IR($CHCl_3$) 2840, 1650, 1610, 1590, 1500, 1460, 1355, 1235, 1170, and 1060 cm^{-1}; NMR ($CDCl_3$) δ 0.53 (d, J = 7.0 Hz, 3), 1.49–2.32 (m, 4), 2.56–2.79 (m, 1), 3.03 (s, 3), 3.70 (s, 3), 3.85 (s, 3), 3.87 (s, 6) 4.11–4.35 (m, 2), 5.44 (s, 1), 5.92 (s, 1), 5.98 (d, J = 4.8 Hz, 1), 6.43 (s, 2); UV (95% EtOH) 243 nm (sh, log ϵ 4.16), 258 (4.28), 291 (sh, 3.68); MS *m/e* (relative intensity, %) 482 (M^+, 1), 208 (81), 79 (100). Anal. ($C_{23}H_{30}O_9S$) C, H.

(2β,3β,3aα,5β)-3,3a,4,5-Tetrahydro-5-methoxy-3-methyl-3a-[3-[(methylsulfonyl)oxy]propyl]-2-(3,4,5-trimethoxyphenyl)-6(2*H*)-benzofuranone (5). A solution of benzofuranone **6** (0.354 g, 0.73 mmol) in methanol (50 mL) containing 5% Rh/C (49 mg) was hydrogenated under an atmospheric pressure of hydrogen. After 105 min, the solution was filtered through a pad of Celite with the aid of dichloromethane and the filtrate was concentrated in vacuo. Flash chromatography (40 mm, 66 g, EtOAc–acetone 9:1 (v/v)) of the mixture gave 0.076 g of the desired product **5** (22% yield, 33% based on recovered starting material) and 0.121 g of unreacted benzofuranone **6**. Crystallization gave analytically pure **5**: mp 149–151 °C ($CHCl_3$–hexane); IR ($CHCl_3$) 1660, 1630, 1600, 1505, 1460, 1355, 1180, and 1130 cm^{-1}; NMR ($CDCl_3$) δ 0.55 (d, J = 7.4 Hz, 3), 1.80–2.15 (m, 5), 2.24 (dd, J = 12.9, 4.8 Hz, 1), 2.62–2.45 (m, 1), 3.08 (s, 3), 3.63 (s, 3), 3.85 (s, 3), 3.88 (s, 6), 3.94 (dd, J = 12.1, 4.8 Hz, 1), 4.48–4.26 (m, 2), 5.58 (s, 1), 5.86 (d, J = 4.8 Hz, 1), 6.46 (s, 2); MS *m/e* (relative intensity, %) 484 (M^+, 17) 406 (17), 221 (53), 79 (100); UV (95% EtOH) 257 nm (log ϵ 4.38). Anal. ($C_{23}H_{32}O_9S$) C, H.

(2β,3β,3aα,5β)-3,3a,4,5-Tetrahydro-5-methoxy-3-methyl-3a-(2-propenyl)-2-(3,4,5-trimethoxyphenyl)-6(2*H*)-benzofuranone (4). To a stirring suspension of 4,4′-dichlorodiphenyl diselenide (39 mg, 0.10 mmol) in absolute ethanol (1 mL) was added slowly, under a heavy argon atmosphere, small quantities of solid $NaBH_4$ until a colorless solution was obtained. The solution was then cooled in an ice bath for 20 min. Benzofurane **5** (53 mg, 0.11 mmol) in THF (1 mL) was then added and the solution was stirred for 55 min. Sodium periodate (0.199 g, 0.93 mmol) in 50% aqueous THF (3 mL) was added and stirring was continued for 25 min. The ice bath was removed and the solution was then heated at 70 °C (oil bath) for 150 min. The solution was diluted with water (10 mL) and extracted with EtOAc (3× 20 mL). The combined organic extracts were washed with 5% $NaHCO_3$ solution (1× 20 mL) and brine (1× 20 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. Flash chromatography (20 mm, 16 g, EtOAc) gave 23 mg (54% yield) of benzofuranone **4**: mp 137–139 °C ($CHCl_3$–hexane); IR ($CHCl_3$) 2825, 1655, 1630, 1590 cm^{-1}; UV (95% EtOH) 260 nm (log ϵ 4.40); NMR ($CDCl_3$) δ 0.54 (d, J = 7.4 Hz, 3), 1.91 (t, J = 12.3 Hz, 1), 2.32 (dd, J = 12.5, 5.2 Hz, 1), 2.45–2.75 (m, 3), 3.60 (s, 3), 3.85 (s, 3), 3.87 (s, 6), 4.01 (dd, J = 12.1, 5.2 Hz, 1), 5.28–5.39 (m, 2), 5.60 (s, 1), 5.85 (d, J = 5.2 Hz, 1), 5.87–6.04 (m, 1), 6.42 (s, 2). Anal. Calcd for $C_{22}H_{28}O_6$: 388.1886. Found: 388.1887.

Megaphone (1): To a cooled (ice bath) and stirring solution of benzofuranone **4** (23 mg, 0.06 mmol) in THF (0.3 mL) was added DIBAH (1 M in hexane, 0.15 mL, 0.15 mmol) via syringe. After 45 min, 3 drops of saturated NH_4Cl solution were added, followed by ether (5 mL), solid NH_4Cl (25 mg), and Celite (0.15 g). The solution was stirred at room temperature for 30 min and filtered through $MgSO_4$ and the cake washed with ether. Concentration of the filtrate in vacuo gave a colorless oil which was dissolved in THF (0.1 mL) containing Et_3N (16 μL, 12 mg, 0.12 mmol). The solution was then cooled to −55 to −60 °C with stirring and methanesulfonyl chloride (9 μL, 13 mg, 0.12 mmol) was added. The mixture was then stirred for 15 min, and 0.2 mL of H_2O/THF/Et_3N (3:2:1) was added. After the solution was warmed to room temperature, it was diluted with Et_2O, washed with water (once) and brine (once), dried ($MgSO_4$), filtered, and concentrated. Flash chromatography (20 mm, 16 g, hexane–EtOAc 1:1 (v/v)) gave 10 mg (42% yield) of megaphone (1): IR (CCl_4) 3600, 3375, 2830, 1665, 1590, 1500, 1460, 1230, and 1005 cm^{-1}; NMR ($CDCl_3$) δ 0.77 (d, J= 7.4 Hz, 3), 1.95 (br q, J = 7.0 Hz, 1), 2.13–2.49 (m, 3), 2.59 (dd, J = 14.7, 6.6 Hz, 1), 3.47 (s, 3), 3.83 (s, 3), 3.88 (s, 6), 4.17–4.28 (m, 1), 4.56–4.79 (br s, 1), 5.03 (br s, 1), 5.24 (br s, 1), 5.29 (br s, 1), 5.73–5.98 (m, 1), 6.03 (dd, J = 10.3, 2.2 Hz, 1), 6.66 (s, 2), 7.00 (d, J = 10.3 Hz), 0.60 (d, J = 7.7 Hz, hemiketal Me), 3.37 (s, hemiketal OMe), 6.47 (s, aromatic hemiketal).

Megaphone Acetate (2). Racemic megaphone acetate (**2**) prepared according to the literature[1] was a colorless oil: IR (CCl_4) 2840, 1745, 1680, 1590, 1510, 1460, 1420, 1230, 1130, 1010, 960, 920 cm^{-1}; NMR ($CDCl_3$) δ 0.93 (d, J = 7 Hz, 3), 1.87 (dd, J = 13.2, 9.9 Hz, 1), 2.13 (s, 3), 2.25–2.40 (m, 3), 2.55 (q, J = 7 Hz, 1), 3.46 (s, 3), 3.82 (s, 3), 3.88 (s, 6), 4.17–4.27 (m, 1), 4.95–5.03 (m, 1) 5.04 (br s, 1), 5.49–5.64 (m, 1), 5.67 (s, 1), 6.01 (dd, J = 10.3, 2.2 Hz, 1), 6.55 (s, 2), 6.91 (dt, J = 10.3, 1.8 Hz, 1).

