a carbon monoxide atmosphere, followed by addition of equimolar benzonorbornadiene and purging with nitrogen in the dark, yielded ketone 11a. Infrared spectra recorded during this experiment showed the same changes as those found during photolysis of Fe(CO)$_5$ in the presence of benzonorbornadiene alone.

(21) C. C. Barraclough. J. Lewis, and R. S Nyholm. *J. Chem. Soc.*, 2582 (1961).

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

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Abstract: Experimental evidence is presented for the oxidation of isopropyl alcohol by chromium(IV) as being an essential step in the chromium(VI) oxidation of this substrate. Equilibrium constants for the formation of mono- and diesters, as well as rate constants for the decomposition of the esters and for the oxidation of isopropyl alcohol by chromium(V) in 97% acetic acid, have been reevaluated and are summarized.

The role of chromium(IV) in chromic acid oxidation has been the subject of a number of investigations. Roček and Radkowsky[2] found that chromium(IV) generated by the reaction of vanadium(IV) with chromium(VI) causes oxidative cleavage of cyclobutanol. Similarly, Rahman and Roček[2b] showed that

(2) (a) J. Roček and A. E. Radkowsky. *J. Amer. Chem. Soc.*, 90, 2986 (1968); (b) M. Rahman and J. Roček, *ibid.*, 93, 5455, 5462 (1971).
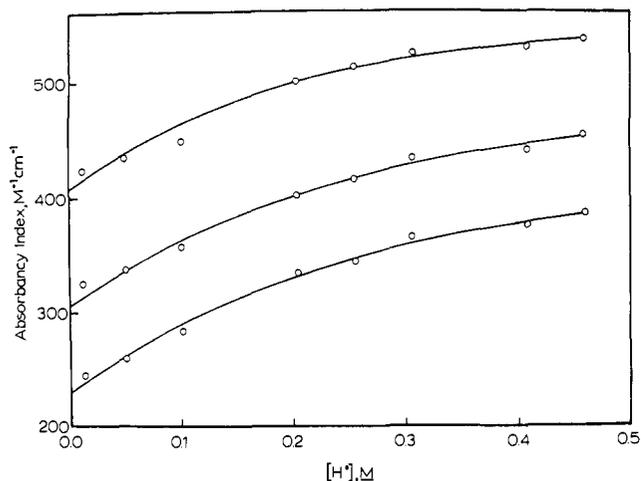
Figure 1. Effect of hydrogen ion concentration on the absorbancy indices for chromium(VI) in 97% acetic acid. The data are for 380 (upper), 385 (center), and 390 mμ (lower) and the lines represent the calculated values. The conditions were: [Cr(VI)] = 7.84 × 10⁻⁴ M, μ = 0.50 M(NaClO₄), T = 15.0°.

Figure 2. Effect of isopropyl alcohol concentration on the initial equilibrium absorbancy index for chromium(VI) in 97% acetic acid. The line represents the calculated values. The conditions were: [Cr(VI)] = 1.0–1.1 × 10⁻³ M, [H⁺] = 0.0125 M, μ = 0.184 M(NaClO₄), T = 15.0°, 385 mμ.
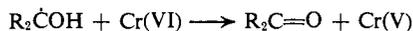
chromium(IV) generated in this fashion reacted with primary and secondary alcohols to give free radicals which may be captured by acrylamide. Nave and Trahanovsky[3] found the oxidative cleavage of alcohols which occurs during chromium(VI) oxidation to have characteristics similar to ceric ion oxidation of these alcohols. These data lead to the conclusion that chromium(IV) is an active oxidant in chromic acid oxidations.

We have reported another approach to determining the relative roles of chromium(VI), (V), and (IV) in the oxidation of isopropyl alcohol.[4] We now wish to present a full account of this investigation. The basis of the experiment is easily seen in comparing two possible schemes (Schemes I and II) for the chromium(VI)

Scheme I

$$R_2CHOH + Cr(VI) \longrightarrow R_2C{=}O + Cr(IV)$$

$$Cr(IV) + Cr(VI) \longrightarrow 2Cr(V)$$

$$2(R_2CHOH + Cr(V) \longrightarrow R_2C{=}O + Cr(III))$$

Scheme II

$$R_2CHOH + Cr(VI) \longrightarrow R_2C{=}O + Cr(IV)$$

$$R_2CHOH + Cr(IV) \longrightarrow R_2\dot{C}OH + Cr(III)$$

$$R_2\dot{C}OH + Cr(VI) \longrightarrow R_2C{=}O + Cr(V)$$

$$R_2CHOH + Cr(V) \longrightarrow R_2C{=}O + Cr(III)$$

oxidation of isopropyl alcohol.[5] If we consider only the reactions up through the formation of chromium(V), the first scheme gives an acetone:Cr(V) ratio of 1:2 whereas the second scheme gives the products in the ratio of 2:1. Thus, an examination of the stoichiometry of the reaction under conditions where the oxidation by chromium(V) is slower than that by chromium(VI) should reveal which of the schemes is correct.

