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 $m\mu$, 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 $m\mu$) 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]

Kenneth B. Wiberg* and Günther Szeimies

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. Received March 30, 1973

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

Table I. Oxidation of Benzaldehyde in 96% Acetic Acid[a]

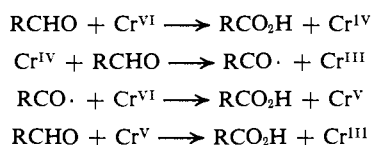| [Aldehyde], M	$k_1' \times 10$, sec^{-1}	$k_2' \times 10$, sec^{-1}	$k_1 = k_1'/[RCHO]$, l. mol^{-1} sec^{-1}	$k_2 = k_2'[RCHO]$, l. mol^{-1} sec^{-1}
0.521	0.790 ± 0.005	0.489 ± 0.010	0.152	0.094
0.296	0.458 ± 0.006	0.277 ± 0.009	0.155	0.094
0.292	0.456 ± 0.006	0.303 ± 0.008	0.156	0.104
0.280	0.423 ± 0.017	0.247 ± 0.014	0.151	0.088
0.273	0.390 ± 0.007	0.229 ± 0.003	0.143	0.084
0.205	0.330 ± 0.008	0.219 ± 0.008	0.161	0.107
0.100	0.177	0.115	0.177	0.115
			Av = 0.156 ± 0.007	0.097 ± 0.009

[a] $[Cr^{VI}] = 0.0025\ M$, $[HClO_4] = 0.3\ M$, temperature 25.0°.

chromium(VI) was obtained by the study of the competitive oxidation of a pair of aldehydes.[4] The observed competition ratio reflected the relative reactivity of the two aldehydes toward each of the active oxidants with weighting factors determined by the stoichiometry of the steps. It was not, however, possible to distinguish between the two following sets of reactions (Schemes I and II). Other possible schemes in which

Scheme I

$$RCHO + Cr^{VI} \longrightarrow RCO_2H + Cr^{IV}$$

$$Cr^{IV} + Cr^{VI} \longrightarrow 2Cr^{V}$$

$$2(Cr^{V} + RCHO \longrightarrow RCO_2H + Cr^{III})$$

Scheme II

$$RCHO + Cr^{VI} \longrightarrow RCO_2H + Cr^{IV}$$

$$Cr^{IV} + RCHO \longrightarrow RCO\cdot + Cr^{III}$$

$$RCO\cdot + Cr^{VI} \longrightarrow RCO_2H + Cr^{V}$$
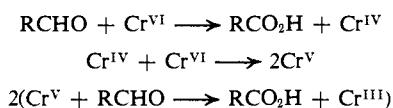
$$RCHO + Cr^{V} \longrightarrow RCO_2H + Cr^{III}$$

chromium(V) is reduced via a one-electron step may be eliminated since such reactions would lead to a branching chain, and hence an autocatalytic reaction.[5] It will be shown later that chromium(V) disappears at a rate directly proportional to the aldehyde concentration. This eliminates schemes in which chromium(V) disproportionates to chromium(VI) and chromium(IV).

We then desire a method by which the reaction of chromium(V) could be followed directly. Our success with a spectrometric study of alcohol oxidation by chromium(VI) and chromium(V)[6] has led us to examine aldehyde oxidation in the same fashion. In the oxidation of benzaldehyde in 96% acetic acid, the absorbance at 520 mμ was found first to increase and then decrease. The absorbance of the intermediate corresponded to that found in the chromic acid oxidation of isopropyl alcohol,[6] and an esr signal due to chromium(V) also was found. Thus it seems clear that the reactions being studied are

$$RCHO + Cr^{VI} \xrightarrow{k_1} RCO_2H + Cr^{IV}$$

$$RCHO + Cr^{V} \xrightarrow{k_2} RCO_2H + Cr^{III}$$
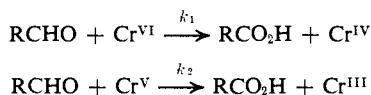
The process by which chromium(IV) is converted to chromium(V) is not specified. However, it must be rapid compared to the other reactions. Unlike the oxidation of alcohols,[6] no preoxidation equilibria could be found spectrometrically.

(4) K. B. Wiberg and W. H. Richardson, *J. Amer. Chem. Soc.*, **84**, 2800 (1962).

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

(6) K. B. Wiberg and H. Schäfer, *J. Amer. Chem. Soc.*, **91**, 927, 933 (1969).

