2728 J. Am. Chem. Soc. 1981, 103, 2728-2733

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 $k'_{1,Fe}$

$$Fe(H_2O)_6^{3+} \overset{K_{Fe}}{\rightleftharpoons} (H_2O)_5FeOH^{2+} + H^+ \tag{26}$$

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

$\simeq 10^4$ 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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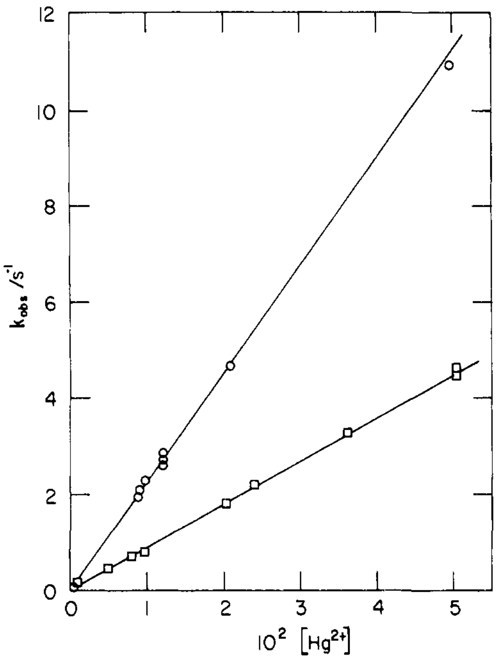

Figure 1. Kinetic data for S_E2 reactions of Hg^{2+} with $CrCH_2OH^{2+}$ (eq 1, circles) and with $CrCH_2OCH_3^{2+}$ (eq 2, squares), plotted as the pseudo-first-order rate constant vs. [Hg^{2+}] at 24.7 °C and varying [H^+], 0.10–1.00 M.

original preparation,[22] which could be seen as a green band at the top of the resin column. The chromium analyses were necessarily carried out at much higher concentrations than were the other analyses or kinetics, but nothing in the results suggests that our findings were altered for this reason.

The concentration of Hg_2^{2+} produced was determined spectrophotometrically (ϵ_{236} 2.80 × 10^4 M^{-1} cm^{-1}), with appropriate blank corrections for other components such as $Co(NH_3)_5F^{2+}$ (ϵ_{236} 770).

Formaldehyde was determined with use of chromotropic acid.[23] Acetone was determined spectrophotometrically after removal of the metal ions by ion exchange. In this medium (0.5 M 2-propanol, 0.05 M perchloric acid), ϵ_{263} 17.7 M^{-1} cm^{-1} for acetone. Acetaldehyde was detected among the products from the UV spectrum after ion exchange; quantitative determination was done by extraction into chloroform in which ϵ_{285} 18.3 M^{-1} cm^{-1}. Mass spectral analysis was used to identify the product of the reaction of $CrCD(CD_3)OC_2D_5^{2+}$ with Hg^{2+}.

Kinetics. The progress of the reactions was monitored spectrophotometrically, with the use of one of the absorption maxima of the organochromium cation near 300 or 400 nm or the 236-nm maximum of Hg_2^{2+}. The reactions were followed with use of Cary Model 14 and Cary Model 219 spectrophotometers or a Canterbury SF-3A stopped-flow spectrophotometer, depending on the time scale of a given reaction. Specific procedures are as follows. For the slow reactions of the relatively stable cations $CrCH(CH_3)OC_2H_5^{2+}$ and $CrCH(CF_3)OH^{2+}$, all components except Hg^{2+} were placed under N_2 in a quartz cell of 5-cm optical path and thermostated at 25 °C for 20–30 min. Reactions were initiated by injecting a deaerated solution of Hg^{2+}. The stopped-flow study of another thermally stable complex, $CrCH_2OCH_3^{2+}$, was done similarly. The remaining three rapidly-reacting complexes, $CrCH_2OH^{2+}$, $CrCH(CH_3)OH^{2+}$ and $CrC(CH_3)_2OH^{2+}$, were prepared in the stopped-flow solution reservoir immediately before use. Owing to their lower stability the thermostating time was significantly reduced for these reactions.