We have previously shown that the above reaction conditions could be achieved in 97% acetic acid as the

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

(4) K. B. Wiberg and S. K. Mukherjee, *J. Amer. Chem. Soc.*, **93**, 2543 (1971).

(5) *Cf.* K. B. Wiberg in "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965, Chapter 11, for a review of the possible reaction schemes for chromic acid oxidation.
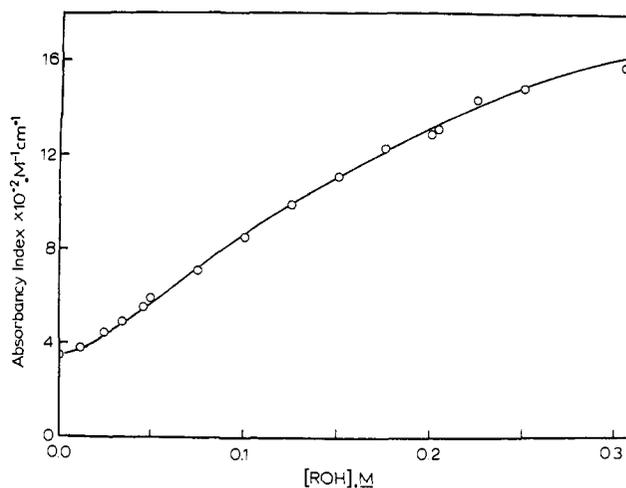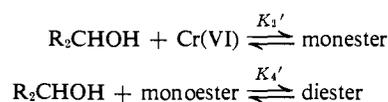
solvent.[4,6] A precise knowledge of the rate constants for the oxidation by chromium(VI) and chromium(V) is needed for a detailed analysis of the stoichiometry of the reaction as a function of time. Therefore, we also have reevaluated these and other related constants dealing with the reaction. This appeared desirable for two reasons. First, the rates of reaction are very sensitive to the solvent composition and we wished to be sure that the stoichiometry experiments were carried out in the same solvent mixture as used for the kinetics. Second, our methods of collecting and analyzing the experimental data have improved considerably making it possible to obtain more precise rate constants than previously possible.

Chromic Acid Ionization Constant. The ionization constant for acetochromic acid was determined using the change in absorbance with acid concentration of three wavelengths (380, 385, and 390 mμ). The ionization constant was found to be 0.24 ± 0.02. A comparison of observed and calculated absorbancy indices is shown in Figure 1.

Esterification Equilibria. The initial rapid changes in absorbance on mixing chromic acid and isopropyl alcohol solutions are due to the formation of the mono- and diesters. The equilibrium absorbancy indices (the values reached before the onset of the oxidation reaction) are shown in Figure 2. The values could be fit to the scheme

$$R_2CHOH + Cr(VI) \underset{}{\overset{K_2'}{\rightleftharpoons}} \text{monester}$$

$$R_2CHOH + \text{monoester} \underset{}{\overset{K_4'}{\rightleftharpoons}} \text{diester}$$

using the constants K_2' = 14.5 M^{-1}, K_4' = 3.63 M^{-1}, $\epsilon(Cr(VI))$ = 347 M^{-1} cm^{-1}, $\epsilon(\text{monoester})$ = 467 M^{-1} cm^{-1}, and $\epsilon(\text{diester})$ = 2900 M^{-1} cm^{-1}. The curve in Figure 2 corresponds to these constants.