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Kinetics and Mechanism of the Oxidation of (α-Hydroxyalkyl)chromium Complexes by Copper(II) and Iron(III) Ions

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Abstract: Copper(II) and iron(III) ions react with (α-hydroxyalkyl)chromium(2+) complexes (alkyl = methyl, ethyl, 2-propyl) in water or in aqueous alcohol solutions leading to the cleavage of the chromium–carbon bond. The immediate products are Cr^{2+}, the reduced metal ion (Cu^+ or Fe^{2+}), and the corresponding aldehyde or ketone. The reactions obey the rate law $-d[CrROH^{2+}]/dt = (k + k'[H^+]^{-1})[CrROH^{2+}][M]$, where M = Cu^{2+} or Fe^{3+}. The dominant k' term has the following values in 1 M aqueous parent alcohol (methanol, ethanol, and 2-propanol, respectively): $CrCH_2OH^{2+}$, $k'_{Cu} = 0.251\ s^{-1}$, $k'_{Fe} = 0.496\ s^{-1}$; $CrCH(CH_3)OH^{2+}$, 1.46, 0.481; $CrC(CH_3)_2OH^{2+}$, 0.574, 1.90. The reactivity toward Cu^{2+} and Fe^{3+} is significantly diminished upon substitution of the OH hydrogen by an alkyl group. Copper(II) does not react with (α-alkoxyalkyl)chromium(2+) complexes at all, while iron(III) shows some reactivity with $k'_{Fe} = 0.0127\ s^{-1}$ ($CrCH_2OCH_3^{2+}$) and $0.0400\ s^{-1}$ ($CrCH(CH_3)OC_2H_5^{2+}$), both in 1 M methanol. A mechanism proposed for the oxidation of (α-hydroxyalkyl)chromium(2+) complexes by copper(II) and iron(III) consists of the oxidant attack at the alcoholic OH group followed by a slow electron-transfer step.

The Fischer–Tropsch process is one in which hydrocarbon fuels and alcohols can be synthesized from mixtures of carbon monoxide and hydrogen obtained from coal and water. The mechanism of the heterogeneous process is not completely understood, however, and this poses one impediment to its commercial development where the distribution of products is crucial.[1] One possible

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mechanism[2] describes the process in terms of a series of active intermediates, including α-hydroxyalkyl derivatives, MCH_2OH, $MCH(CH_3)OH$, etc.

There are not a large number of stable organometallic complexes having this composition, which limits a ready examination of their chemistry. Of the few known examples, many occur only as transients or intermediates. One example is the proposed intermediate $[(OC)_5MnCH(Ph)OH]$ which decomposed to the hydride so rapidly as to escape detection;[3] also, unstable α-hydroxyalkyl complexes of cobalt(III), derivatives of vitamin B_{12}[4] and synthetic macrocyles,[5] have been detected.

A stable compound $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_2OH)$ has recently been isolated.[6] Another set of complexes are the organopentaaquochromium(III) cations containing CH_2OH and related groups bound directly to the chromium.[7] These complexes are hydrolytically unstable,[7,8] like other members of the family $(H_2O)_5CrR^{2+}$, all of which undergo slow protonolysis reactions in acidic solution, e.g., $CrCH_2OH^{2+} + H_3O^+ = Cr^{3+}(aq) + CH_3OH$. The rates of protonolysis are no higher for the α-hydroxyalkyls than for the alkyls, however, and are of little importance in comparison with the reactions being studied.

The chemical reactivity of α-hydroxyalkyls is as yet poorly characterized. We thus undertook a study of selected reactions of the (α-hydroxyalkyl)pentaaquochromium(III) ions, both to explore their chemistry and to complement earlier work on the general reactivity of organochromium cations.[7-9] It soon became apparent that the α-hydroxyalkyl complexes, unlike the simple alkyl analogues, are excellent albeit selective reducing agents. Thus the ions $Fe^{3+}(aq)$ and $Cu^{2+}(aq)$ readily oxidize the $CrROH^{2+}$ ions to aldehyde or ketone, whereas oxygen, hydrogen peroxide (from which they are prepared), and halopentaamminecobalt(III) ions are unreactive. Clearly this sets the $CrROH^{2+}$ complexes apart from the regular alkylchromium ions which are generally unreactive toward oxidizing agents (note, however, that isopropylchromium(III) ion reacts with oxygen[9a]) and even from the benzylchromium(III) ion which reacts with these oxidants only indirectly.[10]

One immediately notes a certain relationship between occurrence of the oxidation of $(H_2O)_5CrCH_2OH^{2+}$ by Fe^{3+} and Cu^{2+} and corresponding reactions of the free radical $\cdot CH_2OH$. The latter processes have been studied by Walling et al.[11] using competition experiments on radicals generated from Fenton's reagent. They have also been studied directly with the use of pulse radiolysis.[12] Some clear differences in mechanism between the reactions of the $CrROH^{2+}$ complexes and the free $\cdot ROH$ radicals are apparent, however, and it is useful to note at the outset that the organochromium complexes are *not* reacting primarily by prior homolytic dissociation to the free radical, although in some instances this does constitute an important additional pathway. Furthermore, coordination of chromium to the radical renders much less likely any mechanism in which the oxidant attacks directly at the α carbon atom; this point should be stressed since it is believed to be the preferred route for reaction of Cu^{2+} and free alkyl radicals.[11b,13-15]

In the present work we report on the stoichiometry, products, and kinetics of oxidation of $(H_2O)_5CrCH_2OH^{2+}$ and substituted analogues by iron(III) and copper(II) ions. The reactions were studied in acidic, aqueous, or semiaqueous (dilute ROH in H_2O) solutions. The alcohol used was usually that from which the given organic radical was itself derived.

Experimental Section

Materials. The complexes $CrCH_2OH^{2+}$, $CrCH(CH_3)OH^{2+}$, $CrCH(CF_3)OH^{2+}$, and $CrC(CH_3)_2OH^{2+}$ were prepared[7] in ca. 80% yield by addition of the stoichiometric quantity of chromium(II) perchlorate solution to an acidic, aqueous solution of hydrogen peroxide containing the desired alcohol[16] (methanol, ethanol, 2,2,2-trifluoroethanol, or 2-propanol). The following UV-visible absorption maxima were found: $CrCH_2OH^{2+}$,[17] λ_{max} 282 nm (ϵ 2.4×10^3 dm^3 mol^{-1} cm^{-1}), 392 (5.7×10^2); $CrCH(CH_3)OH^{2+}$,[17] 296 (2.8×10^3), 396 (6.9×10^2); $CrC(CH_3)_2OH^{2+}$,[17] 311 (2.5×10^3), 407 (7.0×10^2); $CrCH(CF_3)OH^{2+}$, 515 (26.6), 395 (1.7×10^2), and 264 (3.05×10^3). The latter complex is very stable toward protonolysis and is thus easily isolated by ion-exchange chromatography.

The α-alkoxyalkyl complexes were prepared similarly, the previously known[7] $CrCH(CH_3)OC_2H_5^{2+}$ from ~0.1 M aqueous diethyl ether and the new complex $CrCH_2OCH_3^{2+}$ in an aqueous solution saturated with gaseous dimethyl ether. These complexes undergo acidolysis much more slowly than their α-OH analogues but show greater sensitivity toward oxygen. They are easily isolable by ion-exchange chromatography on Dowex 50W-X2, the desired species eluting with 0.65 M $HClO_4$ at ~5 °C under nitrogen. The absorption maxima are as follows: $CrCH_2OCH_3^{2+}$, 530 (15.3), 385 (4.04×10^2), 270 (2.59×10^3); $CrCH(CH_3)OC_2H_5^{2+}$, 390 (4.68×10^2), 290 (2.27×10^3).

Solutions of Cu^{2+}, Fe^{3+}, and Cr^{3+}, prepared from the solid hydrated perchlorate salts, were standardized spectrophotometrically (Cr^{3+}), cerimetrically (Fe^{3+}), or iodometrically (Cu^{2+}). The amount of free perchloric acid in solutions of Fe^{3+} and Cr^{3+} was determined by difference from the total amount of acid released from a column of Dowex 50W-X8 cation-exchange resin (hydrogen ion form). The free acid in Cu^{2+} solutions was determined by direct titration. Solutions of chromium(II) perchlorate were prepared by reduction of Cr^{3+} over zinc amalgam. Hydrogen peroxide solutions were standardized iodometrically, and solutions of $[Co(NH_3)_5F]^{2+}$, $[Co(NH_3)_5Cl]^{2+}$, and $[Co(NH_3)_5Br]^{2+}$ were freshly prepared from their perchlorate salts. All the experiments were performed under an atmosphere of prepurified nitrogen.