The kinetics experiments were carried out at 25 °C and 1.00 M ionic strength, maintained with lithium perchlorate and perchloric acid, either in pure aqueous solution for (alkoxyalkyl)chromium reactions or in 1.0 M aqueous alcohol for (α-hydroxyalkyl)chromium reactions, with use of the parent alcohols, methanol, ethanol, or 2-propanol. Most of the determinations with $CrC(CH_3)_2OH^{2+}$ were done at 0.05 M 2-propanol. The changes in alcohol concentration at these low levels had minimal effect.

The reactions were done with an excess of mercury(II) ions to avoid formation of metallic mercury. In all but one instance the concentration of mercury(II) was sufficiently high that it could be regarded as nearly constant during each kinetic run. Such reactions conformed quite precisely to pseudo-first-order kinetics, and the value of k_{obsd} was calculated with use of standard methods.

Results and Interpretation

The members of this family of organometallic cations react with Hg^{2+} by at least three quite different mechanisms, as manifested by changes in stoichiometry, products, rate equations, and the effects of scavengers for possible intermediates. Because of these variations, each system required individual study in detail. The results for each set of complexes are thus given separately for sake of clarity. It has proved possible to account for the entire set of reactions in terms of characteristic pattern of reactivity which bears a rational relationship to the constitution of a given reactant. For sake of clarity, the mechanistic interpretation for each organochromium ion is given with the experimental findings for each reaction.

$CrCH_2OH^{2+}$ and $CrCH_2OCH_3^{2+}$. Both reactions produce formaldehyde in 100% yield; neither, when carried out in the presence of $Co(NH_3)_5F^{2+}$, gives rise to a detectable quantity of CrF^{2+}. For these reasons and others to be given shortly, it seems quite certain that these complexes both react by direct alkyl transfer from chromium to mercury, as in the S_E2 mechanism of eq 1 and 2, giving rise to organomercury(II) cations.

$$\mathrm{CrCH_2OH^{2+} + Hg^{2+} \rightarrow Cr^{3+} + HgCH_2OH^+} \qquad (1)$$

$$\mathrm{CrCH_2OCH_3^{2+} + Hg^{2+} \rightarrow Cr^{3+} + HgCH_2OCH_3^+} \qquad (2)$$

The latter are susceptible to decomposition, however, and are not isolable from these reactions. The net reactions in each case are eq 3 and 4.

$$\mathrm{CrCH_2OH^{2+} + 2Hg^{2+} = Cr^{3+} + Hg_2^{2+} + HCHO + H^+} \qquad (3)$$

$$\mathrm{CrCH_2OCH_3^{2+} + 2Hg^{2+} + H_2O = Cr^{3+} + Hg_2^{2+} + HCHO + CH_3OH + H^+} \qquad (4)$$

Kinetic determinations for $CrCH_2OH^{2+}$ were done at both 390 nm (λ_{max} for $CrCH_2OH^{2+}$) and 236 nm (Hg_2^{2+}), with identical results. Values of k_{obsd} are directly proportional to [Hg^{2+}] and do not depend on [H^+] as shown in Figure 1. The kinetic data are consistent with the rate law of eq 5, with k_1 = 228 ± 7 M^{-1} s^{-1} at 25.0 °C and 1 M aqueous methanol.

$$-d[\mathrm{CrCH_2OH^{2+}}]/dt = k_1[\mathrm{CrCH_2OH^{2+}}][\mathrm{Hg^{2+}}] \qquad (5)$$

Addition of $Co(NH_3)_5F^{2+}$ has no effect on the reaction rate, k_1 at 5.0 × 10^{-3} M being 247 ± 4 (0.10 M H^+) and 235 ± 4 (0.95 M H^+). In addition, change of nature of the alcohol has no effect; at 0.5 M CH_3OH + 1.0 M 2-C_3H_7OH (the latter added after formation of $CrCH_2OH^{2+}$ was complete), k_1 = 237 M^{-1} s^{-1}.

