

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

The Oxidation of Aromatic Aldehydes by Chromyl Acetate¹BY KENNETH B. WIBERG^{2a} AND PAUL A. LEPSE^{2b}

RECEIVED FEBRUARY 5, 1964

The kinetics and stoichiometry of the oxidation of benzaldehyde by chromyl acetate has been studied. The reaction proceeds in two stages, the first giving chromium(V) and the second giving chromium(IV). Both reactions are first order in benzaldehyde and in the oxidant, show a kinetic isotope effect, and involve oxygen transfer from the oxidant to the aldehyde. The possible mechanisms are discussed.

We have previously examined the kinetics of the chromic acid oxidation of aromatic aldehydes in aqueous acetic acid.³ Oxidations of this type are often carried out in acetic anhydride as the reaction medium, and under these conditions the chromium(VI) is in the form of the neutral, covalent chromyl acetate.⁴ In the present investigation, we have examined the difference in the mode of oxidation of aldehydes between aqueous acetic acid and acetic anhydride as the solvent.

Results

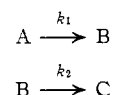
Chromium trioxide in acetic anhydride gives an orange solution of chromyl acetate. The addition of benzaldehyde causes a rapid change in color to dark brown. Titrimetric analysis of the brown solution indicates that 1 equivalent of oxidizing power per chromium still remains and this residual titer decreases only slowly with time. It is apparent that the oxidation does not readily proceed to give chromium(III) as in acetic acid-water, but rather gives chromium(IV) or a 1:2 complex of chromium(VI) and chromium(III). In view of the results of Pungor and Trompler⁵ on the formation of chromium(IV) in sulfuric acid solutions, and the isolation of a number of chromium(IV) compounds,⁶ the production of chromium in this oxidation state seems reasonable. Further, the spectrum of the solution differs from that of a mixture of chromium(III) and (VI).

Isolation of benzoic acid from the reaction mixtures used for the kinetic runs was difficult because of the high solubility of the acid in the aqueous acetic acid medium resulting from the hydrolysis of the solvent. Isotope dilution analysis, using benzoic-C¹⁴ acid, was therefore employed. After allowing the reaction to proceed for a long time, leading to almost complete reduction to chromium(III), 73% of the theoretical amount of benzoic acid was found. This indicates considerable solvent oxidation by an intermediate chromium species, probably Cr(V).⁷ This has previously been observed in aqueous acetic acid.³ Solvent oxidation may be minimized by using an excess of the aldehyde, and this was done in all kinetic runs.

A possible by-product arising from the oxidation of benzaldehyde is benzil which could be formed by the

coupling of two benzoyl radicals. Isotopic dilution analysis indicated the presence of less than 0.036% of the theoretical amount of benzil.

The kinetics of the reaction could be studied both titrimetrically and spectrophotometrically. Some typical spectrophotometric data are shown in Fig. 1. It can be seen from the curve obtained at 440 m μ that an intermediate is formed which then reacts further to give Cr(IV). Since the aldehyde concentration was relatively large, both reactions might be expected to be either first order or pseudo-first order, and might be represented by



If the absorbance of the intermediate were known, the two rate constants could be easily determined.⁸ However, this was not known and all three parameters k_1 , k_2 , and ϵ_b must be evaluated from the absorbance-time data. In practice, ϵ_c must also be evaluated since the "infinity" absorbance changes slowly with time corresponding to the slow reaction of Cr(IV).

The integrated form of the differential equations which represent this system are

$$A = A_0 e^{-k_1 t}$$

$$B = A_0 k_1 (e^{-k_2 t} - e^{-k_1 t}) / (k_2 - k_1)$$

$$C = A_0 - A - B$$

$$\text{Abs.} = \epsilon_a A + \epsilon_b B + \epsilon_c C$$

Approximate values of k_1 could be estimated using the initial slope, k_2 could be estimated from a plot of $\ln(\text{Abs.} - \epsilon_c A_0)$ vs. time for the latter part of the reaction, and $\epsilon_b A_0$ was estimated as somewhat larger than the maximum absorbance, or was estimated from the equation

$$t_{\max} = \frac{1}{k_1 - k_2} \ln \left[1 + \frac{(k_1 - k_2)(\epsilon_b - \epsilon_a)}{k_2(\epsilon_b - \epsilon_c)} \right]$$

The "best" values of k_1 , k_2 , ϵ_b , and ϵ_c were obtained from the initial estimates in two ways. First, the absorbance-time relationship was calculated using the approximate parameters, and the average deviation from the observed values was obtained. Then the parameters were taken one at a time and increased or decreased by 1% per iteration until further varying of any of the parameters effected no further decrease in the average deviation.⁹ The five-dimensional surface

(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 166.

(9) These computations were carried out with the aid of an IBM-709 computer.

(1) This work was supported by the Atomic Energy Commission and by an A. P. Sloan Foundation Fellowship to K. B. W.

(2) (a) Department of Chemistry, Yale University. (b) Taken from a thesis submitted by P. A. L. to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree. National Science Foundation Predoctoral Fellow.

(3) K. B. Wiberg and T. Mull, *J. Am. Chem. Soc.*, **80**, 3022 (1958).

(4) H. L. Krauss, *Angew. Chem.*, **70**, 502 (1958); W. Watanabe, Ph.D. Thesis, University of Chicago, 1948, p. 43.

(5) E. Pungor and J. Trompler, *J. Inorg. Nucl. Chem.*, **5**, 123 (1957).

(6) H. V. Wartenberg, *Z. anorg. allgem. Chem.*, **247**, 135 (1941); R. Scholder and G. Sperka, *ibid.*, **285**, 49 (1956); N. Hagihara and H. Yamazaki, *J. Am. Chem. Soc.*, **81**, 3160 (1959).

(7) Under the same conditions there would have been only 7.2% reaction of chromyl acetate with the specially purified acetic anhydride.

representing the deviation as a function of the four variables appears to be complex with several false minima. The iterative procedure is prone to move into one of these "pot-holes," but this could be checked by varying the final parameters somewhat and repeating the calculation. If the parameters return to the values found the first time, the results are probably correct.

In the second method, a difference quotient equal to the change in deviation on varying the parameter by a small percentage was computed for each parameter. Then, all of the parameters were varied simultaneously, each by an amount proportional to its difference quotient. In effect, the values of the parameters were moved along a vector. When motion in this direction no longer resulted in a decrease in the deviation, the direction for a new vector was computed by the same procedure, and the process was continued until a minimum value of the deviation was obtained.

In order to learn how accurately the values of the parameters could be obtained by these methods, a set of values for the rate constants and extinction coefficients similar to those appropriate for the experimental runs at 465 $m\mu$ was assumed, and a set of absorbancy values was calculated as a function of time. Various sets of "initial estimates," off in varying degree from the correct values, were fed into the computer to determine how close to the correct values they would be moved. Some typical results are summarized in Table I.

