Organic and Biological Chemistry

Reductive Coupling of Benzaldehyde by Chromium(II) Salts

Dennis D. Davis and W. Brooks Bigelow

Contribution from the Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88001. *Received September 27, 1969*

Abstract: Benzaldehyde is reduced by Cr(II) salts in aqueous acidic ethanol to hydrobenzoin and the ethyl ethers of hydrobenzoin. A kinetic study of the reaction indicates a multipath reaction mechanism, with a rate law of the form, $k_{obsd}[Cr(II)] = k_1[Cr(II)][PhCHO][H^+] + k_2[Cr(II)][PhCHO]^2[H^+] + k_3[Cr(II)][PhCHO][H^+][Cl^-] + k_4 \cdot [Cr(II)][PhCHO]^2[H^+][Cl^-]$. A mechanism is proposed which involves initial ligand-transfer reduction of a halohydrin or a protonated hydrate (or hemiacetal) of benzaldehyde. Similar reduction of "dimeric" forms of benzaldehyde addition compounds are suggested to account for two terms in the rate law. An organochromium species is postulated as an intermediate in the formation of the coupled products.

Since the identification and characterization of the benzylchromium ion, $PhCH_2Cr^{2+}$, as an intermediate in the reduction of benzyl chloride by Cr(II) salts,[1] there has been a rebirth of interest in chromous reductions.[2] The present work describes the kinetics and mechanism for the bimolecular reduction of benzaldehyde by Cr(II) salts in aqueous acidic ethanol.

In 1926 Conant and Cutter[3] observed that chromous and vanadous salts reductively coupled benzaldehyde to hydrobenzoin. Aliphatic aldehydes and ketones, aromatic ketones, and esters are unreactive, while typical aromatic aldehydes, α,β-unsaturated aldehydes, and some α,β-unsaturated ketones undergo a one-electron reduction with formation of bimolecular products. Qualitative kinetic evidence showed that the reaction rate increased upon addition of acid and thus they proposed reduction of a protonated carbonyl compound to a radical which subsequently dimerizes. Other reports indicate that benzaldehyde and acetophenone are reduced to the corresponding alcohols by Cr(II) sulfate in aqueous dimethylformamide[4] or by ammoniacal Cr(II) sulfate.[5]

Protolytic reduction and coupling are common reaction paths exhibited by the reactive benzylic[6,7] and certain alkyl halides.[8,9] These classes of compounds proceed through a common intermediate, an organochromium ion, with the products being determined by its subsequent reactions. The formation of both coupled products and protolytic reduction products from the reduction of benzaldehyde suggests that the reaction scheme proposed for the reduction of organic halides may also apply to carbonyl compounds.

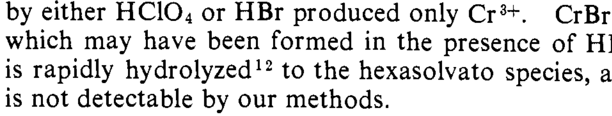
$$RX + 2Cr^{2+} \longrightarrow RCr^{2+} + CrX^{2+} \qquad (1)$$

$$RCr^{2+} + H^+ \longrightarrow RH + Cr^{3+} \qquad (2)$$

$$RCr^{2+} + RX \longrightarrow RR + CrX^{2+} \qquad (3)$$

Results

Benzaldehyde is slowly reduced by Cr(II) in aqueous acidic ethanol at room temperature to give mainly coupled products, with the product distribution depending only slightly upon the acid used. In the presence of HCl, PhCHO is reduced to (mol %, based on starting PhCHO) 69% hydrobenzoin, 11% hydrobenzoin monoethyl ether, 2.6% hydrobenzoin diethyl ether, and 3.5% benzyl alcohol. The reduction in the presence of $HClO_4$ produces 57.5% hydrobenzoin, 21.3% hydrobenzoin monoethyl ether, 2.1% hydrobenzoin diethyl ether, and 1.7% benzyl alcohol. Trace amounts of toluene and benzyl ethyl ether were observed in both cases.