The kinetics of the reaction of $CrCH_2OCH_3^{2+}$ with Hg^{2+} are wavelength dependent. At 385 nm, a single reaction (Figure 1) with an acid-independent rate constant is seen. The value of k_2 at various temperatures is as follows: 20.3 ± 0.1 M^{-1} s^{-1} (0.3 °C), 27.2 (5.2), 52.2 (15.4), 90.5 ± 0.8 (24.7), and 196 ± 1 (40.0).

$$-d[\mathrm{CrCH_2OCH_3^{2+}}]/dt = k_2[\mathrm{CrCH_2OCH_3^{2+}}][\mathrm{Hg^{2+}}] \qquad (6)$$

The activation parameters for k_2 according to activated complex theory are $\Delta H^{\ddagger}$ = 38.6 ± 0.3 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −77.8 ± 1.0 J mol^{-1} K^{-1}.

The absorbance at 270 nm first decreases as $CrCH_2OCH_3^{2+}$ is consumed and then increases. The latter is attributed to the decay of the organomercury cation.

$$\mathrm{HgCH_2OCH_3^+ + H_2O \rightarrow Hg^0 + HCHO + CH_3OH + H^+} \qquad (7)$$

$$\mathrm{Hg^0 + Hg^{2+} \rightarrow Hg_2^{2+}} \quad \text{(very fast)}^{24} \qquad (8)$$

The first stage kinetics agreed with eq 6, and the second stage was best studied at 236 nm where both stages are accompanied

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[22] One of the side reactions is formation of a chromium(III) dimer: Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197. Anderson, L. B.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 1470.

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by an increase in absorbance, but the amplitude of the second is much larger owing to the very large molar absorptivity of Hg_2^{2+}. The rate constant for the second stage, determined by an analysis of the data by a consecutive reaction treatment, is independent of $[Hg^{2+}]$ and $[CrCH_2OCH_3^{2+}]_0$.

$$d[Hg_2^{2+}]/dt = k_7[HgCH_2OCH_3^+] \tag{9}$$

The value of k_7 shows a small inverse acid dependence: at 1.00 M H^+, $k_7 = 8.24 \times 10^{-3}$ s^{-1} and at 0.100 M H^+, 1.6×10^{-2} s^{-1}, both determinations from experiments at 25 °C having $0.7 < 10^5[CrCH_2OCH_3^{2+}]_0 < 8$ M and $0.48 < 10^3[Hg^{2+}] < 1.6$ M. The kinetic analysis yields ϵ_{236} for $HgCH_2OCH_3^+$ as $(8.2 \pm 0.5) \times 10^3$ M^{-1} cm^{-1}. The final spectrum is that of Hg_2^{2+} and as expected from eq 4 has an intensity consistent with the stoichiometry, $[Hg_2^{2+}]_\infty = [CrCH_2OCH_3^{2+}]_0$.

Further confirmation of the chemistry shown by the reactions in eq 2, 4, 7, and 8 comes from a kinetic determination at 385 nm and 24.7 °C, with the concentrations 8.96×10^{-4} M Hg^{2+}, 4.81×10^{-4} M $CrCH_2OCH_3^{2+}$, and 1.0 M H^+, such that $[Hg^{2+}]$ was in less than twofold excess over the organochromium ion. All of the organochromium ion was consumed, as in eq 2, and in accord with the stoichiometry of this reaction the second-order kinetic plot was linear only if a 1:1 stoichiometry was assumed. The rate constant was 87.5 M^{-1} s^{-1}, in good agreement with the value 90.5 ± 0.8 from runs having a large excess of Hg^{2+}. A kinetic plot assuming an initial 1:2 stoichiometry as in the overall reaction of eq 4 was curved and a rate constant could not be evaluated. In essence, these data show that one Hg^{2+} is consumed in each reaction. These observations, coupled with the previously noted result that the ultimate Hg_2^{2+} product is formed only after the $CrCH_2OCH_3^{2+}$ reactant has been consumed, are consistent with eq 2 followed by eq 7.