TABLE I
ACCURACY OF COMPUTED RATE CONSTANTS FOR TWO
CONSECUTIVE FIRST-ORDER REACTIONS^a

Error in initial estimates, %				Error in computed values, %				Av. dev.
ϵ_b	ϵ_c	k_1	k_2	ϵ_b	ϵ_c	k_1	k_2	
A. Method of iterations								
0	0	0	+12	+2.0	0.0	-5.9	+6.8	0.00197
0	0	+19	0	-1.0	0.0	+3.4	-3.0	.00113
0	+10	0	0	-1.0	+6.7	+4.0	+7.2	.00268
+11	0	0	0	0.0	0.0	+1.0	-1.0	.00031
+11	+10	+19	+12	-1.3	+8.9	+4.4	+10.0	.00350
B. Vector method								
+10	+10	+19	+11	+0.5	+4.3	-1.0	+8.7	0.00057
+10	+10	-12	+11	+2.1	+5.8	-5.4	+17.5	.00093
+10	-10	+19	+11	+0.06	+1.1	-0.05	+1.8	.00019
-13	+10	+19	+11	+ .4	+3.6	- .7	+6.9	.00051
+10	+10	-12	-13	- .07	-1.4	- .05	-2.3	.00026
+10	-10	+19	-13	-1.6	-6.9	+4.7	-11.7	.00083

^a The correct values of the parameters were: $\epsilon_a A_0 = 0.346$, $\epsilon_b A_0 = 0.808$, $\epsilon_c A_0 = 0.400$, $k_1 = 2.185 \text{ min.}^{-1}$, $k_2 = 0.3383 \text{ min.}^{-1}$. The absorbance values at 23 different times from 0.2-5.0 min. were used as data. The deviations are given in absorbancy units, and are the minimum values found by the computer. The errors correspond to the first "false minimum" found.

It is apparent that the plot of deviation vs. ϵ_b , ϵ_c , k_1 , and k_2 does not have a sharp lowest minimum with steep sides to the curve, but rather has a shallow minimum with a considerable range of values of these parameters giving deviations close to zero. The value of k_2 may deviate by as much as 20% from the correct value, and k_1 may differ by as much as 6% and still give agreement between calculated and observed absorbancy values within the experimental error. In some experimental runs, the value of ϵ_a was also varied because the absorbancy-time plot did not extrapolate to the true value of $\epsilon_a A_0$ at $t = 0$.

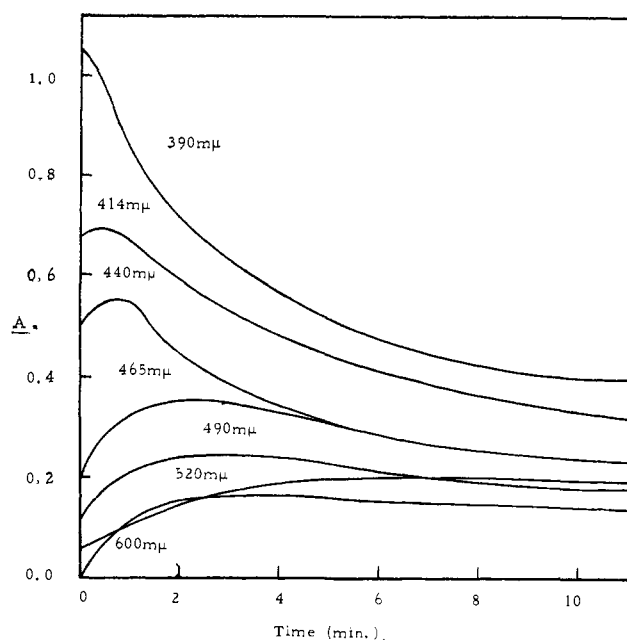


Fig. 1.—Reaction of benzaldehyde with chromyl acetate; absorbance vs. time at several wave lengths.

Values for k_1 , k_2 , ϵ_b , and ϵ_c at 25° were obtained for the chromyl acetate oxidation of benzaldehyde, *p*-nitro-, *m*-nitro-, *p*-chloro-, *m*-chloro-, *p*-methyl- and *p*-methoxybenzaldehyde, benzaldehyde-*d*₁, and *p*-nitrobenzaldehyde-*d*₁. These data are listed in Tables II, III, and IV.

TABLE II
SPECTROPHOTOMETRIC RATE DATA FOR THE CHROMYL
ACETATE OXIDATION OF BENZALDEHYDE AT 390 $m\mu$, $T = 25^\circ$ ^a

[ArCHO]	[Cr ⁶⁺]	ϵ_b	ϵ_c	$k_2/[ArCHO]$, l. sec. ⁻¹ mole ⁻¹
0.0169	0.00054	1117	390	0.112
.0466	.00109	1117	390	.099
.0466	.00083	1117	395	.095
.0466	.00083	1117	400	.095
.0483	.00075	1117	395	.102
.0483	.00075	1117	400	.101
.0966	.00051	1117	400	.107
.0966	.00102	1117	400	.099
.0962	.00092	1117	400	.094
.0962	.00462	1117	400	.091
.1398	.00109	1117	390	.106
.1865	.00109	1117	390	.093

Av. 0.100 ± 0.005

^a At this wave length, the initial reaction characterized by k_1 cannot be studied with accuracy and only k_2 was obtained. The values were obtained by the method of least squares.

It can be seen from Table II that the second step in the oxidation of benzaldehyde has a first-order dependence on the concentrations of both the aldehyde and the oxidant when both are varied over a range of approximately ten. The data of Table III show that the rate constant for this step is independent of the wave length used, and that the first step in the oxidation also has a first-order kinetic dependence on the concentrations of aldehyde and oxidant. The calculated values of ϵ_b and ϵ_c permit one to estimate the spectrum of the two chromium species which are involved, and these data are plotted in Fig. 2.

The *m*- and *p*-chloro substituted and the *m*-nitro substituted aldehydes gave the same kinetic behavior

TABLE III
 SPECTROPHOTOMETRIC RATE DATA FOR THE CHROMYL ACETATE OXIDATION OF BENZALDEHYDE

Wave length, m μ	[ArCHO]	[Cr ⁵⁺]	ϵ_a	ϵ_a^a	ϵ_b	ϵ_c	$k_1/[ArCHO]$	$k_2/[ArCHO]$
390	0.0483	0.00075	1117	1190	905	395	0.41	0.102
414	.0483	.000936	715	800	725	355	.34	.106
440	.0962	.00183	425	495	580	270	.26	.101
465	.0193	.00180	210	235	465	235	.26	.138
465	.0241	.00174	210	235	410	235	.31	.116
465	.0338	.00180	210	250	465	235	.25	.147
465	.0483	.00180	210	215	415	230	.41	.133
465	.0483	.00183	210	235	425	235	.39	.091
465	.0483	.00374	210	230	470	230	.29	.082
465	.0966	.00180	210	240	425	235	.28	.109
490	.0483	.00374	120	135	315	200	.27	.088
490	.0483	.00321	120	125	350	200	.32	.112
520	.0483	.00936	65	50	145	220	.30	.137
550	.0483	.00936	35	35	250	170	.31	.100
600	.0483	.00936	8	10	205	155	.33	.101