A more complete scheme would be

$$AcOCrO_3H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AcOCrO_3^- + H^+ \quad K_1 = k_1/k_{-1}$$

(6) K. B. Wiberg and H. Schafer, *J. Amer. Chem. Soc.*, **91**, 927, 933 (1969).
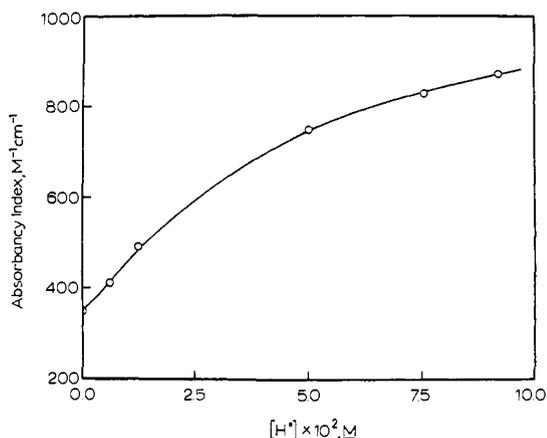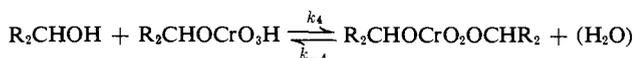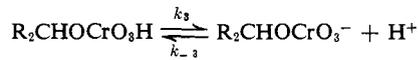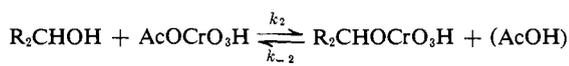
Figure 3. Effect of acid concentration on the initial equilibrium absorbancy index for chromium(VI) in 97% acetic acid containing 0.0351 M isopropyl alcohol. The line represents the calculated values. The conditions were: $[Cr(VI)] = 1.00–1.06 \times 10^{-3}\ M$, $T = 15.0°$, 385 mμ.

$$R_2CHOH + AcOCrO_3H \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2CHOCrO_3H + (AcOH)$$

$$R_2CHOCrO_3H \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R_2CHOCrO_3^- + H^+$$

$$R_2CHOH + R_2CHOCrO_3H \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} R_2CHOCrO_2OCHR_2 + (H_2O)$$

The value of K_1 was determined above. In order to separate K_2' into K_2 and K_3, the effect of acid concentration on the equilibrium absorbancy indices was examined using $[R_2CHOH] = 0.0351\ M$. An analysis of these data (Figure 3) gave $K_3 = 0.019$. The difference between K_1 and K_3 seems to be a reasonable effect of replacing an acetoxy group attached to chromium(VI) by an isopropoxy group. The rates of formation of the mono- and diesters also were fit by the procedure described previously,[6] and a comparison of the calculated and observed rate constants is shown in Figure 4. The final set of constants which describe the preoxidation equilibria follow (A = acetochromic acid, M = monoester, and D = diester). The absorbancy indices are for 385 mμ.

$K_1 = 0.24 \pm 0.02\ M$
$K_2 = 115.4\ M^{-1}\quad k_2 = 13,200\ M^{-1}\quad k_{-2} = 114\ sec^{-1}$
$\phantom{K_2 = 115.4\ M^{-1}\quad k_2 = 13,200\ }sec^{-1}$
$K_3 = 0.019\ M$
$K_4 = 9.21\ M^{-1}\quad k_4 = 710\ M^{-1}\quad k_{-4} = 77\ sec^{-1}$
$\phantom{K_4 = 9.21\ M^{-1}\quad k_4 = 710\ }sec^{-1}$

ϵ_A 529 $M^{-1}\ cm^{-1}$ ϵ_A - 306 $M^{-1}\ cm^{-1}$
ϵ_M 785 $M^{-1}\ cm^{-1}$ ϵ_M - 311 $M^{-1}\ cm^{-1}$
ϵ_D 2900 $M^{-1}\ cm^{-1}$

The concentrations of each species as a function of alcohol concentration are shown in Figure 5.

Oxidation Steps. After the initial very rapid change in absorbance on mixing, there follows two successive oxidation steps in which chromium(VI) is first converted to chromium(V), and then chromium(V) is converted to chromium(III). The first reaction is easily followed at 385 mμ where the absorbance changes are mainly due to the disappearance of chromium(VI). The second may be observed at wavelengths around 510 mμ where the absorbance first rises and then decreases to the value characteristic of chromium(III).
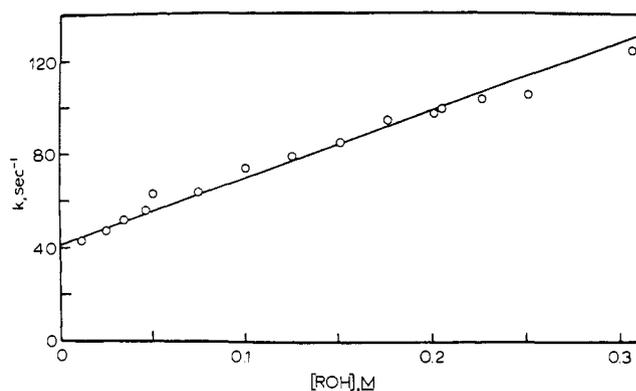