The kinetics of the reaction were studied using a relatively large excess of aldehyde and of mineral acid, leading to a process which may be described as two consecutive pseudo-first-order reactions. The observed

$$Cr^{VI} \xrightarrow{k_1'} Cr^{IV}$$

$$Cr^{V} \xrightarrow{k_2'} Cr^{III}$$
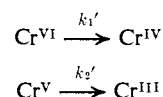
data were fit to such a process using the technique described in the preceding papers.[6] The results are summarized in Table I. Both k_1' and k_2' increased with increasing aldehyde concentrations. The rate constants k_1 and k_2 were obtained by dividing k_1' and k_2' by the aldehyde concentration. Although there may be a small trend toward higher rate constants with lower aldehyde concentrations, the data are quite satisfactorily represented by a first-order dependence on aldehyde concentration.

The oxidation of benzaldehyde-d_1 was examined in the same way. The ratio of k_1/k_2 was affected in such a way that the absorbance increase noted with ordinary benzaldehyde was not found. Rather, there was initially essentially no absorbance change, followed by the normal decrease. In this case, it was difficult to obtain good kinetic parameters. Approximate values which could be derived are given in Table II. From

Table II. Kinetic Isotope Effects in the Chromic Acid Oxidation of Benzaldehyde

[RCDO], M	$100k_1'$, sec	$100k_2'$, sec	$k_1 = k_1'/[ald]$, l. mol^{-1} sec^{-1}	$k_2 = k_2'/[ald]$, l. mol^{-1} sec^{-1}
0.276	0.833	1.17	0.0302	0.0424
0.276	0.733	1.17	0.0266	0.0424
0.276	0.770	1.28	0.0279	0.0464
0.276	0.737	1.17	0.0267	0.0424
0.276	0.800	1.05	0.0290	0.0380
		Av	0.0281 ± 0.0015	0.0423 ± 0.0017

$k_H/k_D\ (Cr^{VI}) = 0.156/0.0281 = 5.6$
$k_H/k_D\ (Cr^{V}) = 0.097/0.0423 = 2.3$

these data, the isotope effect for the chromium(VI) oxidation is $k_H/k_D = 5.6$ and that for the chromium(V) oxidation is $k_H/k_D = 2.3$.

The effect of substituents was now examined, giving the data shown in Table III. A comparison with our previous kinetic data for the oxidation by chromium(VI) in 85% acetic acid, and with the data for oxidation by the intermediate valence chromium species derived from competitive oxidation experiments, is given in Table IV. It can be seen that the present results are in very good agreement with those obtained earlier. The slightly larger substituent effects found in the present case

Table III. Effect of Substituents on the Chromic Acid Oxidation of Aldehydes

Substituent	[RCHO], M	$k_1' \times 10$, sec^{-1}	$k_2' \times 10$, sec^{-1}	k_1, l. mol^{-1} sec^{-1}	k_2, l. mol^{-1} sec^{-1}
p-F	0.128	0.137 ± 0.003	0.102 ± 0.005	0.107	0.080
	0.190	0.227	0.151	0.119	0.080
				Av 0.113 ± 0.006	0.080
m-CH$_3$O	0.128	0.384 ± 0.008	0.238 ± 0.009	0.300	0.186
	0.211	0.615 ± 0.022	0.333 ± 0.016	0.292	0.158
				Av 0.296 ± 0.004	0.172 ± 0.014
m-Cl	0.0712	0.234 ± 0.004	0.126 ± 0.005	0.329	0.177
	0.131	0.434 ± 0.007	0.220 ± 0.012	0.331	0.168
	0.233	0.764 ± 0.006	0.334 ± 0.016	0.328	0.141
				Av 0.329 ± 0.002	0.162 ± 0.014
p-Cl	0.0800	0.197 ± 0.006	0.115 ± 0.015	0.246	0.144
	0.172	0.419 ± 0.019	0.242 ± 0.009	0.243	0.141
	0.360	0.789 ± 0.023	0.434 ± 0.033	0.220	0.121
				Av 0.236 ± 0.011	0.135 ± 0.010
p-CH$_3$	0.102	0.113	0.082	0.111	0.080
	0.113	0.120 ± 0.002	0.089 ± 0.002	0.106	0.079
	0.195	0.194 ± 0.010	0.147 ± 0.006	0.100	0.075
	0.347	0.435	0.304	0.125	0.088
				Av 0.111 ± 0.008	0.081 ± 0.004

Table IV. Summary of Substituent Effects in Benzaldehyde Oxidation

Substituent	$k_{rel}(Cr^{VI})$, sec	Prev. work[4]	$k_{rel}(Cr^V)$, sec^{-1}	$k_{rel}(Cr^{IV} + Cr^V)$,[4] sec^{-1}
p-CH$_3$	0.71	0.69	0.84	0.81
p-F	0.73		0.83	
H	1.00	1.00	1.00	1.00
p-Cl	1.51	1.38	1.39	1.20
m-CH$_3$O	1.90	1.80	1.78	
m-Cl	2.11	1.91	1.68	1.42
ρ^a	0.86	0.74	0.58	0.42