 Av. 0.32 ± 0.04 0.111 ± 0.016

^a These values of ϵ_a minimize the average deviation.

as benzaldehyde. The first step in the oxidation of *p*-nitrobenzaldehyde gave the same behavior as the first step for benzaldehyde, but the second step gave

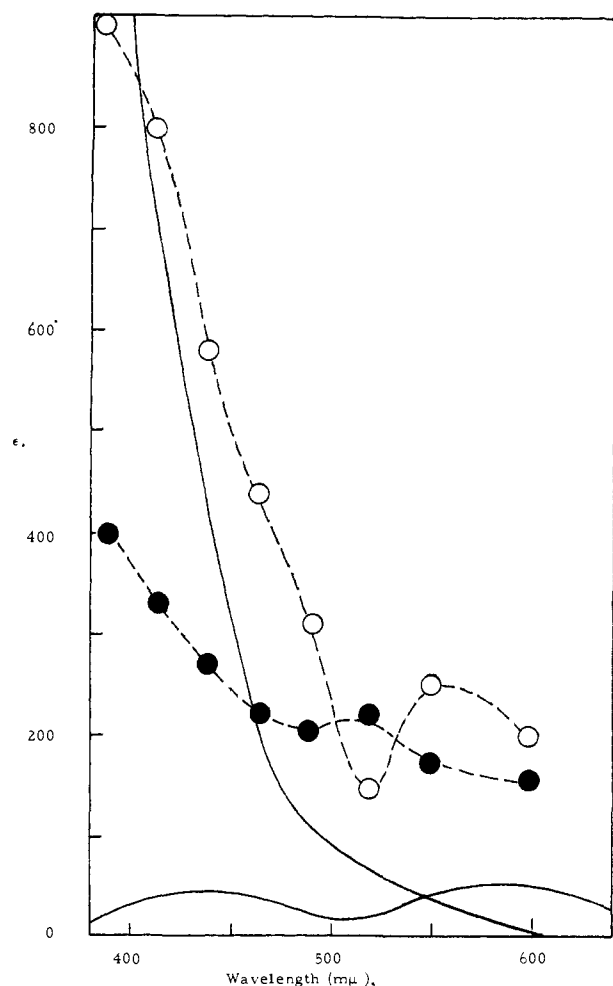


Fig. 2.—Spectra of chromyl acetate (high absorbance solid line), chromic acetate (low absorbance solid line); chromium(V) (open circles), and chromium(IV) (closed circles).

a one-half order dependence on the aldehyde. The second step in the oxidation of *p*-methoxybenzaldehyde gave the same behavior as the second step for benzaldehyde, but the first step appeared to give roughly a

second-order dependence on aldehyde. Finally, the oxidation of *p*-tolualdehyde proceeded faster than any of the other aldehydes and the oxidation appeared to involve the methyl group. We have found that toluene is oxidized by chromyl acetate at a rate comparable to that for benzaldehyde.

All of the data given in the tables are for spectrophotometric runs. The titrimetric runs gave similar rate constants, but the reproducibility was poor, possibly because of the difficulty in completely excluding air during the titrimetric run.¹⁰ In the spectrophotometric runs, it was found that air had little effect on k_1 , but had a large catalytic effect on k_2 .

The data on the effect of substituents are summarized in Table V. Plots of $\log k$ against σ are shown in Fig. 3, and it can be seen that a fair correlation is obtained with ρ for step one being -0.2 , and ρ for step two being -0.9 . The data given in Table IV permit

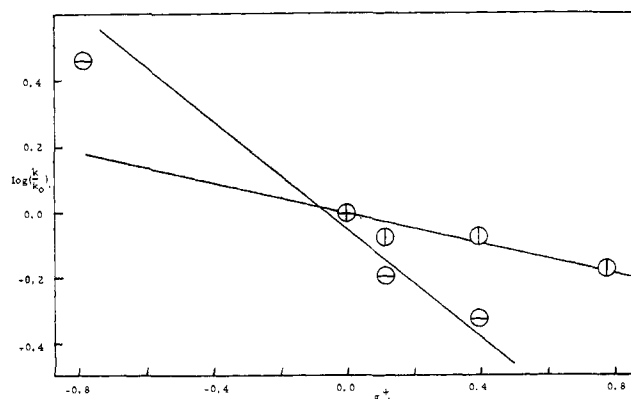


Fig. 3.—Plot of log relative rate against σ^+ .

a calculation of a kinetic hydrogen isotope effect: for benzaldehyde, one finds $k_H/k_D = 2.3$ for step 1, and 3.3 for step 2; for *p*-nitrobenzaldehyde, one finds $k_H/k_D = 9.7$ for step 1 and 2.6 for step 2.

The effect of added acid, base, and salts on the rate of reaction was also studied. Methanesulfonic acid catalyzed both the oxidation of the solvent by chromyl acetate and the conversion of the aromatic aldehyde to the benzal diacetate, making it impractical to study

(10) A detailed account of the titrimetric runs is given in the thesis of P. A. L. and is available through University Microfilms.