Figure 4. Effect of isopropyl alcohol concentration on the rate of formation of chromium(VI) esters in 97% acetic acid. The line represents the rate constants calculated using the constants given in the text.
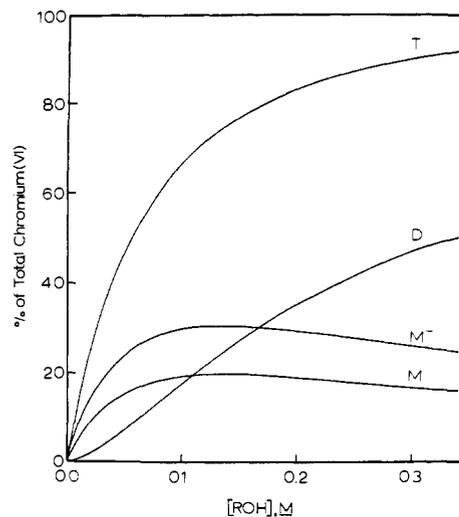

Figure 5. Relative concentrations of monoester (M), monoester anion (M⁻), diester (D), and total esters (T) as a function of isopropyl alcohol concentration.

The rate constants for the appearance and subsequent reaction of chromium(V) can be obtained by an analysis of the absorbance changes at 510 mμ.[6] We had previously used the method of steepest descent for this purpose, but following the suggestion of Wold,[7] we have found more satisfactory results to be obtained by an iterative least-squares fit of the data to the equation

$$y_i = a_1 e^{a_2 t_i} + a_3 e^{a_4 t_i} + a_5$$

where y_i is the observed absorbance value at time t_i, a_2 and a_4 are $-k_1$ and $-k_2$, respectively, and the other a's are combinations of the rate constants and absorbancy indices.[8]

There still remains the problem of extracting five constants from a single set of data. A more satisfactory approach is to employ two or more wavelengths and to fit the data at all wavelengths simultaneously.[8] In one case, this was carried out using data for 22 wavelengths. A good fit was obtained at all wavelengths using the same a_2 and a_4 throughout, indicating

(7) S. Wold, *Acta Chem. Scand.*, **21**, 1986 (1967).
(8) *Cf.* C. Deutsch, "Computer Programs for Chemistry," Vol. 4, D. F. DeTar, Ed., Academic Press, New York, N. Y., 1972, p 243.

that a single set of consecutive reactions could account for all of the observations. The absorbance values for each of the three chromium species calculated in this experiment are shown in Figure 6.

The absorbancy data thus obtained permitted us to choose a smaller set of wavelengths to be used in the remainder of the kinetic experiments. The effect of the alcohol concentration on the rate constants k_1 and k_2 is shown in Table I. It can be seen that the values of

Table I. Effect of Isopropyl Alcohol Concentration on the Rate of Appearance (k_1) and Disappearance (k_2) of Chromium(V) in 97% Acetic Acid Media[a]

10^3[Cr-(VI)], M	[ROH], M	$k_1 \times 10^2$, sec^{-1}	$k_2 \times 10^2$, sec^{-1}
1.40	0.0234	2.71 ± 0.10[b]	1.26 ± 0.01
1.01	0.0351	4.34 ± 0.10	1.74 ± 0.05
1.02	0.0503	5.75 ± 0.12	2.83 ± 0.04
1.04	0.0755	7.37 ± 0.06	2.82 ± 0.01
1.03	0.0935	8.64 ± 0.02	2.12 ± 0.03
1.18	0.0958	8.79 ± 0.08	2.75 ± 0.05
1.08	0.1007	8.83 ± 0.17	2.75 ± 0.38
0.98	0.1258	9.95 ± 0.10	2.73 ± 0.10
1.04	0.1762	11.4 ± 0.1	2.76 ± 0.05
0.84	0.1916	11.3 ± 0.1	3.16 ± 0.09
1.00	0.2050	11.5 ± 0.1	2.95 ± 0.05
1.06	0.3074	11.0 ± 0.2	3.72 ± 0.11

[a] [H$^+$] = 0.0125 M, μ = 0.184 M (NaClO$_4$), T = 15.0 ± 0.1°. [b] Average deviation for a set of three runs.

k_1 at first rise rapidly, and then level off at the alcohol concentrations for which the equilibrium absorbancy indices also level off. The alcohol concentration has a much smaller effect on the values of k_2.