Stoichiometry, Product Analysis, and Kinetics. Many of the inorganic products were separated and identified by chromatography on cation-exchange resin columns (Dowex 50W-X8 or Sephadex CM-25). Formaldehyde was identified by the chromotropic acid test,[18] with quantitative determination by a variation of the silver(I) oxidation procedure[19] in which metal ions were first precipitated by addition of 6 M KOH (without this, the end point is less sharp). A similar method was used for acetaldehyde produced during Cu^{2+} oxidation of $CrCH(CH_3)OH^{2+}$ and $CrCH(CH_3)OC_2H_5^{2+}$, but its high volatility requires rapid analysis, and metal ions were therefore not removed prior to analysis. These results were confirmed by GC analysis. The silver(I) oxidation method gives low results in the presence of iron salts, and the amount of acetaldehyde formed during Fe^{3+} oxidation of the same complexes was de-

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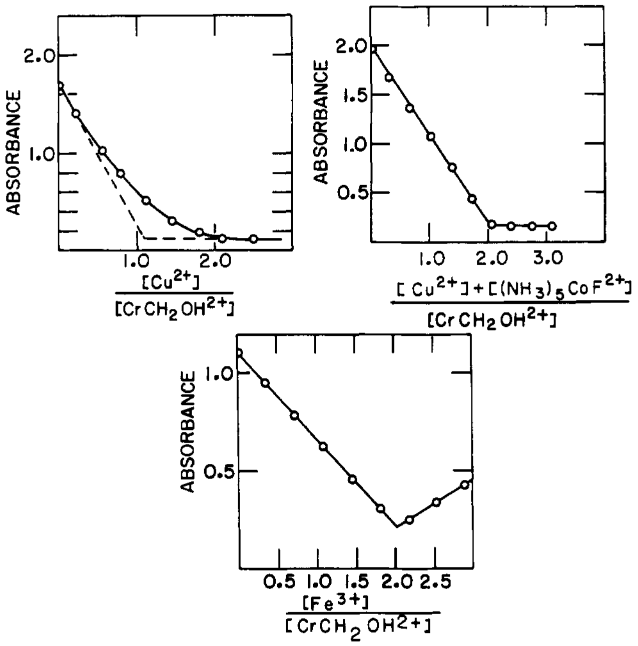

Figure 1. Spectrophotometric titrations of $CrCH_2OH^{2+}$ with Cu^{2+} and with Fe^{3+} at λ 390 nm. The first graph depicts results on the Cu^{2+} reaction in which a variable stoichiometry results since Cu^{2+} is consumed by both $CrCH_2OH^{2+}$ and Cr^{2+} as in eq 4 and 5. At $[Cu^{2+}]/[CrCH_2OH^{2+}] > 2.0$, no organochromium ions remain, consistent with eq 6. When a scavenger for Cr^{2+} such as $Co(NH_3)_5F^{2+}$ is added such that $[Co(NH_3)_5F^{2+}]_0 = [Cu^{2+}]_0$, as in the second graph, eq 5 no longer occurs and the net reaction occurs with a 1:1:1 stoichiometry as in eq 7. The third graph depicts results for Fe^{3+} where the correspondingly more rapid rate of eq 2 compared to eq 1 results in a process of 2:1 stoichiometry as in eq 3.

termined by GC and spectrophotometric analyses after extracting acetaldehyde into chloroform (ϵ_{285} 18.3 dm³ mol⁻¹ cm⁻¹). Accuracy in these determinations is limited to 10%–15% by the uncertainty in the molar absorptivities (and thus the initial concentration) of the organochromium complexes.

Kinetic data were obtained spectrophotometrically with use of Cary Models 14 and 219 recording spectrophotometers equipped with thermostated cell holders, except for $CrC(CH_3)_2OH^{2+}$ where the faster reactions required the stopped-flow technique with use of a Canterbury SF-3A spectrophotometer. The "standard" conditions for these experiments were a temperature of 24.8 °C, an ionic strength of 1.00 M (controlled with lithium perchlorate), and a solvent composition adjusted to 1.0 M alcohol, which amounts to ca. 4–8 vol %. The alcohols used were methanol, ethanol, 2-propanol, and 2,2,2-trifluoroethanol for the respective α-hydroxy complexes and 1.0 M methanol for the complexes $CrCH(CH_3)OC_2H_5^{2+}$ and $CrCH_2OCH_3^{2+}$. A lesser number of experiments were carried out at different temperatures and alcohol concentrations. The kinetics determinations were carried out in the presence of an excess of external oxidant (Fe^{3+} or Cu^{2+}); in every instance the data followed a pseudo-first-order rate law. Plots of ln $(D_t - D_\infty)$ vs. t were excellent straight lines for three half-lives or more and yielded values of k_{obsd} which agreed in duplicate runs to within 1%.

Results

Stoichiometry and Product Analysis. Because these reactions are relatively complex, precise stoichiometric determinations were carried out for each complex. All products were qualitatively identified and their yields determined by quantitative analysis. The results of spectrophotometric titrations of $CrCH_2OH^{2+}$ with Fe^{3+} and with Cu^{2+} are shown in Figure 1. The titration in the former reaction shows two linear segments, with the end point taken at their intersection when the absorbance is at a minimum. This occurs at a concentration ratio $[Fe^{3+}]_0/[CrCH_2OH^{2+}]_0 = 2.0$, beyond which the absorbance rises once again with further iron(III) which itself absorbs appreciably at this wavelength. The indicated end point is consistent with the net reaction given by eq 3; for reasons given shortly, however, we believe this process occurs by a succession of two independent reactions, as given in eq 1 and 2, the net result being the overall reaction of eq 3.

$$Fe^{3+} + CrCH_2OH^{2+} = Fe^{2+} + Cr^{2+} + H^+ + HCHO \quad (1)$$

$$Fe^{3+} + Cr^{2+} = Fe^{2+} + Cr^{3+} \quad (2)$$

$$\text{net: } 2Fe^{3+} + CrCH_2OH^{2+} = 2Fe^{2+} + Cr^{3+} + H^+ + HCHO \quad (3)$$

The spectrophotometric titration with Cu^{2+} is more complex. Figure 1 shows that the extent of reaction, as measured by the absorbance at the organochromium absorption maximum, decreases in a nonlinear fashion with added copper(II). If we consider that an analogous sequence of reactions occurs, as shown in eq 4–6, then the curvature arises from the competitive rates

$$CrCH_2OH^{2+} + Cu^{2+} = Cu^+ + Cr^{2+} + H^+ + HCHO \quad (4)$$

$$Cr^{2+} + Cu^{2+} = Cu^+ + Cr^{3+} \quad (5)$$

$$\text{net: } 2Cu^{2+} + CrCH_2OH^{2+} = 2Cu^+ + Cr^{3+} + H^+ + HCHO \quad (6)$$

of the two steps consuming the limited quantity of copper(II).

In support of this, the known rate[20] of eq 5 can be calculated to be competitive with that of eq 4 under these conditions, whereas in the analogous iron(III) reactions, reaction 2 occurs[21,22] much more rapidly than 1. In further support of this scheme for the Cu^{2+} reaction, a similar titration of $CrCH_2OH^{2+}$ was done, now with an equimolar mixture of Cu^{2+} and $(NH_3)_5CoF^{2+}$. This cobalt complex, which does not react with $CrCH_2OH^{2+}$, oxidizes Cr^{2+} very rapidly[23] ($k = 2.5 \times 10^5$ M⁻¹ s⁻¹) but Cu^+ relatively slowly[24] ($k = 1.1$ M⁻¹ s⁻¹). In comparison, the oxidation of Cr^{2+} by Cu^{2+} is much slower[20] ($k_5 = 0.17 + 0.59[H^+]^{-1}$); thus virtually all the Cr^{2+} should be scavenged and the entire quantity of Cu^{2+} should be available for reaction with $CrCH_2OH^{2+}$ as in eq 4. The results of such a spectrophotometric titration are also shown in Figure 1. Two linear portions were found, giving a sharp end point at $([Cu^{2+}]_0 + [Co(NH_3)_5F^{2+}]_0)/[CrCH_2OH^{2+}]_0 = 2.06$, substantiating a 1:1:1 stoichiometry consistent with the discussion given above and the net reaction shown in eq 7.

$$CrCH_2OH^{2+} + Cu^{2+} + Co(NH_3)_5F^{2+} + 4H^+ = CrF^{2+} + Cu^+ + Co^{2+} + 5NH_4^+ + HCHO \quad (7)$$

The inorganic products of reaction 4 were determined by reaction of $CrCH_2OH^{2+}$ with Cu^{2+} in the presence of $Co(NH_3)_5Cl^{2+}$, a reagent which does not react with (hydroxymethyl)chromium(III) ion but which rapidly[23,24] oxidizes both Cr^{2+} and Cu^+. A solution containing 0.16 mmol of $CrCH_2OH^{2+}$ in 1:1 CH_3OH/H_2O at 0.1 M H^+ was left to react with 0.40 mmol of Cu^{2+} in the presence of 0.40 mmol of $Co(NH_3)_5Cl^{2+}$. The products were 0.15 mmol of $CrCl^{2+}$, 0.27 mmol of Co^{2+}, and 0.37 mmol of Cu^{2+}. The formation of $CrCl^{2+}$ is expected if the reaction of $CrCH_2OH^{2+}$ and Cu^{2+} produces Cr^{2+}. Its detection thus constitutes convincing evidence for Cr^{2+} being formed in the reaction, and the yield, which is 94% of that expected, can be regarded as essentially quantitative. Copper(II) is recovered unchanged (92% recovery), since under the conditions of this experiment the Cu^+ formed in eq 4 is reoxidized by reaction with the cobalt(III) complex. Finally, we note that Co^{2+} arises from reduction of $(NH_3)_5CoCl^{2+}$ by Cr^{2+} and by Cu^+; its yield was 0.27 mmol (84%), a reasonable recovery in this experiment.