$$PhCHO + Cr^{2+} + H^+ \xrightarrow{EtOH-H_2O} \underset{HO\quad OH}{PhCHCHPh} + \underset{HO\quad OEt}{PhCHCHPh} + \underset{EtO\quad OEt}{PhCHCHPh} + PhCH_2OH \qquad (4)$$

Inorganic products[10] were separated by ion-exchange chromatography[10] and measured spectrophotometrically.[11] The reaction in the presence of HCl produced Cr^{3+} (24%) and $CrCl^{2+}$ (64%). Reactions promoted by either $HClO_4$ or HBr produced only Cr^{3+}. $CrBr^{2+}$, which may have been formed in the presence of HBr, is rapidly hydrolyzed[12] to the hexasolvato species, and is not detectable by our methods.

The stoichiometry of the reaction was determined by allowing benzaldehyde to react with excess Cr(II) for several days and back-titrating to determine the amount of Cr(II) consumed. After 1 week at room temperature, 0.037 mol of Cr(II) was consumed by

---

(1) F. A. L. Anet and E. LeBlanc, *J. Amer. Chem. Soc.*, **79**, 2649 (1957).

(2) For reviews on chromous reductions see (a) J. K. Kochi, *Rec. Chem. Progr.*, 27, 207 (1966); (b) J. R. Hanson and E. Premuzic, *Angew. Chem., Int. Ed. Engl.*, 7, 247 (1968).

(3) J. B. Conant and H. B. Cutter, *J. Amer. Chem. Soc.*, **48**, 1016 (1926).

(4) C. E. Castro and W. C. Kray, Jr., *ibid.*, **88**, 4447 (1966).

(5) K. D. Kopple, *ibid.*, **84**, 1586 (1962).

(6) J. K. Kochi and D. D. Davis, *ibid.*, **86**, 5264 (1964).

(7) J. K. Kochi and D. Buchanan, *ibid.*, **87**, 853 (1965).

(8) J. K. Kochi and D. M. Singleton, *J. Org. Chem.*, **33**, 1027 (1968).

(9) C. E. Castro and W. C. Kray, Jr., *J. Amer. Chem. Soc.*, **85**, 2768 (1963).

(10) Throughout this paper solvation of chromium ions by water and alcohol is implied (J. Baltisberger and E. L. King, *ibid.*, **86**, 795 (1964)); a coordination number of six is assumed.

(11) P. J. Elving and B. Zemel, *ibid.*, **79**, 1281 (1957).

(12) F. A. Gunthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

0.040 mol of benzaldehyde, indicating essentially a 1:1 stoichiometry.

Kinetics

The rate of reduction of benzaldehyde by Cr(II) in aqueous acidic ethanol (65 vol % ethanol) was followed by determination of the total reducing species present and by monitoring the disappearance of Cr(II) spectrophotometrically. The data obtained are summarized in Tables I–III. The reduction, in the presence of either HCl or $HClO_4$, is first order in both Cr(II) and H^+. When the reaction is acidified with $HClO_4$, a plot of log k_{obsd} *vs.* log [PhCHO] is linear, with a slope of 1.73, suggesting two parallel reaction pathways, one first order in PhCHO, and one second order in PhCHO. Chloride ion accelerates the rate of reaction, but the reaction is not clearly first order in chloride ion, as shown by a plot of log k_{obsd} *vs.* log $[Cl^-]$, which has a slope of 0.87. Since the reaction will proceed in the absence of chloride ion, but is accelerated by it, the rate law must contain terms for the reaction in the presence and absence of halide ion.

Table I. Rate of Reaction of PhCHO with $Cr(ClO_4)_2$[a]

[PhCHO]	$[H^+]$	$k_{obsd} \times 10^4$ sec
1.29	1.29	6.14
0.97	1.29	3.70
0.65	1.29	1.82
0.32	1.29	0.55
1.29	0.64[b]	2.55
1.29	0.32[b]	1.56

[a] 25°, 65% EtOH. Data obtained titrimetrically, [Cr(II)] = 0.05 *F*. [b] Ionic strength maintained at 1.29 by the addition of $NaClO_4$.