The effect of chromium(VI) concentration on the rate constants is shown in Table II. Again, k_1 responds

Table II. Effect of Chromium(VI) Concentration on the Rate of Appearance (k_1) and Disappearance (k_2) of Chromium(V) in 97% Acetic Acid[a]

10^3[Cr-(VI)], M	[ROH], M	$k_1 \times 10^2$, sec^{-1}	$k_2 \times 10^2$, sec^{-1}
1.90	0.1258	12.3 ± 0.2[b]	3.77 ± 0.05
2.84	0.1258	15.7 ± 0.3	3.88 ± 0.22
2.97	0.1537	12.3 ± 0.1	3.12 ± 0.01
3.90	0.1258	14.1 ± 0.3	3.79 ± 0.09
5.00	0.1258	14.6 ± 0.4	3.55 ± 0.04
5.04	0.0958	13.1 ± 0.2	3.19 ± 0.02
9.96	0.1258	18.5 ± 0.3	3.09 ± 0.02

[a] μ = 0.184 M (NaClO$_4$), T = 15.0 ± 0.1°. [b] Average deviation for a set of three runs.

to the change in concentration, but k_2 does not. An increase in the hydrogen ion concentration affects both k_1 and k_2 (Table III). Finally, the use of isopropyl-α-d_1 alcohol leads to an isotope effect for both k_1 and k_2 (Table IV). The isotope effect appears to depend on both the chromium(VI) and hydrogen ion concentrations.

Since the equilibrium constants for the formation of both mono- and diesters have been obtained, it is possible to obtain the rate constants for the decomposition of each of the esters from the values of k_1. The values thus obtained were k_M = 0.294 sec^{-1} and k_D = 0.174 sec^{-1} (Figure 7). The value for k_D is well determined from this analysis, whereas that for k_M is somewhat less
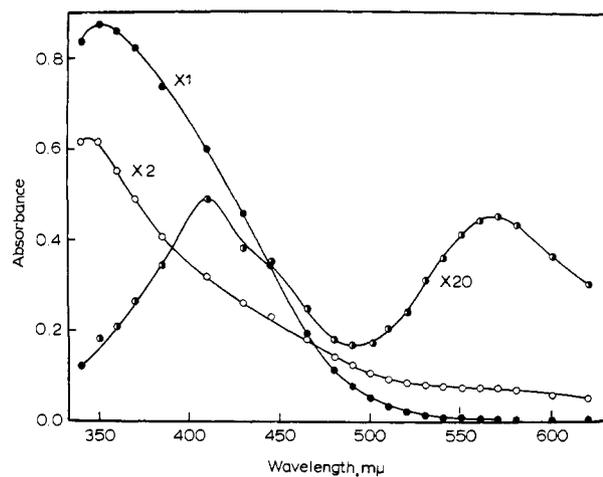

Figure 6. Calculated absorption spectra of chromium(VI) (largely diester) (●), chromium(V) (○), and chromium (III) (◐). The conditions were: [Cr(VI)] = 2.97 × 10^{-3} M, [ROH] = 0.154 M, [H$^+$] = 0.0125 M, μ = 0.184 M(NaClO$_4$), T = 15.0°.

Table III. Effect of Hydrogen Ion Concentration on the Rate of Appearance (k_1) and Disappearance (k_2) of Chromium(V) in 97% Acetic Acid Media[a]

10^3[Cr-(VI)], M	[H$^+$], M	$k_1 \times 10^2$, sec^{-1}	$k_2 \times 10^2$, sec^{-1}
1.01	0.0125	4.34 ± 0.10[b]	1.74 ± 0.05
0.92	0.0250	6.37 ± 0.10	1.34 ± 0.04
1.06	0.0500	13.3 ± 0.1	2.53 ± 0.04
1.02	0.0751	21.9 ± 0.1	3.47 ± 0.05
1.03	0.0920	29.4 ± 0.1	4.40 ± 0.11

[a] [ROH] = 0.0351 M, μ = 0.184 M (NaClO$_4$). T = 15.0 ± 0.1°. [b] Average deviation for a set of three runs.

certain since K_2 could not be as well determined from the experimental data as K_4.

Rate of Formation of Acetone. Having determined the kinetic constants for the reaction, it was possible to calculate the concentration of acetone to be expected as a function of time for each of the two schemes which were presented. This was done by numerical integration of the appropriate set of differential equations. The calculated curves are shown in Figure 8. It can be seen that the two schemes do predict markedly different rates of acetone formation.