Production of Cu^+ from reactions 4 and 5 was confirmed more directly by using a kinetic technique based on its known[24,25] rate of reaction with $Co(NH_3)_5F^{2+}$. In these experiments $CrCH_2OH^{2+}$ was left to react completely with excess Cu^{2+}, sufficient time being allowed for eq 5 to reach completion. A small amount of Co-

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[24] Parker, O. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1968.

[25] The rate constant in this solvent, 1:1 CH_3OH/H_2O, at 25 °C and 1 M ionic strength was found, with use of the established methods,[24] to be 6.23 M⁻¹ s⁻¹. This compares to the value in water at 25 °C and 1 M ionic strength of 1.11 M⁻¹ s⁻¹.

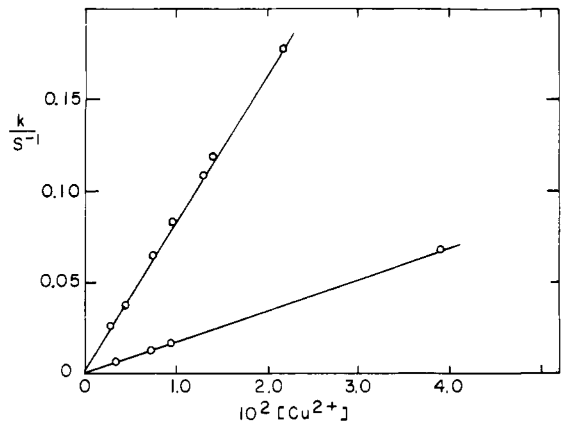

Figure 2. Plots illustrating the linear dependence on $[Cu^{2+}]$ of the pseudo-first-order rate constants for the oxidation of $CrCH_2OH^{2+}$ by Cu^{2+} at two concentrations of H^+: 0.100 M (upper line) and 0.500 M (lower). The small intercepts correspond to the rate constants for acidolysis (eq 11 and 12). Data refer to 1:1 CH_3OH/H_2O at 24.8 °C and 1.00 M ionic strength.

$(NH_3)_5F^{2+}$ was then added, sufficient for a kinetics determination but such that Cu^+ would remain in a pseudo-first-order concentration excess if it were formed in the amount required by eq 4 and 5. The subsequent consumption of cobalt(III) complex was monitored from the absorbance decrease at 510 nm (ϵ_{Co} 45 M^{-1} cm^{-1}) and used to calculate a pseudo-first-order rate constant k_{obsd}. The value of $k_{obsd}/[Cu^+]$, with use of the theoretical value for $[Cu^+]$ calculated from eq 6, was 6.39 M^{-1} s^{-1}. The agreement[25] of this rate constant with that for authentic Cu^+ under identical conditions (6.23 M^{-1} s^{-1}) constitutes qualitative proof of its identify and a quantitative determination of its yield.

Production of Cr^{2+} was also confirmed directly in reactions of $CrCH(CH_3)OH^{2+}$ with Cu^{2+} in the presence of $(NH_3)_5CoF^{2+}$, which produced CrF^{2+}. Oxidation with Fe^{3+} in the presence of $Co(NH_3)_5Br^{2+}$[26] produced $CrBr^{2+}$. After correction for the determined[27] amount of residual Cr^{2+} remaining from the preparation of the organochromium complex, the respective yields of CrF^{2+} and $CrBr^{2+}$ were 98% and 100% of the theoretical values based on eq 4 and 1. Oxidation of $CrCH_2OCH_3^{2+}$ by Fe^{3+} in the presence of $Co(NH_3)_5Cl^{2+}$ produced $CrCl^{2+}$ in 93% yield. The rest of the Cr^{2+} presumably reacted with Fe^{3+} as expected on the basis of the known rates of oxidation of Cr^{2+} by $Co(NH_3)_5Cl^{2+}$[23] and Fe^{3+},[21,22] which are now more nearly competitive.

Formaldehyde was produced quantitatively (106% yield) in the reaction of $CrCH_2OH^{2+}$ with Cu^{2+}. Acetaldehyde was formed quantitatively in the reactions of $CrCH(CH_3)OH^{2+}$ with Cu^{2+} and Fe^{3+}; the respective yields are 111% and 99%. The oxidation of $CrCH(CH_3)OC_2H_5^{2+}$ by Fe^{3+} also forms acetaldehyde (86%) as does decomposition of the complex in the presence of Cu^{2+} (83%) or molecular oxygen. In the case of $CrCH(CH_3)OC_2H_5^{2+}$, the initial product is probably the hemiacetal $HOCH(CH_3)OC_2H_5$ which decomposes to acetaldehyde and ethanol in acidic aqueous solution. That is to say, Cu^{2+} does not react directly with $CrCH(CH_3)OC_2H_5^{2+}$, but this complex is subject to homolytic decomposition, a process which is greatly accelerated by addition of Cu^{2+} since the reaction of Cu^{2+} and the radical $\cdot CH(CH_3)OC_2H_5$ occurs very rapidly, preventing reversal of the homolytic step.

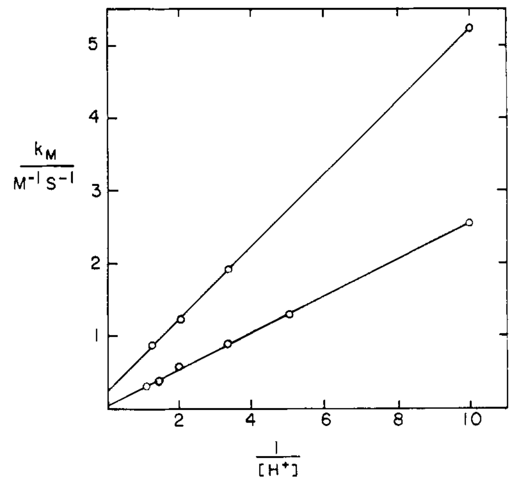

Figure 3. Plots illustrating the rate dependence on hydrogen ion variation. The slopes of the lines in Figure 2 define a second-order rate constant k_M which is a linear function of $1/[H^+]$ according to eq 13. Data refer to reactions of $CrCH_2OH^{2+}$ with Fe^{3+} (upper line) and Cu^{2+} (lower line) at 24.8 °C in 1 M aqueous methanol, 1.00 M ionic strength.

Kinetics of α-Hydroxyalkyl Complexes. The kinetic data yielded values of k_{obsd}, a pseudo-first-order rate constant defined by eq 8.

$$-d[CrR^{2+}]/dt = k_{obsd}[CrR^{2+}] \qquad (8)$$

The reactions of $CrCH_2OH^{2+}$ with Fe^{3+} and Cu^{2+} were studied in 1 M CH_3OH and with Cu^{2+} also in 1:1 CH_3OH/H_2O (ca. 12.3 M CH_3OH). The kinetic data show a linear variation of k_{obsd} with $[Fe^{3+}]_{av}$ or $[Cu^{2+}]_{av}$ at constant $[H^+]$, as illustrated for some typical series of experiments in Figure 2, with a small but finite intercept. The variation of k_{obsd} with concentration of oxidizing agent is thus given by eq 9 and 10. The rate constant k_d, which

$$k_{obsd}{}^{Cu} = k_d + k_{Cu}[Cu^{2+}] \qquad (9)$$

$$k_{obsd}{}^{Fe} = k_d + k_{Fe}[Fe^{3+}] \qquad (10)$$

makes at most a 10% contribution to k_{obsd} (and an average contribution of 4.5%), is believed to represent simply the independently known[7,8] protonolysis of the reactant (eq 11 and 12).

$$CrCH_2OH^{2+} + H_3O^+ = Cr^{3+}(aq) + CH_3OH \qquad (11)$$

$$k_d(25\ °C) = 6.6 \times 10^{-4} + 4.65 \times 10^{-4}[H^+]\ s^{-1} \qquad (12)$$

Values[28] of k_{Cu} and k_{Fe} show a strong inverse dependence on $[H^+]$ such that a plot of k_{Cu} or k_{Fe} vs. $1/[H^+]$ is linear, as illustrated in Figure 3. The relationship can be expressed by eq 13, in which the inverse acid term makes the major contribution under the conditions studied.

$$k_M = k + (k'/[H^+]) \qquad (13)$$

Other oxidizing agents such as $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5OH_2^{3+}$, and H_2O_2 do not at all react with $CrCH_2OH^{2+}$; that is, the rate is simply that attributable to spontaneous acidolysis (eq 11 and 12). In addition, selected divalent cations (Zn^{2+}, Co^{2+}, Ba^{2+}) were added to Cu^{2+} reactions at fairly high concentration (0.27 M) with concomitant reduction in lithium perchlorate concentration to maintain constant ionic strength. The rates were unaffected by these ions. This suggests that no prior association of Cu^{2+} with $CrCH_2OH^{2+}$ occurs to an *appreciable* extent, because if it did then the other redox-inactive M^{2+} ions would be expected to compete with Cu^{2+} in such associations and thus lead to rate retardation by mass-law effects. Of course this does not preclude a small degree of association of Cu^{2+} and $CrCH_2OH^{2+}$ to form

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[26] This complex, which reacts with Cr^{2+} more rapidly than the fluoro complex does,[23] was needed to ensure scavenging of Cr^{2+} by the cobalt(III) complex, considering the rate of oxidation[21,22] of Cr^{2+} by Fe^{3+} according to eq 2.