Table II. Rate of Reaction of PhCHO with $Cr(ClO_4)_2$ and HCl[a]

[PhCHO]	$[H^+]$	$[Cl^-]$	$k_{obsd} \times 10^4$ sec
1.29	1.29	1.29	28.0
0.97	1.29	1.29	17.0
0.65	1.29	1.29	8.2
0.104	1.29	1.29	2.7[b]
0.091	1.29	1.29	3.7[b]
1.29	1.29	0.97[c]	22.2
1.29	1.29	0.65[c]	15.0
1.29	1.29	0.32[c]	9.94
1.29	0.65	0.65[c]	7.89

[a] 25°, 65% EtOH. Data obtained titrimetrically. [b] From second-order plot of the data; $k_{obsd} = k_2[PhCHO]$. [c] Ionic strength maintained by the addition of $NaClO_4$.

Table III. Spectrophotometric Rate of Reaction of PhCHO with $Cr(ClO_4)_2$[a]

[PhCHO]	$[H^+]$	$[Cl^-]$	$k_{obsd} \times 10^4$ sec
1.29	1.29	1.29	26.5
0.65	1.29	1.29	10.0
1.29	1.29	0.65[b]	22.5
1.29	0.65	1.29	13.3
1.29	1.29	0[c]	6.5

[a] Data obtained at 750 nm in 65% EtOH at 25.0°. [b] Ionic strength maintained by the addition of $NaClO_4$. [c] Acidified with $HClO_4$.

When the reaction is acidified with HCl, the apparent order in PhCHO, as determined by a plot of log k_{obsd} *vs.* log [PhCHO], is 1.77, again suggesting parallel reaction pathways. Consistent with the nonintegral kinetic orders exhibited by PhCHO and chloride ion, the following rate law is indicated, where k_{obsd} is the

$$\text{rate} = k_{obsd}[Cr(II)] = k_1[Cr(II)][PhCHO][H^+] + k_2[Cr(II)][PhCHO]^2[H^+] + k_3[Cr(II)][PhCHO][H^+][Cl^-] + k_4[Cr(II)][PhCHO]^2[H^+][Cl^-] \quad (5)$$

observed pseudo-first-order rate constant, and k_1, k_2, k_3, and k_4 are the rate constants for the individual terms in the rate law and contain equilibrium constants for any prior equilibria. When the reaction is conducted in the presence of $HClO_4$ only, $[Cl^-] = 0$ and the rate law becomes

$$\text{rate} = k_{obsd}[Cr(II)] = k_1[Cr(II)][PhCHO][H^+] + k_2[Cr(II)][PhCHO]^2[H^+] \quad (6)$$

Rearrangement leads to

$$\frac{k_{obsd}}{[PhCHO][H^+]} = k_1 + k_2[PhCHO] \quad (7)$$

If eq 7 is valid, a plot of $k_{obsd}/[H^+][PhCHO]$ *vs.* [PhCHO] should be linear with a slope of k_2 and an intercept of k_1. A linear plot is indeed obtained with slope $2.4 \times 10^{-4}\ M^{-3}\ sec^{-1}$ and an intercept of $5.9 \times 10^{-5}\ M^{-2}\ sec^{-1}$. Again rearranging eq 5

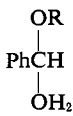
$$\frac{k_{obsd}}{[PhCHO][H^+]} = k_1 + k_2[PhCHO] + k_3[Cl^-] + k_4[PhCHO][Cl^-] \quad (8)$$

At constant $[Cl^-]$, a plot of $k_{obsd}/[H^+][PhCHO]$ *vs.* [PhCHO] should be linear with a slope of $k_2 + k_4[Cl^-]$ and an intercept of $k_1 + k_3[Cl^-]$. Such a plot is linear with slope $1.2 \times 10^{-3}\ M^{-3}\ sec^{-1}$, and an intercept of $1.4 \times 10^{-4}\ M^{-2}\ sec^{-1}$. Using the previously obtained values of k_1 and k_2, and solving for k_3 and k_4, the values of $k_3 = 6.3 \times 10^{-5}\ M^{-3}\ sec^{-1}$ and $k_4 = 7.6 \times 10^{-4}\ M^{-4}\ sec^{-1}$ are obtained.