On the other hand, identical kinetics were found for the reaction of $CrCH_2OH^{2+}$ and Hg^{2+} at 390 and 236 nm. The clear implication in this case is that the analogous intermediate $HgCH_2OH^+$ (assuming it is formed in the reaction) has a much shorter lifetime (eq 10) than $HgCH_2OCH_3^+$. This is quite reasonable considering the same stability order has been found for organocobalt compounds which also decompose by two-electron reactions.[10,25]

$$HgCH_2OH^+ \rightarrow Hg^0 + HCHO + H^+ \tag{10}$$

$CrC(CH_3)_2OH^{2+}$. This reaction produces $Cr(H_2O)_6^{3+}$, Hg_2^{2+}, and acetone in 1:1:1 amounts; addition of $Co(NH_3)_5F^{2+}$ after reaction is complete produced no further reaction. The stoichiometry under these conditions is thus

$$CrC(CH_3)_2OH^{2+} + 2Hg^{2+} = Cr^{3+} + (CH_3)_2CO + Hg_2^{2+} + H^+ \tag{11}$$

On the other hand, the stoichiometry is sharply altered when $Co(NH_3)_5F^{2+}$ is present during the entire reaction. Acetone is still formed quantitatively but now CrF^{2+} and not Cr^{3+} is produced, and the yield of mercurous ions is nearly halved: $[Hg_2^{2+}]_\infty/[CrC(CH_3)_2OH^{2+}]_0 \approx 0.57 \pm 0.05$. The stoichiometric reaction in the presence of $Co(NH_3)_5F^{2+}$ can thus be formulated as eq 12.

$$CrC(CH_3)_2OH^{2+} + Hg^{2+} + Co(NH_3)_5F^{2+} + 4H^+ = CrF^{2+} + (CH_3)_2CO + {}^1/_2Hg_2^{2+} + Co^{2+} + 5NH_4^+ \tag{12}$$

Quantitative production of CrF^{2+} proves that Cr^{2+} occurs as an intermediate in the reaction. On the other hand, formation of Cr^{3+} in the absence of the cobalt complex clearly indicates that in its absence Cr^{2+} is efficiently oxidized by an intermediate in the reaction. The reaction between Cr^{2+} and Hg^{2+}, which occurs[26] at a rate given by $+d[Cr^{3+}]/dt = (0.05 + 1.47[H^+]^{-1})[Cr^{2+}][Hg^{2+}]$ at 25 °C, 2 M ionic strength, occurs far too slowly to account for conversion of Cr^{2+} to Cr^{3+} under the reaction conditions. We suggest that this intermediate is Hg^+, itself produced along with Cr^{2+} in an initial reaction. The sequence of reactions proposed to occur in the *absence* of $Co(NH_3)_5F^{2+}$ is given by eq 13–15.

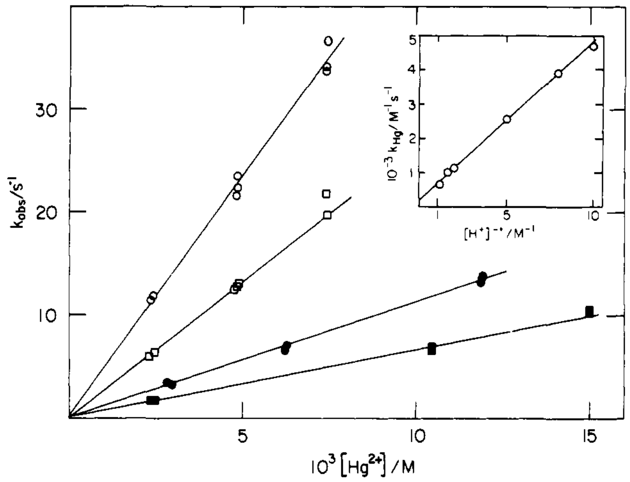

Figure 2. Variation of k_{obsd} for the reaction between $CrC(CH_3)_2OH^{2+}$ and Hg^{2+} with $[Hg^{2+}]$ at various $[H^+]$ according to eq 19: open circles, 0.10 M H^+; open squares, 0.20; filled circles, 0.50; filled squares, 0.94. Inset: plot of k_{Hg} vs. $1/[H^+]$ according to eq 20.