TABLE IV
SPECTROPHOTOMETRIC RATE DATA FOR THE CHROMYL
ACETATE OXIDATION OF SUBSTITUTED BENZALDEHYDES, 25°

Substituent	Wave length, m μ	[Ar-CHO]	[Cr ⁶⁺]	k_1 /[ArCHO] l. mole ⁻¹ sec. ⁻¹	k_2 /[ArCHO]
<i>m</i> -Cl	465	0.0189	0.00191	0.38	0.050
	465	.0472	.00191	.26	.048
	465	.0943	.00191	.26	.050
	390	.0227	.00105		.049
	390	.0448	.00082		.052
	390	.0895	.00082		.053
	390	.1895	.00105		.054
	390	.3790	.00105		.049
				0.29 ± 0.05	0.051 ± 0.002
	<i>p</i> -Cl	465	0.0193	0.00167	0.30
465		.0483	.00167	.29	.064
465		.0966	.00167	.24	.064
465		.193	.00167	.24	.056
390		.0475	.000819		.053
390		.0950	.000819		.055
				0.27 ± 0.03	0.062 ± 0.007
<i>m</i> -NO ₂		465	0.0193	0.00178	0.25
	465	.0483	.00178	.18	.0143
	465	.0960	.00178	.20	.0140
	465	.193	.00178	.19	.0177
	440	.0483	.00191		.0139
	440	.0966	.00191		.0141
	440	.0966	.00165		.0137
	440	.193	.00191		.0158
	440	.193	.00165		.0161
	440	.386	.00165		.0159
				0.21 ± 0.03	0.0150 ± 0.0011
	<i>p</i> -NO ₂	465	0.0193	0.00176	0.27
465		.0483	.00176	.29	.0127 ^a
465		.0966	.00176	.35	.0127 ^a
465		.0965	.00205	.32	.0119 ^a
465		.0965	.00510	.33	.0118 ^a
465		.0965	.0101	.33	.0107 ^a
465		.193	.00176	.38	.0107 ^a
440		.0232	.00148		.0112 ^a
440		.0483	.01170		.0112 ^a
440		.0483	.00154		.0114 ^a
440		.0966	.00154		.0112 ^a
440		.0966	.00170		.0117 ^a
440		.193	.00148		.0118 ^a
				0.32 ± 0.02	0.0115 ± 0.0005
<i>p</i> -MeO	465	0.0196	0.00181		0.319
	465	.0489	.00181		.316
	465	.0978	.00181		.304
	390	.0235	.00086		.303
	390	.0470	.00086		.303
				0.309 ± 0.007	
<i>p</i> -H- α -d	390	0.0974	0.000784	0.136	0.0296
	390	.1948	.000784	.151	.0303
	390	.3897	.000784	.151	.0305
			0.146 ± 0.007	0.0301 ± 0.0004	
<i>p</i> -NO ₂ - α -d	465	0.0193	0.00156	0.027	0.0044 ^a
	465	.0483	.00156	.032	.0044 ^a
	465	.0483	.00156	.031	.0042 ^a
	465	.0966	.00156	.032	.0050 ^a
			0.031 ± 0.002	0.0045 ± 0.0003	

^a These values are k_2 /[ArCHO]^{1/2}.

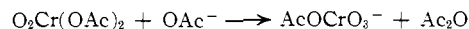
TABLE V
EFFECT OF SUBSTITUENTS ON THE CHROMYL ACETATE
OXIDATION OF BENZALDEHYDE

Compound	k_1 /[ArCHO]	k_2 /[ArCHO]
Benzaldehyde	0.32	0.100
Benzaldehyde- <i>d</i>	.146	.0301
<i>m</i> -Chlorobenzaldehyde	.29	.051
<i>p</i> -Chlorobenzaldehyde	.27	.062
<i>m</i> -Nitrobenzaldehyde	.21	.0150
<i>p</i> -Nitrobenzaldehyde	.32	.0115 ^a
<i>p</i> -Nitrobenzaldehyde- <i>d</i>	.031	.0045 ^a
<i>p</i> -Methoxybenzaldehyde309

^a These values are k_2 /[ArCHO]^{1/2}.

the effect of acid on the oxidation of benzaldehyde. The diacetate was found to be resistant to oxidation. The addition of 5 to 10% of acetic acid had no effect on the rate of reaction. Similarly, benzoic acid had no effect.

Sodium acetate converted chromyl acetate to a different chromium(VI) species as indicated by the change in spectrum. At the same time, the rate of oxidation was markedly reduced. The addition of 1 equivalent of sodium acetate stopped the reaction. The reaction with acetate ion is probably



The addition of chromic acetate had no effect on the rate of reaction. Both manganous ion and cerous ion effected reduction of chromyl acetate making induced oxidation experiments impractical for this reaction.

The kinetic data, although helpful, do not supply much information about the detailed nature of the activated complex. Thus, we were led to examine the possibility of oxygen transfer between chromyl acetate and benzaldehyde. It seemed possible that chromyl acetate, unlike chromic acid in water, would give a negligibly slow oxygen transfer with its solvent, acetic anhydride. This was tested by equilibrating chromium trioxide with water containing 1.7% excess oxygen-18. After drying, the chromium trioxide was dissolved in acetic anhydride, and diphenyl sulfide was added to one portion. After 1 and 2 hr., diphenyl sulfide was added to other portions of the chromyl acetate solution. Diphenyl sulfide reacts very rapidly with chromyl acetate to give diphenyl sulfone, which hopefully might be formed with complete oxygen transfer.

After isolation and purification, the diphenyl sulfone was analyzed for its oxygen-18 content by the method of Doering and Dorfman.¹¹ The diphenyl sulfone formed immediately after preparing the chromyl acetate solution contained 1.087 \pm 0.004% O¹⁸, the material formed after 1 hr. standing contained 1.010 \pm 0.003% O¹⁸ and after 2 hr. the diphenyl sulfone formed had 0.971 \pm 0.005% O¹⁸. Thus the exchange is quite slow.

Benzaldehyde was allowed to react with labeled chromyl acetate (0.806% excess O¹⁸), giving benzoic acid with 0.274% excess O¹⁸. When benzoic acid having 1.272% excess O¹⁸ was dissolved in acetic anhydride and treated under the conditions used for the reaction and subsequent hydrolysis, without adding chromyl acetate, the recovered acid had 0.826% excess O¹⁸ indicating a loss of 35% of the label (presumably *via* mixed anhydride formation and partial benzoyl-oxygen bond cleavage in the hydrolysis). If one assumes that the same extent of exchange will occur subsequent to the oxidation of benzaldehyde, the above data indicate 104 \pm 5% oxygen transfer.

p-Nitrobenzaldehyde was oxidized in the same fashion using chromyl acetate having 0.883% excess O¹⁸. The acid formed had only 0.021% excess O¹⁸. When *p*-nitrobenzoic acid (0.281% excess O¹⁸) was dissolved in acetic anhydride and reisolated as above, it was found to have 0.090% excess O¹⁸, indicating 76% loss of the label. Making the same assumption

(11) W. von E. Doering and E. Dorfman, *J. Am. Chem. Soc.*, **75**, 5595 (1953).

about exchange as above, the data indicate $20 \pm 3\%$ oxygen transfer.

Finally, an attempt was made to determine the nature of the chromium intermediate which was first formed. The electron spin resonance spectra of reaction mixtures of chromyl acetate with benzaldehyde were examined: no spectrum corresponding to an organic free radical, with $g = 2.00+$, could be observed, but spectra corresponding to a chromium species with $g = 1.973 \pm 0.004$ was found. The spectrum was found to decrease with time, becoming unobservable after about 1 hr. from the time of initiation of the reaction.

If the species giving the observed spectrum were Cr(III), one would expect its concentration, and hence the intensity of the spectrum, to increase with time. A Cr(IV) species, having two unpaired electrons and $S = 1$, would be expected to give a broad spectrum with two peaks of low intensity because of the breadth. Such a spectrum has been observed for chromium dioxide.¹² With the spectrometer used in this work, having a relatively low sensitivity, no spectrum could be observed from a 20% solution of chromium tetra-*t*-butoxide¹³ in carbon tetrachloride.