A check on consistency using eq 8 and data obtained at constant [PhCHO] = 1.29 *F* and varying $[Cl^-]$ gives a slope of $1.1 \times 10^{-3}\ M^{-3}\ sec^{-1}$, which agrees very well with the value of $1.0 \times 10^{-3}\ M^{-3}\ sec^{-1}$ calculated from the previously determined values of k_3 and k_4 (eq 8). By extrapolating to $[Cl^-] = 0$, an intercept of $2.6 \times 10^{-4}\ M^{-3}\ sec^{-1}$ is obtained, corresponding to the experimentally determined quantity, $k_1 + k_2[PhCHO] = 3.4 \times 10^{-4}\ M^{-3}\ sec^{-1}$ (eq 7).

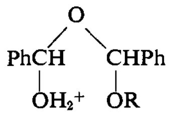
Discussion

The one-electron reduction of benzaldehyde to hydrobenzoin and its ethers proceeds by a complex mechanism involving at least four terms in the rate law. Each involves proportionality to acid concentration, suggesting that the actual reacting species is not benzaldehyde itself, but rather a protonated form, most reasonably a protonated hydrate or hemiacetal. Moreover, the major component of the chromic species formed in the reduction is $CrCl^{2+}$, which is highly indicative of a ligand-transfer reduction from a moiety containing bound halogen.[2a] Structures **1**–**4** are addition compounds of benzaldehyde whose reduction will adequately account for the experimental observations.



1

$PhCH(OR)(OH_2^+)$

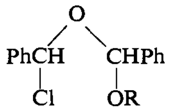


2

$PhCH(OH_2^+)OCH(OR)Ph$

PhCH(OR)Cl

3



4

$PhCH(Cl)OCH(OR)Ph$

R = H or Et

In the perchloric acid promoted reaction, reduction of **1** and **2** proceeds by ligand transfer of water to form an α-alkoxy- or α-hydroxybenzyl radical.

$$\mathbf{1} + Cr^{2+} \xrightarrow{\text{slow}} \underset{\mathbf{5}}{PhCH(OR)} + Cr^{3+} \tag{9}$$

$$\mathbf{2} + Cr^{2+} \xrightarrow{\text{slow}} \underset{\mathbf{6}}{PhCHOCH(OR)Ph} + Cr^{3+} \tag{10}$$

In halide-containing media, **3** and **4** are also present and reduced by ligand transfer of chloride, accounting for the four-term rate law.

$$\mathbf{3} + Cr^{2+} \xrightarrow{\text{slow}} \mathbf{5} + CrCl^{2+} \tag{11}$$

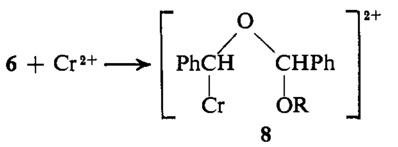
$$\mathbf{4} + Cr^{2+} \xrightarrow{\text{slow}} \mathbf{6} + CrCl^{2+} \tag{12}$$

The ligand-transfer reduction of a hydrate, hemiacetal, or halohydrin also explains the observation that carbonyl compounds known to form a hydrate or hemiacetal, such as benzaldehyde or benzalacetone, are readily reduced, while compounds such as acetone are not reduced.[3]

The influence of halide ions on Cr(II) reductions has been noted and discussed previously.[13,14] Castro[13] found that chloride was essential in the acid promoted reductive dimerization of 1,1-diphenylethylene or diphenylmethylcarbinol by $CrSO_4$. Under slightly different conditions, Slaugh and Raley observed that VSO_4 or $Cr(ClO_4)_2$ in nonhalogen acid media reduce diphenyl- and triphenylcarbinols to the corresponding polyphenylethanes. These observations in addition to our kinetic results clearly indicate the presence of two reduction pathways, one involving chloride ion. We have chosen to indicate both as inner sphere or bridging reductions; however, ligand transfer can only be demonstrated for the path involving chloride. Evidence for inner sphere transfer of water is by analogy to other Cr(II) reductions, mainly in inorganic systems.[15]