[27] A determination of the amount of chromium(II) remaining after its reaction with a hydrogen peroxide in stoichiometrically equivalent quantity in the presence of ethanol is required since the yield of the organochromium product is never quantitative. For $CrCH(CH_3)OH^{2+}$, for example, yields are 64–66% of theoretical. This determination was carried out by the rapid addition of an excess of $Co(NH_3)_5F^{2+}$. The absorbance was measured at λ 510 nm and the amount of Cr^{2+} calculated from the change in $[Co(NH_3)_5F^{2+}]$. A correction has been made for the absorbance of CrF^{2+} and Co^{2+} formed in the reaction. Rapid work is required since this organochromium ion decomposes fairly rapidly, especially in the absence of excess Cr^{2+}.

[28] Tabulations of individual rate constants and concentrations are available in the supplementary material.

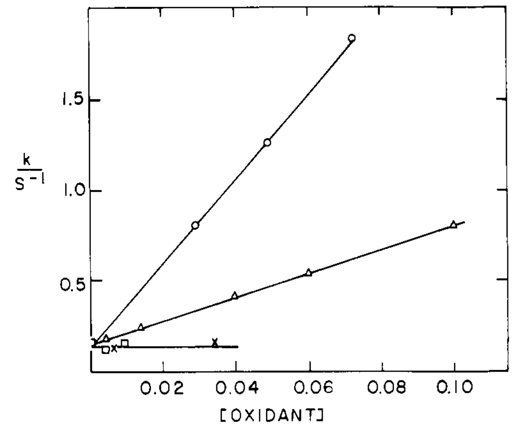

Figure 4. Kinetic data for reactions of $CrC(CH_3)_2OH^{2+}$ at $[H^+] = 0.100$ M (24.8 °C, 1.00 M ionic strength). The plot depicts the linear variation of the pseudo-first-order rate constant with the concentration of the oxidant, showing data for Fe^{3+} (circles) and Cu^{2+} (triangles). The intercepts of these lines correspond to the rate constant for unimolecular homolysis, which is the same value as found in solutions of those oxidizing agents which do not react directly with the (α-hydroxyalkyl)chromium ions such as H_2O_2 (squares) and $Co(NH_3)_5Cl^{2+}$ (X's).

Table I. Parameters for the Dependence of Oxidation Rate Constants[a] on $[H^+]$

complex	$k_{Cu}/M^{-1}\ s^{-1}$	$k_{Fe}/M^{-1}\ s^{-1}$
$CrCH_2OH^{2+}$ [b]	0.063 (35) + 0.810 (17)/$[H^+]$	
$CrCH_2OH^{2+}$ [c]	0.036 (7) + 0.251 (3)/$[H^+]$	0.22 (1) + 0.496 (6)/$[H^+]$
$CrCH(CH_3)OH^{2+}$ [d]	0.68 (12) + 1.46 (5)/$[H^+]$	0.71 (2) + 0.481 (5)/$[H^+]$
$CrC(CH_3)_2OH^{2+}$ [e]	0.77 (4) + 0.574 (13)/$[H^+]$	3.79 (34) + 1.90 (8)/$[H^+]$
$CrCH(CF_3)OH^{2+}$ [f]	$2 \times 10^{-4}/[H^+]$	0 + 0.127 (1)/$[H^+]$[g]
$CrCH(CH_3)OC_2H_5{}^{2+}$ [c]	no reaction	0.082 (7) + 0.0400 (21)/$[H^+]$
$CrCH_2OCH_3{}^{2+}$ [c]	no reaction	0.0062 (18) + 0.0127 (5)/$[H^+]$

[a] At 24.8 °C and 1.0 M ionic strength. Numbers in parentheses represent standard deviations of the last digit(s) of the given parameter. [b] In 1:1 v/v $CH_3OH:H_2O$. [c] In 1 M aqueous methanol. [d] In 1 M aqueous ethanol. [e] In 1 M aqueous 2-propanol. [f] In 1 M aqueous 2,2,2-trifluoroethanol. [g] Value in water is $K_{Fe} = 62\ (11) \times 10^{-4} + 0.114\ (1)/[H^+]$.

a highly reactive intermediate present at very low concentration; indeed this is just what we suggest later as the most plausible mechanism.

The other organochromium cations react similarly, except that the intercepts of plots corresponding to Figure 2 contain, in addition to the rate constant for protonolysis, a contribution from the homolysis reaction

$$CrC(R,R')OH^{2+} \xrightarrow{k_{hom}} Cr^{2+} + \cdot C(R,R')OH \quad (14)$$

The effect of homolysis is quite prominent for $CrC(CH_3)_2OH^{2+}$ where the intercept of Figure 4 (0.133 s^{-1}) in fact consists largely of the homolysis reaction (0.127 s^{-1}). A complete study of the homolysis reactions will be reported elsewhere.[29] This point aside, the rate constants k_{Cu} and k_{Fe} for the other complexes parallel those for $CrCH_2OH^{2+}$ in two important respects: they are of a very similar magnitude[30] and show the same variation with $[H^+]$ (eq 13). Values for all complexes are summarized in Table I.

Table II. Temperature Dependence of the Rate Constants[a] and Activation Parameters for Oxidation of $CrCH_2OH^{2+}$ [b]

	Cu^{2+}		Fe^{3+}	
T, °C	$k/M^{-1}\ s^{-1}$	k'/s^{-1}	$k/M^{-1}\ s^{-1}$	k'/s^{-1}
32.0	0.051 (1)	0.598 (1)	0.44 (2)	1.26 (1)
24.8	0.036 (7)	0.251 (3)	0.22 (1)	0.496 (6)
9.7	0.0052 (8)	0.0380 (3)	0.079 (3)	0.0664 (10)
$\Delta H^\ddagger$, kJ mol^{-1}	74.8 (9.4)	86.1 (0.5)	49.3 (2.8)	92.9 (0.9)
$\Delta S^\ddagger$, J mol^{-1} K^{-1}	−23.7 (32.2)	32.7 (1.7)	−90.9 (9.5)	61.2 (3.1)

[a] At 1.0 M ionic strength and 1 M aqueous methanol.
[b] Numbers in parentheses are the standard deviations of the last digit(s).

Solvent, Temperature, and Isotopic Variations. Since a different alcohol cosolvent was used for the kinetic studies of each complex, that alcohol being the parent alcohol from which the complex was derived, we asked whether these solvent changes were significant. Experiments in which solvent and solvent composition were varied were done under a set of standard conditions: 3.00×10^{-2} M Cu^{2+}, 8.0×10^{-4} M $CrCH_2OH^{2+}$, and 0.500 M H^+ at 24.8 °C and 1.00 M ionic strength. The kinetic data followed the same form as given above in 1 M CH_3OH (where $k_{obsd} = 1.64 \times 10^{-2}\ s^{-1}$). Values of k_{obsd} are as follows: $2.04 \times 10^{-2}\ s^{-1}$ (2 M CH_3OH), $2.31 \times 10^{-2}\ s^{-1}$ (1 M CH_3OH + 1 M C_2H_5OH), and $2.31 \times 10^{-2}\ s^{-1}$ (1 M CH_3OH + 1 M i-C_3H_7OH). Because these rate constants thus appear insensitive to the particular alcohol chosen, the values at 1 M ROH for the different complexes containing different alcohols as solvent components are taken to be strictly comparable. The overall alcohol content is, however, a significant variable, with $k_{obsd} = 1.64 \times 10^{-2}\ s^{-1}$ (1 M CH_3OH), $2.04 \times 10^{-2}\ s^{-1}$ (2 M CH_3OH), and $5.1 \times 10^{-2}\ s^{-1}$ (1:1 CH_3OH/H_2O, ca. 12.3 M).