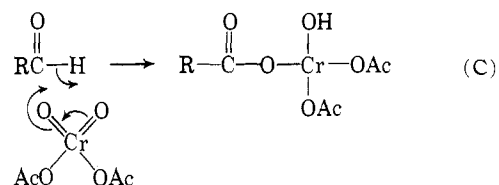
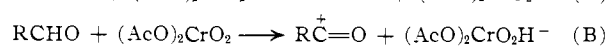
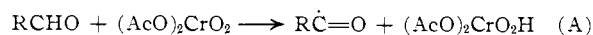
A Cr(V) species, with one unpaired electron, $S = 1/2$, would be expected to give rise to an e.s.r. spectrum with one main peak. Such a spectrum has been observed with the hypochromate ion, CrO_4^{-3} , with $g = 1.97$.¹² The spectrum was not observed at temperatures above 20°K. due to temperature dependent spin-orbit coupling, which broadens the spectrum so much at higher temperatures that it cannot be seen. The spin-orbit coupling, however, is dependent upon the symmetry of the species. If the Cr(V) species were rendered unsymmetrical, as in $(\text{AcO})_2\text{Cr}(\text{OH})\text{O}$, the spectrum might be seen at room temperature. For example, Chien and Boss¹⁴ could not observe an e.s.r. spectrum between 90 and 330°K. for vanadium tetrachloride and other symmetrical V(IV) compounds (isoelectronic with Cr(V)), but well resolved spectra were observed at 300°K. from the unsymmetrical $\text{VCl}_2(\text{OR})_2(\text{ROH})$ where R is *n*- or *t*-butyl. It appears that the e.s.r. spectra of the oxidation reaction mixtures must arise from a Cr(V) species.

The same spectrum could be observed in the absence of benzaldehyde, and presumably also arises from the known slow oxidation of acetic anhydride by chromyl acetate. The e.s.r. results do not necessarily demonstrate that a Cr(V) species is formed in the oxidation of benzaldehyde, but do show that such a species is formed in the reduction of chromyl acetate. It seems reasonable to assume that the chromium species initially formed in the oxidation of benzaldehyde is Cr(V).

Discussion

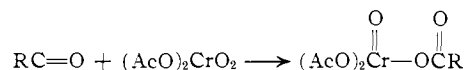
The oxidation of benzaldehyde by chromyl acetate has been found to proceed in two steps. The first probably forms Cr(V) and the second leads to Cr(IV). Both reactions have rates which are first order in benzaldehyde and in the oxidant; both give a kinetic isotope effect, oxygen transfer from the oxidant, and a small negative value of ρ .

The observation of a kinetic isotope effect indicates that carbon-hydrogen bond cleavage occurs in the rate-determining step. The possible mechanisms for this step are



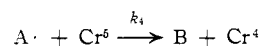
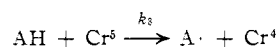
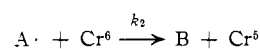
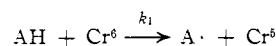
The formation of an acylium ion as in B would require that the reaction have a relatively large value of ρ , which is not in agreement with the experimental findings. Both A and C are satisfactory for the reaction of Cr(VI), but C is unlikely for the oxidation by Cr(V) since reduction to Cr(III) would then occur. We have observed that Cr(III) is not oxidized to Cr(IV) (the observed final chromium species) by Cr(VI) or any other species present in the reaction mixture. It is therefore concluded that Cr(V) reacts *via* process A, and it will be assumed that Cr(VI) reacts similarly.

The initial reaction would be followed by reaction with another Cr(VI) or Cr(V) to give a mixed anhydride



The fate of the mixed anhydride cannot be determined. It may react with the solvent to give benzoic acetic anhydride which will be hydrolyzed on working up the reaction mixture.

With these conclusions in mind, the reaction sequence may be written as



where AH is the aldehyde, A· is the acyl radical, and B is the acid derivative which is formed. The rate expressions are

$$d[\text{AH}]/dt = -k_1[\text{AH}][\text{Cr}^6] - k_3[\text{AH}][\text{Cr}^5]$$

$$d[\text{A}\cdot]/dt = k_1[\text{AH}][\text{Cr}^6] + k_3[\text{AH}][\text{Cr}^5] - k_2[\text{A}\cdot][\text{Cr}^6] - k_4[\text{A}\cdot][\text{Cr}^5]$$

$$d[\text{Cr}^6]/dt = -k_1[\text{AH}][\text{Cr}^6] - k_2[\text{A}\cdot][\text{Cr}^6]$$

$$d[\text{Cr}^5]/dt = k_1[\text{AH}][\text{Cr}^6] + k_2[\text{A}\cdot][\text{Cr}^6] - k_3[\text{AH}][\text{Cr}^5] - k_4[\text{A}\cdot][\text{Cr}^5]$$

Using the steady state approximation, the concentration of A· may be eliminated from the expressions giving

$$\frac{d[\text{Cr}^6]}{dt} = -k_1[\text{AH}][\text{Cr}^6] - k_2[\text{AH}] \frac{k_1[\text{Cr}^6] + k_3[\text{Cr}^5]}{k_2[\text{Cr}^6] + k_4[\text{Cr}^5]}$$

(12) A. Carrington, D. J. E. Ingram, D. Schonland, and M. C. R. Symons, *J. Chem. Soc.*, 4710 (1956).

(13) N. Hagihara and H. Yamazaki, *J. Am. Chem. Soc.*, **81**, 3160 (1959).

(14) J. C. W. Chien and C. R. Boss, *ibid.*, **83**, 3767 (1961).

$$\frac{d[\text{Cr}^5]}{dt} = k_1[\text{AH}][\text{Cr}^6] - k_3[\text{AH}][\text{Cr}^5] + (k_2[\text{Cr}^6] - k_4[\text{Cr}^5])[\text{AH}] \frac{k_1[\text{Cr}^6] + k_3[\text{Cr}^5]}{k_2[\text{Cr}^6] + k_4[\text{Cr}^5]}$$

The rate equations thus derived may be compared with those which were, in effect, assumed when obtaining the rate constant for the reactions of Cr(VI) and Cr(V) from the experimental data

$$d[\text{Cr}^6]/dt = -2k_1[\text{AH}][\text{Cr}^6]$$

$$d[\text{Cr}^5]/dt = 2k_1[\text{AH}][\text{Cr}^6] - 2k_3[\text{AH}][\text{Cr}^5]$$

It is difficult to estimate the effects of including all four rate constants on the results calculated on the two-step basis. Therefore resort was made to the use of numerical integration to obtain the concentrations of each species as a function of time for some assumed values of k_2 and k_4 . The results are presented in Table VI.