The amount of acetone formed at different times was determined by mixing the two reacting solutions and then quenching the reaction by the addition of chromium(II). When the latter was added immediately after mixing, essentially no acetone was found, indicating that quenching was efficient. The concentration of acetone in the reaction solutions was determined by adding a known amount of methyl ethyl ketone as an internal standard, and analyzing the solution by gas chromatography. When the reaction was allowed to proceed to completion, 1.50 ± 0.02 mol of acetone were found per mole of chromium(VI) used. The experimental data are summarized in Table V.

The observed acetone concentrations are indicated in Figure 8. The data fit well the second scheme and clearly rule out the first. This result is in good accord with other studies which have used different methods to show that chromium(IV) will react with alcohols.[2,3]

Figure 8 also contains lines indicating the time at which the absorbance at 510 mμ reached a maximum

Table IV. Rate Constants and Deuterium Isotope Effect for the Appearance (k_1) and Disappearance (k_2) of Chromium(V) in 97% Acetic Acid[a]

10^3[Cr(VI)], M	[ROH], M	[H$^+$], M	$k_1 \times 10^2$, sec^{-1}	$k_2 \times 10^2$, sec^{-1}	$k_1{}^H/k_1{}^D$	$k_2{}^H/k_2{}^D$
1.01	0.1258	0.0125	9.95 ± 0.12	2.15 ± 0.05	6.5	3.3
1.01	0.1264[b]	0.0125	1.53 ± 0.09	0.649 ± 0.017		
4.28	0.1258	0.0125	12.4 ± 0.2	2.98 ± 0.05	4.7	3.7
4.24	0.1264[b]	0.0125	2.63 ± 0.09	0.802 ± 0.010		
1.00	0.1258	0.0920	40.9 ± 0.1	5.22 ± 0.18	9.4	4.3
1.00	0.1264[b]	0.0920	4.35 ± 0.06	1.22 ± 0.06		

[a] μ = 0.184 M (NaClO$_4$), T = 15.0 ± 0.1°. [b] Isopropyl-α-d alcohol.
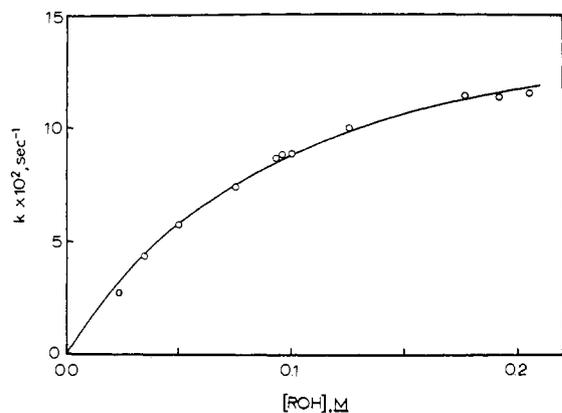

Figure 7. Effect of isopropyl alcohol concentration on the rate of oxidation by chromium(VI). The line represents the calculated values using k_M = 0.294 sec^{-1} and k_D = 0.174 sec^{-1}.

Table V. Stoichiometry of the Chromic Acid Oxidation of Isopropyl Alcohol as a Function of Time in 97% Acetic Acid[a]

Time, sec	[Cr(VI)], mmol/l.	Peak area ratio	[Acetone]$_{obsd}$, mmol/l.	% of acetone formed
2.64	5.06	0.191 ± 0.009	2.85 ± 0.14	38
2.88	5.02	0.197 ± 0.014	2.93 ± 0.21	39
4.39	4.98	0.256 ± 0.028	3.82 ± 0.41	51
5.26	5.00	0.320 ± 0.009	4.76 ± 0.13	64
6.09	5.00	0.296 ± 0.003	4.41 ± 0.06	59
8.90	5.00	0.300 ± 0.009	4.46 ± 0.13	60
9.18	5.06	0.345 ± 0.004	5.13 ± 0.07	68
9.40	5.02	0.329 ± 0.001	4.90 ± 0.01	65
9.70	5.06	0.357 ± 0.025	5.32 ± 0.38	70
12.05	5.00	0.353 ± 0.004	5.25 ± 0.06	70
13.04	5.04	0.379 ± 0.008	5.64 ± 0.12	75
14.19	5.06	0.409 ± 0.001	6.08 ± 0.02	80
16.48	5.04	0.394 ± 0.002	5.86 ± 0.03	78
18.18	5.04	0.388 ± 0.009	5.77 ± 0.14	76
∞	5.06	0.510 ± 0.020[b]	7.59 ± 0.29	100

[a] [ROH] = 0.1258 M, [H$^+$] = 0.0125 M, μ = 0.184 M (NaClO$_4$), T = 15 ± 0.05°, average deviation for a set of at least three runs. [Methyl ethyl ketone] was constant throughout. [b] Average of 15 determinations.

and the time at which the concentration of chromium(V) reaches a maximum. At the absorbance maximum, 55% of the maximum amount of acetone had been formed (26% derived from each of Cr(VI) and Cr(IV) and 3% from Cr(V)), and at the chromium(V) maximum, 67% of the maximum amount of acetone had been formed (31% from each of Cr(VI) and Cr(IV), and 6% from Cr(V)).