Activation parameters were determined for both reactions of $CrCH_2OH^{2+}$ with temperature varied from 5–32 °C. In each series the form of the kinetic equation required values at several hydrogen ion concentrations at a given temperature. To provide the best statistical analysis of the data, it was necessary to perform a nonlinear least-squares analysis[32] of k_M as a simultaneous function of $[H^+]$ (according to eq 13) and of temperatures (assuming an activated complex theory form for k and k'). The activation parameters so obtained are given in Table II. Great weight should not be attached to values associated with the rate constant k considering its contribution to k_M is so minor (particularly for Cu^{2+}). We note here, and will subsequently consider, the great similarity in values of k' for Cu^{2+} and Fe^{3+} and in their activation parameters as well.

Kinetic determinations were carried out on the reaction of Cu^{2+} and $CrCD_2OH^{2+}$, prepared from the reaction of CD_3OH in H_2O. The rate constants were the same, within experimental error, as those found for $CrCH_2OH^{2+}$.

Related Complexes. The complexes $CrCH(CF_3)OH^{2+}$, $CrCH_2OCH_3{}^{2+}$, and $CrCH(CH_3)OC_2H_5{}^{2+}$ were examined in reactions carried out at 25 °C. They show little if any direct reaction with Cu^{2+}. $CrCH(CF_3)OH^{2+}$ is exceptionally stable toward acidolysis, which is typical of the effect of electronegative halogen substituents, and toward homolysis (with $Co(NH_3)_5Cl^{2+}$, $k_{hom} = 3 \times 10^{-5}\ s^{-1}$). There appears to be a direct but very slow reaction with Cu^{2+} ($k_{obsd} = 3.93 \times 10^{-4}\ s^{-1}$ at 0.193 M Cu^{2+}, 0.1 M H^+); by way of comparison, under the same conditions, $CrCH(CH_3)OH^{2+}$ would have $k_{obsd} = 3.0\ s^{-1}$. With the as-

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(29) Bakač, A.; Kirker, G. W.; Espenson, J. H., manuscript in preparation.

(30) The detection of the reaction of $CrC(CH_3)_2OH^{2+}$ and Fe^{3+} was interfered with by the competing reequilibration of the monomer–dimer equilibrium, $2Fe^{3+} + 4H_2O = Fe_2(OH)_2{}^{4+} + 2H^+$, which occurs[31] on a similar time base. The problem was avoided by adjustment of the $[H^+]$ in each of the separate reservoirs of the equal-volume stopped-flow instrument such that the iron(III) species are at equilibrium both before and after dilution. The condition is circumvented in a run having a final $[H^+] = X/2^{1/2}$ if $[H^+]$ in the solutions of $CrC(CH_3)_2OH^{2+}$ and Fe^{3+} are $(2^{1/2} - 1)X$ and X, respectively.

(31) Conocchioli, T. J.; Hamilton, E. J., Jr.; Sutin, N. *J. Am. Chem. Soc.* **1965**, *87*, 926.

(32) The computer program was based on the report from Los Alamos Scientific Laboratory, LASL 2367 + Addenda.

(33) The difficulty with the reaction of eq 17 is not that $Cr^+(aq)$ is completely unknown but that it is too unstable a species to be generated by this reaction. Pulse radiolysis experiments to produce $Cr^+(aq)$ have been reported: Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton, Trans.* **1974**, 2559.

sumption that the k' term of eq 13 dominates, these results permit estimation of a very rough upper limit: $k' \simeq 2 \times 10^{-4}$ s^{-1} for $CrCH(CF_3)OH^{2+} + Cu^{2+}$. The reaction of $CrCH_2OCH_3^{2+}$ with Cu^{2+} is even slower. At 0.1 M $HClO_4$ and 0.3 M Cu^{2+}, k_{obsd} 2.1 × 10^{-5} s^{-1}, at least a part of which could be ascribed to acidolysis and/or homolysis. $CrCH(CH_3)OC_2H_5^{2+}$ shows only homolysis, reacting indirectly in the presence of Cu^{2+}, $Co(NH_3)_5Cl^{2+}$, or $Co(NH_3)_5H_2O^{3+}$ at a rate ($k_{obsd} = (2.04 \pm 0.02) \times 10^{-3}$ s^{-1}) independent of the nature or concentration of the oxidizing agent and of [CH_3OH] (0–1 M) and [H^+] (0.1–0.85 M).

Iron(III) reacts with all three of these complexes at appreciable rates, although in each case the reaction is much slower than that between Fe^{3+} and the complexes considered in the preceding section. In the case of $CrCH(CH_3)OC_2H_5^{2+}$, k_{obsd} is a linear function of [Fe^{3+}] with an intercept of $(2.28 \pm 0.14) \times 10^{-3}$ s^{-1}, the same as the value for homolysis. The slope gives the value of k_{Fe} at a given [H^+]. These rate constants[28] vary with [H^+] according to eq 13, with $k = 0.082 \pm 0.007$ M^{-1} s^{-1} and $k' = 0.0400 \pm 0.0021$ s^{-1} at 24.8 °C, 1 M CH_3OH, and 1 M ionic strength. Several kinetic experiments were done with $CrCD(CD_3)OC_2D_5^{2+}$, prepared from diethyl-d_{10} ether. Within the experimental error the rate constants for the oxidation of this complex by iron(III) did not differ from the ones measured for $CrCH(CH_3)OC_2H_5^{2+}$.

The oxidation of $CrCH_2OCH_3^{2+}$ by iron(III) also follows mixed-second-order kinetics. The acid dependence of this reaction is again well described by eq 13 with $k = (6.2 \pm 1.8) \times 10^{-3}$ M^{-1} s^{-1} and $k' = (1.27 \pm 0.05) \times 10^{-2}$ s^{-1} at 25.2 °C, 1 M CH_3OH, and 1 M ionic strength.

Oxidation of $CrCH(CH_3)OC_2H_5^{2+}$ and $CrCH_2OCH_3^{2+}$ by Fe^{3+} was also studied in pure aqueous solution with the use of complexes isolated by ion-exchange chromatography without the addition of methanol. The rate constants measured at low iron(III) concentrations (~0.01 M) were almost identical with the ones obtained at 1 M CH_3OH. However, a plot of k_{obsd} vs. [Fe^{3+}] showed some curvature so that the rate constants at the high end of [Fe^{3+}] (~0.10 M) were 10–20% lower than expected. The magnitude of the effect is acid independent ruling out any significant comcomplex formation between Fe^{3+} and organochromium complexes which would be expected to show some acid dependence. No further study of this effect was done in view of its relatively small influence on the rate constants and the fact that plots of k_{obsd} vs. [Fe^{3+}] were precisely linear in 1 M alcohol, the standard medium for all the reactions studied.

The complex $CrCH(CF_3)OH^{2+}$ also reacts directly with Fe^{3+} at an appreciable rate; the values[28] of k_{Fe} are inversely proportional to [H^+]

$$-d[CrCH(CF_3)OH^{2+}]/dt = k'[CrCH(CF_3)OH^{2+}][Fe^{3+}]/[H^+] \quad (15)$$

with $k' = 0.127 \pm 0.001$ s^{-1} (24.8 °C, 1 M CF_3CH_2OH in water) and 0.114 ± 0.001 s^{-1} (24.8 °C, water).

Interpretation and Discussion

Comparison of Chromium and Cobalt Complexes. Two unusual modes of reactivity are combined in the chemistry of the α-OH alkyl chromium complexes: (1) the very large reversal in their apparent (or kinetic) stability relative to the organocobalt (N_4 chelate) analogues[4,5] and (2) reactions with selected one-electron oxidizing agents (Cu^{2+}, Fe^{3+}) but not with oxidants in general (e.g., H_2O_2, O_2, $Co(NH_3)_5X^{2+}$) (alkyl complexes do not react with any of these reagents, except in special cases).[9a,10] The cobalt(III) complexes decompose by a two-electron process[5] (eq 16) which

$$(N_4Chel)CoCH_2OH^{2+} \rightarrow [(N_4Chel)Co^I]^+ + H^+ + HCHO \quad (16)$$

is almost certainly[33] unavailable to the chromium complex (eq 17). On the other hand, an overall two-electron change can be

$$(H_2O)_5CrCH_2OH^{2+} \nrightarrow Cr^+(aq) + H^+ + HCHO \quad (17)$$

realized if a suitable external oxidant and the chromium each suffer one-electron reduction, thus accounting for eq 1 and 4. The suitability of some oxidants but not others appears to be closely related to the question of mechanism and in particular for these metal ion oxidants to their ligand substitution rates.