$$CrC(CH_3)_2OH^{2+} + Hg^{2+} \rightarrow Cr^{2+} + Hg^+ + (CH_3)_2CO + H^+ \tag{13}$$

$$Cr^{2+} + Hg^+ \rightarrow Cr^{3+} + Hg^0 \tag{14}$$

$$Hg^0 + Hg^{2+} \rightarrow Hg_2^{2+} \tag{15}$$

The changes noted upon addition of $Co(NH_3)_5F^{2+}$ imply that the Cr^{2+} intermediate reacts preferentially with $Co(NH_3)_5F^{2+}$ rather than Hg^+. The mechanism thus consists of eq 13 and 16,

$$Cr^{2+} + Co(NH_3)_5F^{2+} + 5H^+ \rightarrow CrF^{2+} + Co^{2+} + 5NH_4^+ \tag{16}$$

followed either by dimerization of Hg^+ (eq 17) or by its oxidation

$$2Hg^+ \rightarrow Hg_2^{2+} \tag{17}$$

of $CrROH^{2+}$ (eq 18). We return later to the question of whether

$$CrC(CH_3)_2OH^{2+} + Hg^+ \rightarrow Cr^{2+} + Hg^0 + (CH_3)_2CO + H^+ \tag{18A}$$

$$Hg^0 + Hg^{2+} \rightarrow Hg_2^{2+} \tag{18B}$$

eq 17 or 18 applies.

Consider first the results of kinetics studies without added $Co(NH_3)_5F^{2+}$ where the following concentration ranges were examined: $0.5 < 10^4[CrC(CH_3)_2OH^{2+}]_0 < 1.6$, $2.5 < 10^3[Hg^{2+}] < 15.1$, and $0.10 < [H^+] < 0.94$ M, with [2-propanol] = 0.050 M.[27] The pseudo-first-order rate constant varies with $[Hg^{2+}]$, as depicted in Figure 2, according to eq[28] 19. The mercury-

$$k_{obsd} = k_I + k_{Hg}[Hg^{2+}] \tag{19}$$

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(25) Schrauzer, G. N.; Ribeiro, A.; Lee, L. P.; Ho, R. K. Y. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 807.

(26) Doyle, J.; Sykes, A. G. *J. Chem. Soc. A* **1968**, 215.

(27) Initial studies in which reagent was made up in 1 M 2-propanol were not as reproducible as in other systems, and we suspected that the reaction of Hg^{2+} and $(CH_3)_2CHOH$[16] might be the cause. Consequently, we adopted a procedure wherein the organochromium ion was prepared at lower alcohol concentration, 0.1 M, and mercury(II) was not in contact with the alcohol until the instant of mixing the two solutions in the stopped-flow instrument. The alcohol concentration was kept low to minimize any mixing artifact.

(28) The intercept designated k_I may, in the absence of added $Co(NH_3)_5F^{2+}$, be equal to the unimolecular homolysis rate of $CrC(CH_3)_2OH^{2+}$, k_{hom}. However, k_I cannot be assessed, given the dominant direct reaction of Hg^{2+}, accurately enough to permit an exact comparison. The values of k_I in the presence of added cobalt complex (0.20 ± 0.03 s^{-1}) may be somewhat larger than the k_{hom} (0.14 s^{-1}),[19] as might be expected. The corresponding situation for $CrCH(CH_3)OC_2H_5^{2+}$, where the direct reaction is much slower, is clearer (see text).

dependent term shows an inverse dependence on $[H^+]$ as shown in Figure 2 and eq 20, with $a = (1.66 \pm 0.14) \times 10^2\ M^{-1}\ s^{-1}$ and

$$k_{Hg} = a + b[H^+]^{-1} \qquad (20)$$

$b = (4.67 \pm 0.07) \times 10^2\ s^{-1}$. The latter is the dominant term under the conditions employed. Comparison with the findings when $CrC(CH_3)_2OH^{2+}$ reacts with Fe^{3+} or Cu^{2+}[1,2] is the basis upon which eq 13 was written as the rate-limiting step, noting that its rate constant is given by eq 20.