The conclusions reached above are independent of the mechanism by which chromium(V) is converted to chromium(III). The reaction appears to be an oxidation rather than disproportionation since it shows a
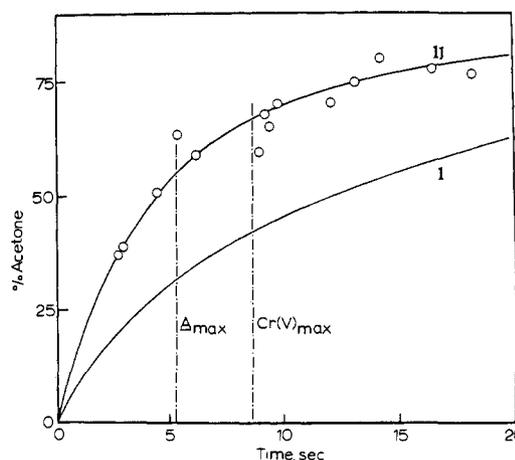

Figure 8. Rate of formation of acetone in the chromic acid oxidation of isopropyl alcohol in 97% acetic acid. Curve I represents the calculated values for Scheme I and curve II is for Scheme II. The conditions were: [Cr(VI)] = 0.0050 M, [ROH] = 0.126 M, [H$^+$] = 0.0125 M, μ = 0.184 M (NaClO$_4$), T = 15.0°.

kinetic isotope effect. Except at very low alcohol concentrations, the rate of disappearance of chromium(V) appears to be independent of the alcohol concentration.

An examination of Figure 5 shows that most of the chromium(VI) is in the form of the mono- or diester rather than acetochromate ion at alcohol concentrations greater than 0.05 M. Thus, the reaction of the radical with chromium(VI) probably will lead to a chromium(V) having an isopropoxy group attached. This will especially be the case if one makes the reasonable assumption that the chromium(VI) anions are less reactive than the neutral species. The lack of kinetic dependence on alcohol concentration then suggests that it is largely the alcohol group which is attached to the chromium(V) which undergoes electron transfer in the conversion of chromium(V) to chromium(III).

Experimental Section

Reagents. Acetic acid was purified and the water content was determined as described previously.[9] The solvent for the reactions was prepared by mixing 3093.9 g of 99.71% acetic acid with 68.5 g of anhydrous sodium perchlorate and 86.5 g of water. The perchloric acid solution was prepared by mixing 3093.9 g of 99.71% acetic acid with 79.25 g of perchloric acid (70.87%) and 63.4 g of water. The concentration of perchloric acid was found to be 0.184 M. The ionic strength of the sydium perchlorate solutiod was 0.184 M.

Fisher analytical reagent grade chromium trioxide was dried and stored over phosphorus pentoxide. Isopropyl alcohol was Fisher reagent grade. Isopropyl-α-d alcohol was prepared as described previously.[6]

Kinetics. A solution of isopropyl alcohol in 97% acetic acid was mixed with a solution of chromium trioxide in 97% acetic acid

(9) K. B. Wiberg and T. Mill. *J. Amer. Chem. Soc.*, **80**, 3022 (1958).

containing perchloric acid using a stopped flow apparatus.[10] Two path lengths, 7 or 2 mm, were used. The output of the photomultiplier amplifier was sampled by an analog to digital converter attached to a PDP-8 computer. The computer was programmed to accept up to 128 data points using two selected time intervals. In the oxidation studies, approximately half the points were collected before the time at which the absorbance reached a maximum at 510 mμ, and the remaining points were collected using a longer time interval, thus permitting the second half of the reaction to be better defined. An infinity reading was taken at a time corresponding to essentially complete reaction.