Mechanism of $CrC(R,R')OH^{2+}$ Reactions. Site of Proton Ionization. The predominant term in the rate equation shows an inverse dependence upon [H^+]. The major question in a consideration of mechanism is which acidic group on the reactants ionizes in forming the activated complexes. Three possibilities are evident: (a) a water molecule on the oxidant; (b) a water molecule coordinated to the organochromium reagent; (c) the acidic proton of the OH group of the α-hydroxyalkyl ligand. In the first case the active oxidizing species are implied to be $(H_2O)_5CuOH^+$ and $(H_2O)_5FeOH^{2+}$; in the second, a reaction of $[(H_2O)_4Cr(OH)(CRR'OH)]^+$ is implied. The third suggestion corresponds to the formation of the intermediates $[(H_2O)_5CrC(R,R')OCu^{3+}]$ and $[(H_2O)_5CrC(R,R')OFe^{4+}]$. The case we propose to make in the subsequent paragraphs of this section is that the first two possibilities provide less convincing explanations of our findings than the third.

A very narrow range of k' values was found (Table I). Values of k' proved to be quite insensitive to the structural differences among the three organochromium ions and to use of Cu^{2+} or Fe^{3+}. Considering the first suggestion (a), rate-limiting attack of $CuOH^+$ and $FeOH^{2+}$, it is noted that the two parent aquo complexes differ so greatly in acidity [$pK_a(Cu^{2+}) \approx 8$ and $pK_a(Fe^{3+}) = 2.78$] yet the net reaction rates are about the same. Were this mechanism adopted and the bimolecular rate constants calculated, then k'_{CuOH^+} ($=k'_{Cu}/K_{a,Cu(II)}$) would be very much greater than $k'_{FeOH^{2+}}$ ($=k'_{Fe}/K_{a,Fe(III)}$), by a factor of ca. 10^5, which is the opposite of the order expected from the oxidizing strengths. The mechanism is further discounted because a similar hydroxo complex, $Co(NH_3)_5OH^{2+}$, is unreactive.

The second suggestion (b) invokes the preequilibrium ionization of water coordinated to the organochromium ion; the ionization constants, although unknown, will be very close to one another. This seems to afford one facile explanation for the narrow reactivity range but leads to other difficulties.

The mechanism would then consist of the steps

$$(H_2O)_5CrROH^{2+} \rightleftharpoons HOCr(OH_2)_4ROH^+ + H^+ \quad K_{a,Cr} \quad (18)$$

$$Cu^{2+}(aq) + HOCr(OH_2)_4ROH^+ \rightarrow [CuOHCr(OH_2)_4ROH]^{3+} \quad (19)$$

This formulation does not readily account for the rates of the Cu^{2+} and Fe^{3+} being nearly identical. If eq 19 is rate limiting (and followed by *rapid* internal electron transfer), then Cu^{2+} and Fe^{3+} which have very different ligand substitution rates would be expected to have very different reaction rates since $k_{Cu,19} \gg k_{Fe,19}$. On the other hand, if the reaction of eq 19 is viewed as a preequilibrium (assuming iron(III) substitution occurs rapidly enough to permit such a view), then one would need to argue that the rate similarities come about because the "internal electron-transfer processes" are nearly the same in each case. These metals and organic radicals[34] differ greatly in their reduction potentials. Considering that both metals are to be reduced, such intermediates would require a difficult but not impossible sequence of electron transfers: from carbanion to chromium, from chromium to iron. Related to this mechanism is another process in which the conjugate base complex $[HOCr(H_2O)_4C(R,R')OH]^+$ is involved in rate-limiting ligand substitution. This could indeed explain the close coincidence of all rates, but it would lead to an activated complex (with a bridging H_2O between Cr and Cu or Fe?) which makes it difficult to account for subsequent reactions, especially formation of Cr^{2+}. Chelation of the conjugate base species and the oxidizing metal ion, via Cr–OH and COH groups, is yet another possibility. It is not possible to rule out all of these formulations on the basis of the data at hand.

The arguments for possibility (c) involving ionization of the alcohol OH group are the following. The first step (which turns out to be a rapid preequilibrium) establishes a small steady-state

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(34) Rao, P. S.; Hayon, E. *J. Am. Chem. Soc.* **1975**, *97*, 2986.

concentration of a reactive intermediate which in turn undergoes unimolecular decomposition to the final products. This proposal is shown for Cu^{2+} in eq 20 and 21, and a similar scheme is easily written for Fe^{3+}.

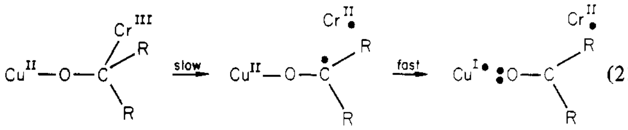
$$Cu^{2+}(aq) + (H_2O)_5CrC(R,R')OH^{2+} \underset{k_{-1,Cu}}{\overset{k_{1,Cu}}{\rightleftharpoons}} [(H_2O)_5CrC(R,R')OCu^{3+}] + H^+ \quad (20)$$

$$[(H_2O)_5CrC(R,R')OCu^{3+}] \xrightarrow{k_{2,Cu}} Cr^{2+}(aq) + Cu^+(aq) + (R,R')C{=}O \quad (21)$$

The rate law derived from this mechanism, with the steady-state approximation made for the intermediate, is given by eq 22. Provided $k_{-1}[H^+] \gg k_2$, eq 22 simplifies to a form consistent with the major pathway and allows us to identify k' of eq 13 as the composite k_1k_2/k_{-1}. The second step of each mechanism is, in effect, rate limiting.

$$-d[CrC(R,R')OH^{2+}]/dt = k_1k_2[CrC(R,R')OH^{2+}][M]/(k_{-1}[H^+] + k_2) \quad (22)$$

The key issue remains the similarity of all the values of k', which we presume is not coincidental. The rate in every case may be governed by the rate of electron transfer to chromium(III).


(23)

This scheme appears to be the best formulations for the copper(II) reactions, particularly so considering that the ether-derived complexes $CrROR^{2+}$ show no reaction whatever with Cu^{2+}. On the other hand, the iron reactions may occur by similar reactions, but in this case a mechanism involving rate-limiting ligand substitution reactions of $FeOH^{2+}$ must be given considerable weight as well.

Comparisons with Free Radical Oxidations. The process shown in eq 20–23 bears a strong resemblance to that proposed[35] for the oxidation of alcohols by the strong one-electron oxidizing agent $Co(H_2O)_6^{3+}$. These reactions also show an inverse acid dependence and have been interpreted as proceeding through an activated complex having the structure $[(R,R')CHOCo]^{\ddagger}$. The various α-(hydroxyalkyl)chromium complexes react at very similar rates, as has also been observed for some reactions of the parent free radicals. The reactions[12b] of the free radicals $HO\dot{C}(R,R')$ with Cu^{2+}, for which good evidence exists to support the suggestion[13,14,15b] of organocopper intermediates, react at nearly identical rates; values of $10^{-7}k$ are 16 ($\cdot CH_2OH$), 9.4 ($CH_3\dot{C}HOH$), and 5.2 $M^{-1}\ s^{-1}$ ($(CH_3)_2\dot{C}OH$). Of course, one must argue the similarity not only of the k_2 values but also of the k_1/k_{-1} ratios, for they together determine the experimental rate constant k'. The latter is not difficult to reconcile for either metal ion separately since the equilibrium constants for eq 20 are not likely to vary significantly with the substituents considering that pK_a's for the parent α-hydroxyalkyl radicals are quite similar.[36,37] Considering that the kinetic data require that Fe^{3+} or Cu^{2+} be weakly bound, i.e., $k_1/k_{-1} \ll 1$, large differences between the two metal ions may not be required.

It is useful to return to a point touched upon earlier, comparison of the present reactions with the mechanism of apparently analogous reactions[12b] of the parent carbon-centered free radicals.

$$\cdot C(R,R')OH + Cu^{2+} = (R,R')CO + Cu^+ + H^+ \quad (24)$$

$$\cdot C(R,R')OH + Fe^{3+} = (R,R')CO + Fe^{2+} + H^+ \quad (25)$$

These two reactions differ markedly from one another and are different as well from the reactions of these metal ions with $CrC(R,R')OH^{2+}$. The reactions of Cu^{2+} with the free radical occur by attack directly at the coordinatively unsaturated carbon atom and proceed via organocopper intermediates. On the other hand, the iron(III) reactions do not involve formation of $FeC(R,R')OH^{2+}$ (for one thing, substitution at iron(III) occurs too slowly). In addition, the reactions are independent of $[H^+]$, and even if substitution rates permitted an intermediate, $C(R,R')OFe^{3+}$ is not indicated by the kinetic data. It is thus concluded[11,12b] that the reactions of Fe^{3+} in eq 25 occur by outer-sphere electron transfer, a conclusion supported by the kinetic effects of the R,R′ substituents since the rate constants increase with the stability of the corresponding carbonium ions.

H^+-Independent Pathway. The less important pathway, that represented by k of eq 13, is proposed to be a parallel process occurring by a similar mechanism but without deprotonation. As so often happens when a basic site exists in a substrate, the degree of protonation may not be a critical feature of the mechanism.