The lifetime of **5** and **6** in solution should be short due to their reaction with chromous ion, an efficient radical trap.[6,16] Trapping of either **5** or **6** leads to the formation of a carbon–chromium bond.

$$\mathbf{5} + Cr^{2+} \longrightarrow \underset{\mathbf{7}}{PhCH(OR)Cr^{2+}} \tag{13}$$



(14)

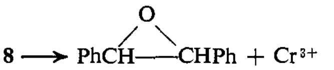
8

Organochromium species formed in a similar manner have been proposed for the reduction of benzal chloride,[4,17] benzylic halides,[1,6,9,18] alkyl halides,[8,9,19] vicinal halides,[20] geminal dihalides,[4,21] and alkylmercuric salts.[22] Reactions available to **7** and **8** include protolytic reduction, coupling, or cyclization.

$$\mathbf{7} + H^{+} \longrightarrow PhCH_2OH + Cr^{3+} \tag{15}$$

$$\mathbf{7} + \mathbf{1} \longrightarrow \underset{\mathbf{9}}{PhCH(OR)CH(OR)Ph} + Cr^{3+} \tag{16}$$

$$\mathbf{7} + \mathbf{3} \longrightarrow \mathbf{10} + CrCl^{2+} \tag{17}$$



(18)

The reactions shown in eq 15–17 account for the observed products. Stilbene oxide formed in eq 18 is not observed; however, under the reaction conditions it is opened to hydrobenzoin and hydrobenzoin ethyl ether. Hydrobenzoin is not converted to its ethers under these conditions nor is stilbene oxide deoxygenated[23] to stilbene in aqueous acidic ethanol.

The fraction of chloride ligand transfer, calculated from the rates of the third and fourth terms in eq 5 relative to the total rate, is 40%, accounting for the fact that only half of the total chromic ions are formed in the initial ligand-transfer step. The chromic products contain at least 65% $CrCl^{2+}$ and thus eq 17 must account for a portion of the reactions producing coupled products. The possibility of the organochromium ion coupling with benzaldehyde itself to produce at least some of the coupled products cannot be ruled out by data presented here.

We have assumed throughout this discussion that the second-order terms in benzaldehyde appearing in the rate law are due to the presence of **2** and **4**.

Conclusion

The results presented in this paper support the mechanism shown by eq 9–18 for the one-electron reduction of benzaldehyde by Cr(II). This work extends the generality of the ligand-transfer mechanism, commonly shown for organic halides, to the carbonyl class of compounds represented by benzaldehyde.

Experimental Section

Materials. Chromium(II) perchlorate was prepared by the reaction of electrolytic chromium metal (99.996% Cr, metallic basis, Varlacoid Corp.) with dilute perchloric acid[24] under a nitrogen atmosphere. **Caution**: concentrated (>1 *M*) solutions of $Cr(ClO_4)_2$ must be prepared at ice-bath temperatures, since the reaction mixture will vigorously decompose water at room temperature. The solutions may be safely stored at room temperature. Benzaldehyde (Baker Reagent) was vacuum distilled from zinc dust immediately prior to use. *meso*-Hydrobenzoin was prepared by the reduction of benzoin[25,26] with $LiAlH_4$ in tetra-

---

[13] C. E. Castro, *J. Amer. Chem. Soc.*, **83**, 3262 (1961); C. E. Castro and R. D. Stephens, *ibid.*, **86**, 4358 (1964); C. E. Castro, R. D. Stephens, and S. Moje, *ibid.*, **88**, 4964 (1966).

[14] L. H. Slaugh and J. H. Raley, *Tetrahedron*, **20**, 1005 (1964).

[15] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 479–487.

[16] J. K. Kochi and P. E. Mocaldlo, *J. Org. Chem.*, 30, 1134 (1965).