^{a} The ρ values are defined for the p-CH$_3$, H, p-Cl, and m-Cl substituents which lead to a very good correlation with σ. The points for p-F fell well below the line whereas those for m-CH$_3$O fell well above the lines.

probably result from the change in solvent from 85% acetic acid to 96% acetic acid. It is known that a decrease in dielectric constant of the solvent normally increases the magnitude of substituent effects.[7]

Finally, the oxidation of several aliphatic aldehydes are examined, giving the data in Table V. Here again,

Table V. Chromic Acid Oxidation of Aliphatic Aldehydes

Aldehyde	[RCHO], M	k_1, l. mol^{-1} sec^{-1}	k_2, l. mol^{-1} sec^{-1}
Pivaldehyde	0.0610	10.4 ± 0.1	1.85 ± 0.05
	0.0918	10.4 ± 0.1	1.85 ± 0.03
	0.181	11.1 ± 0.1	1.92 ± 0.17
	0.234	11.3 ± 0.7	1.79 ± 0.06
		Av 10.8 ± 0.4	1.85 ± 0.04
Isobutyraldehyde	0.0801	27.6 ± 2.3	4.06 ± 0.05
	0.135	29.5 ± 0.1	4.24 ± 0.03
	0.212	30.6 ± 1.6	4.35 ± 0.07
	0.302	28.5 ± 0.1	3.81 ± 0.20
		Av 29.1 ± 1.0	4.12 ± 0.18
n-Butyraldehyde	0.0877	31.1 ± 0.1	3.98 ± 0.03
	0.166	32.0 ± 0.0	3.85 ± 0.19
	0.282	32.9 ± 1.9	3.51 ± 0.09
		Av 32.0 ± 0.6	3.78 ± 0.18

a two-step process was found and the rate constants for oxidation by chromium(VI) and chromium(V) could

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

be derived. No evidence for an aldehyde–chromium-(VI) complex could be found.

Having these data in hand, we may now consider the mechanism of the reaction. Let us first compare the effect of substituents on k_1 with the results previously obtained in the chromyl acetate oxidation of aldehydes.[8] The chromyl acetate reaction gave ρ -0.2, and led to the formation of chromium(V) as an intermediate. The negative value of ρ, along with a kinetic hydrogen isotope effect and oxygen transfer from the Cr=O bond of the oxidant to the product, benzoic acid, suggested the reactions in Scheme III. In this case, Cr(IV) was

Scheme III

$$\underset{O}{\overset{O}{R\overset{\|}{C}H}} + (AcO)_2CrO_2 \longrightarrow R\overset{O}{\overset{\|}{C}}\cdot + (AcO)_2CrO_2H$$

$$R\overset{O}{\overset{\|}{C}}\cdot + (AcO)_2CrO_2 \longrightarrow R\overset{O}{\overset{\|}{C}}OCrO(OAc)_2 \xrightarrow{H_2O} R\overset{O}{\overset{\|}{C}}OH + (AcO)_2CrO_2H$$

$$R\overset{O}{\overset{\|}{C}}H + (AcO)_2CrO_2H \longrightarrow R\overset{O}{\overset{\|}{C}}\cdot + (AcO)_2Cr(OH)_2$$

$$R\overset{O}{\overset{\|}{C}}\cdot + (AcO)_2CrO_2H \longrightarrow R\overset{O}{\overset{\|}{C}}OCr(OAc)_2(OH) \xrightarrow{H_2O} R\overset{O}{\overset{\|}{C}}OH + (AcO)_2Cr(OH)_2$$

stable and did not effect further oxidation. Further evidence for this scheme was found in the observation that triphenylacetaldehyde is completely cleaved to triphenylmethanol and carbon monoxide using chromyl acetate. This is characteristic of oxidations which proceed *via* a hydrogen atom abstraction mechanism. Oxidations which proceed *via* an ester mechanism give triphenylacetic acid.[8]

The large difference in the value of ρ between the chromyl acetate oxidation and that in aqueous acetic acid ($+0.9$) indicates a change in mechanism. The observation that n-butyraldehyde is 200 times as reactive toward chromium(VI) as benzaldehyde also would not be expected for a hydrogen atom abstraction. On the other hand, the rate difference would be expected

(8) K. B. Wiberg and P. A. Lepse, *J. Amer. Chem. Soc.*, **86**, 2612 (1964).

for a process in which chromic acid adds across the carbonyl group giving a chromate ester as an intermediate. It is known that whereas aliphatic aldehydes are largely hydrated in aqueous solution,[9] benzaldehyde does not undergo significant hydration. The same factor should apply to the addition of chromic acid across the carbonyl group; a higher concentration of the chromate intermediate would be expected with the aliphatic aldehydes than with the aromatic aldehydes. Similarly, any other mechanism involving the aldehyde hydrate as an intermediate[10] would accommodate the rate difference between aliphatic and aromatic aldehydes.