Treatment of Kinetic Data. In a typical run, 100 data points were collected using a ratio of first to second time intervals of 1 : 4. In the very rapid esterification runs, the first time interval was normally 2 msec. At all but the lowest alcohol concentrations, the rate constants and equilibrium absorbancy indices were calculated by a least-squares fit to the equation[8]

$$y = a_1 e^{a_2 t} + a_3 e^{a_4 t} + a_5$$

where y is the observed absorbance at time t, a_2 and a_4 are rate constants for two consecutive reactions, and $a_1, a_3,$ and a_5 are combinations of rate constants and absorbancy indices. In the esterification studies, a_2 corresponded to the rate constant for ester formation, and a_4 corresponded to its decomposition to acetone.

The equilibrium parameters for esterification, K_2', K_4', ϵ (monoester), and ϵ (diester), were obtained by starting with a set of approximate values and adjusting them to give a good fit to the equilibrium absorbancy indices using the method of steepest descent.[6] An rms deviation of 1% was reached. The parameters of the more complete esterification scheme were obtained in a similar fashion. Starting with a set of approximate values for the rate constants, the absorbance-time curves were calculated by numerical integration.[11] The rate constants were then adjusted so as to give a good match to the observed absorbance-time curve. The equilibrium constants derived above were used as constraints on the rate constants.

The oxidation studies were carried out in the same fashion as above, using correspondingly longer time intervals. The rate constants, k_1 and k_2, were obtained by the least-squares fitting procedure referred to above. The decomposition into rate constants

for decomposition of mono- and diesters were carried out using the equilibrium constants derived from the esterification studies.

Stoichiometry Experiments. A rapid-mixing reactor containing three thermostated glass hypodermic syringes was constructed. Two of the syringes were attached to a common drive plate, and the third syringe was independent. The isopropyl alcohol solution was placed in one of the paired syringes and the chromium trioxide solution was placed in the other. The third syringe contained a solution of chromium(II) in acetic acid. The reaction was initiated by driving the paired syringes which ejected the mixed solution into a stirred vessel. An electronic timer was started automatically when the drive stopped. After an appropriate time, the third syringe was driven, and the electronic timer was automatically stopped when the drive stopped.[12] A known amount of methyl ethyl ketone was added to the reaction solution, and the ratio of acetone to methyl ethyl ketone was determined by gas chromatography using a 25% Carbowax 400 on C-22 silocel column and a flame ionization detector.

Chromic Acid Ionization Constant. The change in absorbance with acid concentration was determined at three wavelengths (380, 385, 390 mμ) using a Cary 15 spectrometer. The ionization constant, K_1, was calculated at each wavelength using

$$K_1 = \frac{\epsilon_T - \epsilon_{AH}}{\epsilon_{A^-} - \epsilon_H}[H^+]$$

where ϵ_T is the observed absorbancy index, ϵ_{A^-} is that for the acetochromate ion, and ϵ_{AH} is that for acetochromic acid. The value of ϵ_{A^-} was obtained from solutions containing sufficient sodium acetate to neutralize the chromic acid, and the value of ϵ_{HA} was estimated by fitting the observed data to an asymptotic form of the above equation.

Supplementary Material Available. Tables containing additional data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm. 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036 Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-1884.

(10) J. M. Sturtevant, "Rapid Mixing and Sampling Techniques in Biochemistry," B. Chance, Ed., Academic Press, New York, N. Y., 1964, p 89.

(11) The Runge-Kutta method was used for the numerical integration.

(12) L. S. Hegedus and A. Haim [*Inorg. Chem.*, 6, 664 (1967)] have shown that the Cr(II)–Cr(VI) reaction is complete within the time of mixing.

Oxidation of Aldehydes by Chromium(VI) and by Chromium(V) in 96% Acetic Acid[1]

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Abstract: The chromic acid oxidation of benzaldehyde in 96% acetic acid has been found to produce chromium(V) as an intermediate. The rate constants for the chromium(VI) and chromium(V) oxidations were obtained for benzaldehyde as well as for substituted benzaldehydes, benzaldehyde-d_1, and a group of aliphatic aldehydes. The data are compared with the previously obtained data on the oxidation of benzaldehyde by chromium(VI) and the intermediate valence chromium species.

Earlier, we reported the kinetics of the chromic acid oxidation of aromatic aldehydes in aqueous acetic acid.[2,3] The kinetic study led to information on only

the first step in the oxidation, whereas participation by intermediate oxidation states of chromium is almost certainly involved. Information concerning the rapid oxidation which follows the relatively slow oxidation by

(3) *Cf.* G. T. E. Graham and F. H. Westheimer, *J. Amer. Chem. Soc.*, 80, 3030 (1958), for a study of the reaction in aqueous solution.