$CrCH(CH_3)OC_2H_5^{2+}$, $CrCH_2OCH_3^{2+}$, and $CrCH(CF_3)OH^{2+}$. Our findings that Cu^{2+} reacts with these three complexes very slowly or not at all is easily rationalized in terms of the mechanism proposed. $CrCH(CF_3)OH^{2+}$ is expected to react slowly because the strong electron-withdrawing nature of the CF_3 substituent on the α-carbon atom greatly reduces the rate of internal electron-transfer step depicted in eq 23. Failure of the ether-derived complexes to react with Cu^{2+} is consistent with the lack of access to an analogous activated complex but might equally well be attributed to the inability of this derivative to undergo an oxidation process of the same sort.

These ideas must be tempered, however, by the results for the reaction of the same complexes with iron(III). In all three instances Fe^{3+} does react with these complexes, albeit more slowly than with the parent hydroxyalkyls. More to the point, however, the form of the rate law and the identity of the products of both groups of reactions are parallel. In the case of the (α-ethoxyethyl)chromium ion, the initial product of reactions with Fe^{3+} is probably the hemiacetal $HOCH(CH_3)OC_2H_5$, which under the acidic conditions decomposes to ethanol and acetaldehyde, the latter being determined as the quantitative product of this reaction. Analogously formaldehyde is produced in a quantitative yield in the oxidation of (methoxymethyl)chromium by iron(III). There appear to be at present several possibilities for these reactions that we cannot completely distinguish. The first is that the reaction of $CrCH(CF_3)OH^{2+}$ occurs by the same mechanism as the hydroxyalkyls and is found to be significant for Fe^{3+} but not for Cu^{2+} as a reflection of the great difference in oxidizing strength. For the (methoxymethyl)- and (α-ethoxyethyl)chromium ions, however, a preequilibrium analogous to eq 20 clearly cannot occur. The inverse acid path for these reactions must therefore either occur by a different mechanism than ascribed to reactions of $CrC(R,R')OH^{2+}$ and Fe^{3+} or our assignment of the latter is erroneous. The support for that assignment cannot be regarded as overwhelming; nonetheless, this dilemma has caused us to consider other possibilities. One such possibility consists of direct attack of $FeOH^{2+}$. The reaction site might be the α-carbon itself (consistent with hemiacetal formation), in which case $CrCH_2OCH_3^{2+}$ should react more rapidly. The experimental rates are very similar for the two complexes, with $CrCH(CH_3)OC_2H_5^{2+}$ being actually slightly more reactive than $CrCH_2OCH_3^{2+}$.

These considerations suggest that the OH-bridged activated complex for the iron(III) (only) reactions may be important: $[FeOHCrROH^{4+}]^{\ddagger}$, although iron(III) could also attack at the oxygen atom of the bound ether. These possibilities seem much less realistic ones for Cu^{2+}, considering the lower acidity of the coordinated water molecules and the weaker oxidizing strength.

Mechanism of the Preequilibrium Step. We remarked earlier that the mechanism by which the intermediate forms according to eq 20 is immaterial in the present context, considering that this step occurs rapidly compared to the overall reaction. Without further consideration, however, the proposal as written for iron(III) in analogy to eq 20 might be taken as a basis for objection since $k_{1,Fe}$, although difficult to calculate exactly, would greatly exceed

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(37) The argument we make concerning the value of k_1/k_{-1} does not depend on the mechanism by which equilibrium is established; this point was made in the context of the reaction of $Co(NH_3)_5OH_2^{3+}$ and $Cr^{2+}(aq)$ which also occurs by an inverse-acid pathway (Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264).

the maximum value ever found for a substitution reaction of $Fe(H_2O)_6^{3+}$. On the other hand, if the process is being viewed as a reaction of $FeOH^{2+}$, as in eq 26 and 27, then a value of $k'_{1,Fe}$

$$Fe(H_2O)_6^{3+} \xrightleftharpoons{K_{Fe}} (H_2O)_5FeOH^{2+} + H^+ \qquad (26)$$

$$CrC(R,R')OH^{2+} + FeOH^{2+} \xrightleftharpoons[k'_{-1,Fe}]{k'_{1',Fe}} [CrC(R,R')OFe]^{4+} \qquad (27)$$

$\simeq 10^4$ M^{-1} s^{-1}, typical of such substitutions, is compatible with the present kinetics and leads to $k_{2,Fe}/k'_{-1,Fe} \leq 0.1$, consistent with the assignment of the second step as rate limiting. Similar arguments concerning substitution rates could be applied to the formation of the alternative activated complex suggested for the reactions of iron(III), $[FeOHCrC(R,R')OH]^{4+}$.

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Supplementary Material Available: Listings of individual rate constants and concentrations (10 pages). Ordering information is given on any current masthead page.

Concurrent Electrophilic and Oxidative Pathways for Reactions of α-Hydroxyalkyl and α-Alkoxyalkyl Complexes of Chromium(III) with Mercury(II) Ions

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Abstract: The reactions of Hg^{2+} with a number of α-hydroxyalkyl and α-alkoxyalkyl complexes of chromium(III) were studied. The lowest members of both series, $CrCH_2OH^{2+}$ and $CrCH_2OCH_3^{2+}$, react with Hg^{2+} in an acid-independent electrophilic substitution reaction with the reaction constant $\rho = -10$. The organomercurials formed are unstable and decompose rapidly to yield Hg^0. All the other organochromium complexes studied react with Hg^{2+} in acid-dependent electron-transfer reactions. (α-Hydroxyisopropyl)chromium ion, $CrC(CH_3)_2OH^{2+}$, undergoes a one-electron transfer reaction, producing Cr^{2+} and Hg^+ with k (M^{-1} s^1) = 166 + 467/[H^+], while (α-ethoxyethyl)chromium ion, $CrCH(CH_3)OC_2H_5^{2+}$, reacts in a two-electron redox process, yielding Cr^{3+} and Hg^0, k (M^{-1} s^{-1}) = 0.535/[H^+]. (α-Hydroxyethyl)chromium ion, $CrCH(CH_3)OH^{2+}$, reacts by both routes, k (M^{-1} s^{-1}) = 4.11/[H^+], with ~15% participation from the one-electron path and ~85% from the two-electron path. The effect of Cr^{2+} and $Co(NH_3)_5F^{2+}$ (a specific scavenger for Cr^{2+}) on the kinetics and stoichiometry of the reactions is discussed.

The chemistry of α-hydroxyalkyl complexes is presently an active area.[1-11] We have examined the reactions of Hg^{2+} with such chromium(III) cations, whose formulas we represent as $(H_2O)_5CrROH^{2+}$, along with related α-alkoxyalkyl complexes, $(H_2O)_5CrROR'^{2+}$. Mercury(II) ion is a useful reagent because it can function either as an electrophilic reagent, as it does with alkyls[12,13] which react by the S_E2 mechanism,[14,15] in which the rate is pH independent and subject to strong steric influence, or as an oxidizing agent,[16,17] not attacking directly at carbon. In the latter case[1,2] the major kinetic term is proportional to $[H^+]^{-1}$, and the rate very nearly the same for all of the $CrROH^{2+}$ complexes examined. Because there is a considerable variation in structure among the complexes studied, the mechanism of the reactions with Hg^{2+} changes along the series requiring a detailed study of each complex, which is the subject of the present article.

Experimental Section

Materials. The complexes were prepared as before,[2] with excess Cr^{2+} added in some instances to stabilize against homolysis.[18,19] Other reagents have been described previously.[12,20]

Product Analysis. A complete analysis was carried out for the products of each reaction separately in view of the wide differences found among the various members of the series. Any Cr^{2+} formed was converted to CrF^{2+} by reaction with $Co(NH_3)_5F^{2+}$, either present during the reaction of $CrROH^{2+}$ and Hg^{2+} or added immediately upon its completion.[21] The CrF^{2+} fraction was then separated by ion exchange and determined spectrophotometrically from its known absorption spectrum. In some instances the yield of Co^{2+} was also determined with use of a spectrophotometric analysis based upon conversion to $Co(NCS)_4^{2-}$ in aqueous acetone (ϵ_{623} 1.83 × 10^3 M^{-1} cm^{-1}). Similarly $Cr(H_2O)_6^{3+}$ was separated by ion exchange. The latter was usually some 10%-15% lower than expected, the difference assumed to arise from incomplete recovery from the resin column and from the dimeric ion Cr_2O^{4+}, formed in the

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(21) This cobalt complex is an effective scavenger for Cr^{2+} in these reactions not only because it reacts rapidly with Cr^{2+} (k = 2.5 × 10^5 M^{-1} s^{-1}) but also because it does not react with $CrROH^{2+}$ complexes or (unlike other $Co(NH_3)_5X^{2+}$ and CrX^{2+} complexes) with Hg^{2+}.

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