TABLE VI
RESULTS OF NUMERICAL INTEGRATION FOR TWO- AND FOUR-STEP SCHEMES

k_1	k_2	k_3	k_4	$t_{\text{max. sec.}}$	$[\text{Cr}^5]_{\text{max}}/[\text{Cr}^5]_0$
0.17	0.053	100	100	100	0.46
.17	.053	200	200	98	.46
.17	.053	500	500	96	.46
.17	.053	1000	1000	96	.46
.17	.053	500	100	109	.62
.17	.053	100	500	88	.28
.34	.106	0	0	104	.58

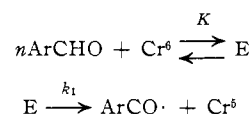
The last line gives the results for the two-step scheme, and the value of t_{max} (the time at which the maximum concentration of Cr(V) is reached) agrees with that experimentally observed. It may be noted that the results are not particularly sensitive to the magnitude of k_2 and k_4 , but are sensitive to their ratio. If k_2 and k_4 were approximately equal, both k_1 and k_3 should be increased slightly to give accord with the experimental data. If k_2 were somewhat greater than k_4 , the values of k_1 and k_3 would be correct. Only if k_4 were greater than k_2 would they be considerably in error. Considering the nature of the reaction in question, it would be reasonable to expect k_2 to be somewhat greater than k_4 since the Cr(VI) species would statistically have twice as good a possibility to react as compared to the Cr(V) species and, except for the steric factor, the reaction probability of oxidants reacting with a free radical would be expected to be high and approximately equal (diffusion controlled). Since it is not possible to measure k_2 and k_4 , we are forced to assume that the values of k_1 and k_3 obtained from the kinetic analysis are approximately correct.

Although it could hardly be considered as definitive, the result of the oxidation of triphenylacetaldehyde by chromyl acetate gives some support for the above mechanism. The reaction gave 90% of the theoretical amount of triphenylcarbinol and carbon monoxide, and no triphenylacetic acid. This may be compared with other oxidations: permanganate gave essentially only triphenylacetic acid, chromic acid in aqueous acetic acid gave 61% triphenylcarbinol and 24% triphenylacetic acid, and ceric ion gave only triphenyl-

carbinol.¹⁵ These data suggest that the ester mechanism for aldehyde oxidation leads to triphenylacetic acid, and that other mechanisms lead to triphenylcarbinol and carbon monoxide.

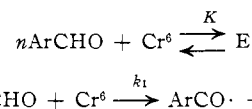
There is, however, an indication that the initial reaction between chromyl acetate and benzaldehyde is complex formation. As the concentration of benzaldehyde is increased, the extrapolated value of ϵ_a diverges increasingly from that of chromyl acetate suggesting that a comparatively rapid reaction between the aldehyde and chromyl acetate occurs before appreciable oxidation is effected.

Two formulations are possible. In the first, a complex E is rapidly formed and decomposes to give chromium(V).



Under pseudo-first-order conditions, the integrated rate expression for this case is the same as that for the simpler set of steps given previously except that the value of ϵ_a is replaced by $(\epsilon_a + \epsilon_e K b^n)/(1 + K b^n)$ where b is the concentration of benzaldehyde (a constant), K is the equilibrium constant for the first step, and ϵ_e is the absorptivity index of the complex. At the same time, k_1 is replaced by $k_1 K b^n/(1 + K b^n)$.

In the second, the complex is nonreactive and does not lead to products



The same integrated rate expression is obtained, but here ϵ_a is replaced by $(\epsilon_a + \epsilon_e K b^n)/(1 + K b^n)$ and k_1 is replaced by $k_1/(1 + K b^n)$.

It can be seen that either of these cases would give the same result for the extrapolated value of the absorptivity index at $t = 0$.

$$\epsilon_a' = \frac{\epsilon_a + \epsilon_e K b^n}{1 + K b^n}$$

This may be rearranged to

$$(\epsilon_a' - \epsilon_a)/b^n = \epsilon_e K - \epsilon_a' K$$

Therefore, if the correct value of n were chosen, a plot of $(\epsilon_a' - \epsilon_a)b^n$ against ϵ_a' would give a straight line with a slope $-K$ and an intercept $\epsilon_e K$. For a group of runs made at 5°, with $[\text{ArCHO}] = 0.048$ to $0.24 M$, the deviation between ϵ_a' and ϵ_a could be obtained with sufficient precision to test the expression (Table VII).

TABLE VII
DATA FOR EVALUATION OF EQUILIBRIUM CONSTANT FOR THE FORMATION OF THE INITIAL COMPLEX

Wave length, m μ	T , °C.	$[\text{C}_6\text{H}_5\text{CHO}]$	$[\text{Cr(VI)}]$	ϵ_a	ϵ_a'
465	5	0.0483	0.00188	212	285
465	5	.0966	.00264	212	345
465	5	.193	.00264	212	435
465	5	.241	.00188	212	470

Using $n = 1$, a linear relationship was found (Fig. 4) leading to the values $K_{5^\circ} = 2.5 \pm 0.1$ l./mole and

(15) K. B. Wiberg and W. Richardson, *J. Am. Chem. Soc.*, **84**, 2800 (1962).

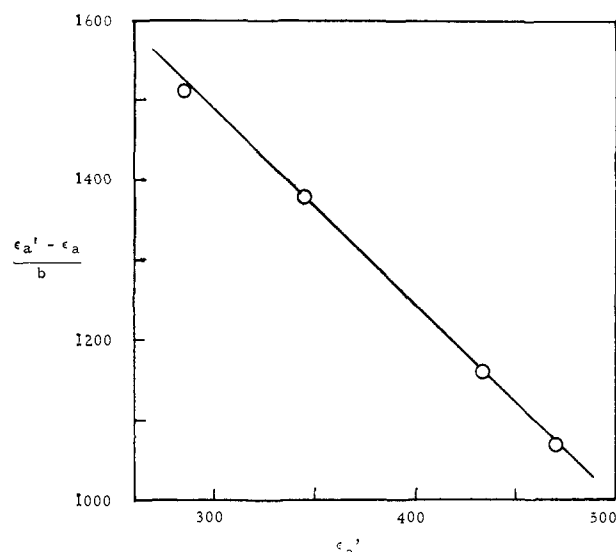


Fig. 4.—Evaluation of the equilibrium constant for the benzaldehyde-chromyl acetate complex.

$\epsilon_e = 900 \pm 10$, at 465 $m\mu$. Assuming ϵ_e to be temperature independent, data at 25° led to $K_{25^\circ} = 1.4 \pm 0.2$ l./mole. Under the conditions used in the experiments at 25°, the amount of complex present was negligible.

Chromyl acetate would be expected to behave in a fashion similar to that of chromyl chloride. It has been observed in the oxidation of hydrocarbons by the latter that a complex is probably formed before the oxidation step.¹⁶ Thus complex formation may be quite general for chromyl compounds. However, the nature of the complexes remains to be determined.

It seems appropriate to compare the oxidation of benzaldehyde by chromyl acetate and by chromic acid. In the latter reaction, ρ is +1.02, whereas in the former $\rho = -0.2$ or -0.9 depending on which step is being considered. The chromic acid oxidation is acid catalyzed, whereas there is no obvious acid catalysis of the chromyl acetate reaction.