[17] J. F. Neumer and S. Aktipis, Abstracts, 136th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 9Q.

[18] H. Lux, D. Sarre, and I. Schaffelholder, *Chem. Ber.*, **97**, 2301 (1964).

[19] J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, **92**, 137 (1970).

[20] W. C. Kray and C. E. Castro, *ibid.*, **86**, 4603 (1964); J. K. Kochi and D. M. Singleton, *ibid.*, **90**, 1582 (1968).

[21] A. Aurgiyah and C. E. Castro, *J. Org. Chem.*, **34**, 1504 (1969).

[22] R. J. Ouellette and B. G. van Leuwen, *ibid.*, **30**, 3967 (1965).

[23] $Cr(en)^{2+}$, however, will reduce stilbene oxide to stilbene. See J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968).

[24] H. Lux and G. Illman, *Chem. Ber.*, **91**, 2143 (1958).

hydrofuran (THF). *trans*-Stilbene oxide was prepared by the reaction of peroxyacetic acid with *trans*-stilbene.[27]

erytho-Hydrobenzoin monoethyl ether was prepared by refluxing *trans*-stilbene oxide in ethanol with a tenfold excess of sodium ethoxide. Two crystallizations of the product from pentane at Dry Ice temperature gave white crystals: mp 51–52° (lit.[28] 45–50°); nmr (CCl_4) δ 7.05 (m, 10, Ph), AB pattern centered about 4.42 (J = 6 Hz, Δ = 29 Hz, 2, $PhCH$); 3.25 (m, 2, OCH_2CH_3); 2.50 (s, 1, OH); 1.00 (t, J = 7 Hz, 3, OCH_2CH_3). *meso*-Hydrobenzoin diethyl ether was prepared by a Williamson reaction from *meso*-hydrobenzoin and ethyl iodide. A dispersion of 1.2 g of 50% NaH in mineral oil (0.025 mol of NaH) was washed with hexane and placed in a 100-ml flask with 40 ml of dry THF. A solution of 2.0 g (0.009 mol) of *meso*-hydrobenzoin in 10 ml of dry THF was slowly added, and the solution was refluxed for 1 hr. Ethyl iodide (4.7 g, 0.03 mol) was added, and the solution was refluxed overnight.

The reaction mixture was poured into 100 ml of H_2O, acidified (H_2SO_4), and extracted with two 50-ml portions of benzene. The benzene was washed with two 50-ml portions of H_2O, dried ($CaCl_2$), and evaporated, giving a yellow oil which solidified on standing. The solid was dissolved in benzene and passed through a 3-cm column of neutral alumina. Evaporation of the eluent gave 1.73 g (69%) of white crystals, mp 55.5–57.0°. Crystallization from pentane at Dry Ice temperature raised the melting point to 60.5–62.0° (lit.[29] 66–66.3°): nmr (CCl_4) δ 7.18 (s, 10, Ph); 4.10 (s, 2, $PhCH$); 3.10 (m, 4, OCH_2CH_3); 0.90 (t, J = 6 Hz, 6, OCH_2CH_3).

Reduction of Benzaldehyde. Benzaldehyde (5.0 g, 0.047 mol) was mixed with 50 ml of 95% ethanol and a stoichiometric amount of acid (HCl or $HClO_4$), and the solution was swept with nitrogen. An approximately 10% excess of 3 M $Cr(ClO_4)_2$ was added *via* syringe, and the mixture was allowed to stand for 3 days.

The mixture was poured into 100 ml of H_2O and extracted with three 100-ml portions of $CHCl_3$. The $CHCl_3$ was washed (H_2O), dried (Na_2SO_4), and evaporated under reduced pressure, with the solvent being collected. Evaporation of the solvent produced a pale yellow oil containing some white solid. Fractional crystallization of the oil from ethanol produced *meso*-hydrobenzoin. Mixing this product with authentic *meso*-hydrobenzoin produced no melting point depression.