If the chromate ester or the aldehyde hydrate is the intermediate, the value of ρ for the oxidation step with the aromatic aldehydes must be about -1.[11] This value agrees well with ρ^* of 1.2 found by Roček[10] for the oxidation of aliphatic aldehydes in aqueous solution where they are extensively hydrated. It is not possible to distinguish between reaction *via* the chromate ester and *via* direct attack of chromic acid on the aldehyde hydrate on the basis of the present evidence. However, the similarity between aldehyde and alcohol oxidations leads us to prefer the ester mechanism.

The ester must decompose *via* an effective two-electron change. However, the reaction need not involve a single step, but could occur as in eq 1–3.[12]
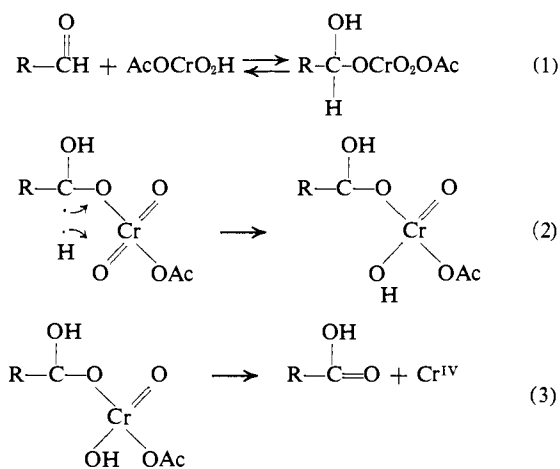
Equation 2 would be rate controlling, and eq 3 would be expected to be very rapid. This mechanism is attractive in that chromium(VI) would then react in the same fashion (*i.e.*, *via* hydrogen atom abstraction) in both aqueous acetic acid and acetic anhydride. The purpose of the ester would be to bring the reactants together. It also presents a convenient way in which chromium(VI) can bring two electrons into two different orbitals in going to chromium(IV). The direct two-electron process would ultimately require spin inversion

of one of the two electrons in order to give the normal chromium(IV) species. The process described above would also account for the value of ρ since it is known that most hydrogen atom abstraction reactions give small negative values of ρ. The direct process in which two electrons are transferred simultaneously is not, however, ruled out.

We shall now consider the oxidation by chromium(V). The effect of substituents observed for oxidation by this species is similar to that found with chromium(VI) (ρ 0.9) and is quite different than that for the chromium(V) oxidation step in the chromyl acetate oxidation (ρ -0.9). In addition, aliphatic aldehydes are more quickly oxidized by chromium(V) than are aromatic aldehydes, again suggesting that the hydrate is the species which is involved in the oxidation. Thus, oxidation by chromium(V) appears very similar to oxidation by chromium(VI), and the same mechanism involving an ester intermediate is probably involved.

The role of chromium(IV) is not established by this investigation. However, Roček and Ng[13] have obtained evidence indicating that chromium(IV) reacts *via* Scheme II. This permits an estimation of the value of ρ for chromium(IV) oxidation using the substituent effects observed herein and the competitive oxidation data,[4] and ρ 0.4 is found. Roček and Ng[13] studied the chromium(IV) oxidation in a different manner and obtained ρ 1.0 in 70% acetic acid. Considering the differences in reaction media used to obtain the several data involved in this estimation, the reaction constants are in satisfactory agreement.

Chromium(IV) almost certainly reacts *via* a one-electron process giving chromium(III) and an organic radical. The positive value of ρ indicates that the free aldehyde is not the active reductant since this would lead to a negative value of ρ as found in the chromyl acetate oxidation of aldehydes. Thus, it appears that the aldehyde hydrate is the species which reacts with chromium(IV).

Experimental Section

(9) R. P. Bell and J. C. Clunie, *Trans. Faraday Soc.*, **48**, 393 (1952).
(10) J. Rocek, *Tetrahedron Lett.*, **No. 5**, 1 (1959).
(11) The value of ρ for the addition of hydrogen cyanide to aromatic aldehydes is $+2$,[7] and the addition of water should give a similar value of ρ.
(12) K. B. Wiberg in "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965, p 162.

(13) J. Roček and C.-S. Ng, private communication.
(14) J. M. Sturtevant in "Rapid Mixing and Sampling Techniques in Biochemistry," B. Chance, Ed., Academic Press, New York, N. Y., 1964, p 89.