It has been proposed that the chromic acid oxidation of aldehydes proceeds *via* an ester intermediate in analogy with the permanganate oxidation of aldehydes.¹⁷ Is it possible that the chromic acid oxidation also involves a hydrogen atom abstraction? The answer is probably no. Two pieces of evidence point to the aldehyde hydrate (or an equivalent structure) as an intermediate in the reaction. First, this is probably necessary in order to explain the effect of substituents on the reaction.¹⁸ Second, the oxidation rate for benzaldehyde is not increased as rapidly by a decrease in water concentration in acetic acid-water mixtures as is the oxidation of isopropyl alcohol, suggesting that a molecule of water is involved in some kinetically important stage in the oxidation of benzaldehyde. Thus, hydrogen abstraction would have to occur on the hydrate of the aldehyde rather than on the aldehyde itself. This appears quite unreasonable since the hydrate is in low concentration compared to the aldehyde, and since the acyl radical should be more easily formed than its hydrate. Some suggestive

evidence in favor of the ester mechanism comes from the observation that the oxidation of triphenylacetaldehyde by chromic acid leads to triphenylacetic acid in an amount corresponding to the fraction of the reaction which is affected by chromium(VI). The oxidation of this aldehyde by permanganate (which probably involves an ester mechanism) gives only triphenylacetic acid, whereas other reagents such as ceric ion and chromyl acetate give only triphenylcarbinol.

The above conclusions about the chromyl acetate oxidation of benzaldehyde probably also apply to the oxidation of *m*- and *p*-chlorobenzaldehydes and *m*-nitrobenzaldehyde. The oxidation of *p*-methoxybenzaldehyde was different, but this may result from ring oxidation as a competing reaction. The case of *p*-nitrobenzaldehyde is interesting in that it gave a much higher kinetic isotope effect for the oxidation by chromyl acetate than did benzaldehyde, it gave a much lower degree of oxygen transfer, and it gave a different kinetic behavior for the second oxidation step. These data suggest a change in mechanism, but the data are not yet sufficient to define properly the change.

Experimental

Materials.—Benzaldehyde was Matheson Coleman and Bell "chlorine free" product. It was purified immediately before use by distilling 5 to 10 ml. through a small one-piece distillation apparatus under a nitrogen atmosphere, taking a center cut of 3 to 5 ml., and redistilling. Another method involved the formation of the bisulfite addition compound, regeneration of the aldehyde, and distillation. No difference could be noted in the results using these two methods of purification.

The liquid substituted benzaldehydes were doubly distilled, under nitrogen, immediately before use: *p*-methoxybenzaldehyde (Matheson), b.p. 143–144° at 39 mm. and 247–248° at 760 mm.; *p*-methylbenzaldehyde (Matheson practical grade purified *via* the bisulfite addition compound), b.p. 105–106° at 34 mm. and 204–205° at 760 mm.; *m*-chlorobenzaldehyde (L. Light and Co., purified *via* the bisulfite addition compound), b.p. 122–122.5° at 45 mm., and 213–214° at 760 mm. The solid aldehydes *p*-chloro- (Eastman), *m*-nitro- (Eastman), and *p*-nitrobenzaldehyde (prepared according to Lieberman and Connor¹⁹) were washed with 10% sodium carbonate to remove the acidic impurity, recrystallized twice from ethanol-water mixtures, and sublimed at 1–2 mm. pressure at a temperature slightly higher than the melting point.

Chromium trioxide, reagent grade, was recrystallized from water, dried over phosphorus pentoxide at 100° and 1 mm., and stored over phosphorus pentoxide.

The commercial, reagent grade acetic anhydride was found to contain a small amount of impurity which reduced chromyl acetate. A solution of chromium trioxide in this acetic anhydride lost 5% of its titer in 1 hr. at 0°. Distillation did not remove the impurity. Therefore, the anhydride was distilled through an 11-plate bubble cap column to remove acetic acid, and 10 g. of chromium trioxide was added to each liter of the solvent. After standing for 3 days, acetic anhydride was distilled from the mixture at 35° and 8 mm. or 28° and 5 mm. using a 15-cm. glass helix-packed column, and a system which did not use grease to seal the ground joint connections. It was important to keep the temperature below 50° during the distillation; above this temperature an explosive reaction occurred in which the chromium was reduced to chromium(III). Solutions of chromium trioxide in acetic anhydride prepared in this fashion gave no observable decomposition at 0° for 8 hr.; at 25° the titer decreased about 1.2% per hour. The acetic anhydride was stored under nitrogen.

p-Nitrobenzaldehyde-*d*₁.—To a stirred solution of 2.00 g. of lithium aluminum deuteride in 100 ml. of anhydrous ether was added 13.8 g. of ethyl benzoate. After heating to reflux for 2

[16] O. H. Wheeler, *Can. J. Chem.*, **38**, 2137 (1960).

[17] K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958).

[18] K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960); J. Rócek, *Tetrahedron Letters*, **No. 5**, 1 (1959).

[19] S. V. Lieberman and R. Connor, "Organic Syntheses," Coll. Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 441.

hr., 35 ml. of 30% Rochelle salt solution was added. The ether layer was separated and the residue was extracted with ether. The combined ether solution was dried over anhydrous sodium sulfate, and the ether was removed using a rotary evaporator giving 8.0 g. (79%) of crude benzyl- d_2 alcohol.

To 8.0 g. of benzyl- d_2 alcohol was added 20 ml. of glacial acetic acid and 20 ml. of acetic anhydride. The mixture was heated on a steam cone for 6 hr., 250 ml. of water was added, and after the hydrolysis of the acetic anhydride was complete, the solution was extracted with four 50-ml. portions of ether. The ether solution was washed several times with 10% sodium carbonate solution and with saturated sodium sulfate. The ether was removed using a rotary evaporator giving 10.7 g. (97%) of crude benzyl- d_2 acetate.

The acetate (10.7 g.) was added dropwise, over a period of 30 min., to 30 ml. of fuming nitric acid maintained at a temperature below -10° by cooling in an ice-salt bath. The addition of 200 ml. of ice water, followed by suction filtration, yielded 13.0 g. of a mixture of a solid and a yellow oil, which appeared to be largely the *p*- and *o*-isomers, respectively. Recrystallization from 95% ethanol gave 4.4 g. (32%) of *p*-nitrobenzyl- d_2 acetate, m.p. 75.1–76.4°. ²⁰

A solution of 2.21 g. of *p*-nitrobenzyl- d_2 acetate and 1.66 g. of sodium hydroxide in a mixture of 20 ml. of purified dioxane and 25 ml. of deuterium oxide was allowed to stand at room temperature for 12 hr. The volume was reduced to 20 ml. by distillation under reduced pressure. The brown solid was filtered and recrystallized from water giving 1.45 g. (86%) of *p*-nitrobenzyl- d_2 alcohol as white crystals, m.p. 90.7–92.2°.