Products (hydrobenzoin, hydrobenzoin monoethyl ether, hydrobenzoin diethyl ether, benzyl alcohol, and toluene) were identified by comparison of gas–liquid partition chromatography (glpc) retention times of the silyated (Tri-Sil, Pierce Chemical Co.) reaction mixture with those of authentic materials and by coinjection with authentic materials. In addition, the coupled products were identified by comparison of R_f values with those of authentic material, using silica gel plates developed with toluene. No separation between *erythro* and *threo* isomers could be obtained in either case.

Products were measured by gas–liquid partition chromatography (glpc) on an Aerograph Model 600-C gas chromatograph with flame-ionization detector, using a 5 ft × $^1/_8$ in. column of 5% SE-30 on firebrick. The coupled products were analyzed at 165°, while benzyl alcohol was analyzed for at 110°.

Hydrobenzoin was measured by treatment of an aliquot of the product mixture in benzene with an excess of $Pb(OAc)_4$, and back-titration of remaining $Pb(OAc)_4$.[30] The gas chromatograph was then calibrated for the ethers relative to hydrobenzoin. Benzyl alcohol was measured relative to added β-phenylethanol.

Inorganic products were determined from three reactions acidified with HCl, HBr, and $HClO_4$. After 24 hr, an aliquot was withdrawn, placed in an equal volume of H_2O, and extracted with $CHCl_3$. The clear aqueous solution was placed on a column of Dowex 50W-X8 cation exchange resin, H^+ form, and eluted with 3 M $HClO_4$. The products were analyzed on a Cary Model 14 spectrophotometer. The reaction in the presence of HCl produced (mol %, based on starting Cr) 63.5% $CrCl(H_2O)_5^{2+}$ and 23.6% $Cr(H_2O)_6^{3+}$. The reactions acidified with HBr and $HClO_4$ produced $Cr(H_2O)_6^{3+}$ as the only detectable chromium species. Recovery of Cr was essentially quantitative.

The stoichiometry was determined by reacting PhCHO with an excess of $Cr(ClO_4)_2$ and back-titrating the remaining Cr(II). Benzaldehyde (2.0 ml of 2.00 M PhCHO in 95% EtOH) was placed in a rubber serum capped test tube and acidified (HCl), and the solution was swept with nitrogen. A 20.0-ml aliquot of 0.463 M $Cr(ClO_4)_2$ was added *via* syringe, and the solution was allowed to stand for 1 week. Titration of the remaining Cr(II) showed that 0.0037 mol of Cr(II) had been consumed by 0.0040 mol of PhCHO. The stoichiometry was therefore assumed to be 1:1. The amount of acid consumed was not measured.

Kinetic Measurements. The reaction of PhCHO with Cr(II) was followed by quenching aliquots in dilute $FeCl_3$ solution and titrating the Fe(II) produced to the ferrous 1,10-phenanthroline end point with 0.01 M Ce(IV).[9] The disappearance of Cr(II) was followed spectrophotometrically in a Beckman Model DU spectrophotometer at 750 nm. The appearance of Cr(III) gave a complex curve and was not followed. Both the disappearance of titer and the disappearance of Cr(II) gave good pseudo-first-order plots to 90% completion. The results of the kinetic measurements are summarized in Tables I–III. Rates were reproducible to within 5%.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

---

(25) H. Gilman, Ed., "Organic Syntheses," Coll. Vol. I, 2nd ed, Wiley, New York, N. Y., 1967, p 94.

(26) L. A. Pohoryles, S. Sarel, and R. Ben-Shoshan, *J. Org. Chem.*, 24, 1878 (1959).

(27) N. Rabjohn, Ed., "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 860.

(28) J. Read and I. G. M. Campbell, *J. Chem. Soc.*, 2377 (1930).

(29) B. I. Mikhantev and L. P. Pavlov, *Zh. Obshch. Khim.*, 30, 402 (1960); *Chem. Abstr.*, 54, 24541 (1960).

(30) J. S. Fritz and G. S. Hammond, "Quantitative Organic Analysis," Wiley, New York, N. Y., 1957, p 250; R. Criegee, *Ber.*, 64B, 264 (1931).