To a solution of 1.75 g. of dinitrogen tetroxide in 6 ml. of carbon tetrachloride was added 2.39 g. of *p*-nitrobenzyl- d_2 alcohol. The mixture was stoppered and maintained at 0° for 15 min., and at room temperature for 72 hr. Volatile material was removed under reduced pressure giving 2.4 g. of a mixture of *p*-nitrobenzoic acid and *p*-nitrobenzaldehyde. The acid was extracted with 10% sodium carbonate solution, and the aldehyde was recrystallized from water giving 0.75 g. (32%) of *p*-nitrobenzaldehyde- d_1 . The aldehyde was further purified *via* the bisulfite addition compound and sublimation at 2 mm. pressure, and had m.p. 104.0–105.0°. The infrared spectrum showed bands at 4.75 and 4.87 μ (aldehyde C–D) and no bands at 3.58 and 3.70 μ (aldehyde C–H).

Solutions.—Because of the slow oxidation of the solvent by chromyl acetate, solutions of this reagent were prepared immediately before each experiment. Chromium trioxide dissolves quite slowly in acetic anhydride; therefore the solutions were prepared by adding a large excess of chromium trioxide to the acetic anhydride, swirling until the color of the solution indicated that the concentration was at or above the desired level, filtering the solution through a glass wool plug, and analyzing for the Cr(VI) concentration. The solution was diluted to the desired concentration and again analyzed for Cr(VI).

Aldehyde solutions were also prepared immediately before use because of the rapid air oxidation of the aldehydes in solution. Freshly distilled benzaldehyde gave a negative starch-iodide test for peroxides, but immediately on being dissolved in acetic anhydride it gave a positive test. Benzaldehyde was measured volumetrically using a calibrated 0.25-ml. syringe. Solutions of the other aldehydes were prepared by direct weighing.

Kinetic Method.—The chromyl acetate solution was placed in one arm of an inverted U-tube which was attached to a spectrometer cell at its center. The aldehyde solution was placed in the other arm. The solutions were degassed in the reaction vessel at a pressure of 10^{-3} mm. using a mercury diffusion pump. The temperature of the solution was brought to 25° using a thermostated water bath, and the reaction vessel was inverted to allow the solutions to mix and flow into the spectrometer cell. The cell was placed in a thermostated water bath placed in the light path of a Beckman DU spectrometer, and the change in optical density with time was noted.

(20) The reported m.p. for unlabeled material is 78° : F. Beilstein and A. Kuhlberg, *Ann.*, **147**, 339 (1868).

Oxygen-18 Labeling Experiments.—Preparation of Chromium Trioxide- O^{18} .—To 2.0 ml. of water containing 1.70% O^{18} was added 1.0 g. of chromium trioxide. The solution was allowed to stand for 20 hr. before distilling the water under reduced pressure. The residue was dried at 100° and 1 mm. over phosphorus pentoxide.

Reaction of Diphenyl Sulfide with Chromyl Acetate- O^{18} .—Diphenyl sulfide was purified by distillation, the fraction boiling at 122 – 123° at 5 mm. being collected. The reactants for each run consisted of 0.10 g. of diphenyl sulfide and 0.20 g. of chromium trioxide- O^{18} in 20 ml. of acetic anhydride under a nitrogen atmosphere. For the first run, chromium trioxide and diphenyl sulfide were added to the acetic anhydride simultaneously. For the second, the diphenyl sulfide was added 1 hr. after the chromium trioxide (most of this hour was required for solution of the chromium trioxide to be effected), and for the third, the diphenyl sulfide was added 2 hr. after the chromium trioxide. The reaction appeared to proceed almost instantaneously. After an additional hour, each reaction mixture was quenched with a solution of 0.16 g. of arsenous acid in 25 ml. of water. After hydrolysis of the acetic anhydride had occurred, the mixture was extracted with three 12-ml. portions of methylene chloride. The methylene chloride solution was washed with two 8-ml. portions of water and with 8 ml. of saturated sodium chloride solution, and was dried over anhydrous sodium sulfate. Evaporation of the solvent gave 0.11 g. (96%) of diphenyl sulfone, m.p. 123.5 – 124.3° . Each product was recrystallized from 75% ethanol and dried at 56° and 0.8 mm. over phosphorus pentoxide. Analysis of the three samples for O^{18} content gave 1.087, 1.010, and 0.971%, respectively. Based on the quantities used in the equilibration of chromium trioxide with water, the maximum O^{18} content of the diphenyl sulfone would be 1.38%. Water picked up by chromium trioxide during weighing and transfer and exchange occurring during the dissolving of the chromium trioxide in acetic anhydride would reduce this value. Considering this, 90% or more oxygen transfer from chromyl acetate to diphenyl sulfide occurred. In the absence of other data, this will be assumed to be 100%, and this assumption is in agreement with the results of the oxidation of benzaldehyde.

Reaction of Benzaldehyde with Chromyl Acetate- O^{18} .—A solution of 0.20 ml. of benzaldehyde in 2 ml. of acetic anhydride was prepared and 0.25 g. of chromium trioxide- O^{18} was dissolved in 16 ml. of acetic anhydride over the course of an hour. Each solution was degassed and then mixed. After 1 hr. at room temperature the solution was poured into 20 ml. of water containing 0.08 g. of arsenous acid. After hydrolysis of the acetic anhydride had occurred, the mixture was extracted with three 8-ml. portions of methylene chloride. The methylene chloride solution was washed with water to remove most of the acetic acid, and was extracted with two 5-ml. portions of 10% sodium carbonate solution. The sodium carbonate solution was heated on a steam cone to drive off methylene chloride, and then acidified with concentrated hydrochloric acid. The solid was filtered and washed with a little water giving 0.171 g. (76%) of benzoic acid. The acid was dried over phosphorus pentoxide and sublimed at 90° and 2 mm., and had m.p. 121.8 – 122.2° .

Reaction of *p*-Nitrobenzaldehyde with Chromyl Acetate- O^{18} .—To a solution of 0.13 g. of *p*-nitrobenzaldehyde in 13 ml. of acetic anhydride was added 0.13 g. of chromium trioxide- O^{18} under a nitrogen atmosphere. After 2.5 hr., acetic anhydride was distilled from the mixture at 6 mm. pressure until the volume was reduced to 4 ml. Ice-water (30 ml.) was added, and after the hydrolysis of the acetic anhydride the solid was filtered giving 0.116 g. (79%) of *p*-nitrobenzoic acid.

Isotopic Dilution Analysis.—To separate arms of a reaction vessel similar to that used for the kinetic runs was added 9 ml. of a 0.174 *M* solution of chromyl acetate in acetic anhydride, and a solution of 0.250 g. (2.41 mmoles) of benzaldehyde in 4 ml. of acetic anhydride containing 0.1170 g. of benzoic acid- C^{14} (0.959 mmoles, 2440 d.p.m./mg.). After degassing, the solutions were mixed and allowed to stand for 10 hr. The benzoic acid was isolated as described above.