A study of the kinetics in the presence of $Co(NH_3)_5F^{2+}$ established that the rate law was the same as in its absence. The rate constants are *independent* of the concentration of the cobalt complex, $(2.5\text{–}5.0) \times 10^{-3}$ M, but the values (particularly b) are appreciably different: $a_{Co} = (0.85 \pm 0.18) \times 10^2\ M^{-1}\ s^{-1}$ and $b_{Co} = (6.53 \pm 0.12) \times 10^2\ s^{-1}$. The rate constant in the absence of $Co(NH_3)_5F^{2+}$ is simply $k_{Hg} = k_{13}$; in its presence, however, $k_{Hg(Co)}$ is either k_{13} (if eq 17 applies) or $2k_{13}$ (if eq 18 applies). The experimental value is $b_{Co}/b \simeq 1.4$, suggesting that eq 17 and 18 are competitive over the range of steady-state concentrations of Hg^+ prevalent in these experiments, with some 40% of Hg^+ on the average reacting by eq 18 and the balance dimerizing.

Evidence has been cited above that reaction of Hg^+ with Cr^{2+} (eq 14) occurs much more rapidly than its dimerization (eq 17) in those runs where Cr^{2+} was not converted to CrF^{2+} by addition of $Co(NH_3)_5F^{2+}$. This work then provides documentation of this conclusion, which had been assumed by Doyle and Sykes as applicable during their study[26] of the reaction between Hg^{2+} and Cr^{2+}.

The value of b ($467\ s^{-1}$) greatly exceeds the corresponding rate constants[1,2] for Fe^{3+} ($1.90\ s^{-1}$) and for Cu^{2+} ($0.574\ s^{-1}$). The difference is particularly striking in that the similarity of the latter values to one another (and indeed to the rate constants for other (α-hydroxyalkyl)chromium ions reacting with Fe^{3+} and Cu^{2+}) was quite noteworthy. The mechanism for term b of eq 20 is believed to be that shown in eq 21 and 22, such that $b = K_{21}k_{22}$ if the

$$CrC(CH_3)_2OH^{2+} + Hg^{2+} \rightleftharpoons CrC(CH_3)_2OHg^{3+} + H^+ \qquad (21)$$

$$CrC(CH_3)_2OHg^{3+} \rightarrow Cr^{2+} + (CH_3)_2CO + Hg^+ \qquad (22)$$

dinuclear intermediate is present only at low concentration. Hg^{2+} generally shows much higher binding constants for ligands than does Cu^{2+} or Fe^{3+}. The consequently greater value so presumed for K_{21} would be reflected in a larger rate constant b, as observed.

$CrCH(CH_3)OH^{2+}$ and $CrCH(CH_3)OC_2H_5^{2+}$. The reactions of these two substrates with Hg^{2+} show many effects in common, and so will be discussed together. Both systems produce Cr^{3+}, acetaldehyde, and Hg_2^{2+} in 1:1:1 amounts, regardless of the presence of $Co(NH_3)_5F^{2+}$.

$$CrCH(CH_3)OH^{2+} + 2Hg^{2+} = Cr^{3+} + Hg_2^{2+} + CH_3CHO + H^+ \qquad (23)$$

$$CrCH(CH_3)OC_2H_5^{2+} + 2Hg^{2+} + H_2O = Cr^{3+} + Hg_2^{2+} + CH_3CHO + C_2H_5OH + H^+ \qquad (24)$$

The finding that Cr^{2+} is not produced at all in the latter reaction and not appreciably[29] in the former was made by the lack of CrF^{2+} found among the products when the reaction was run in the presence of $Co(NH_3)_5F^{2+}$. This result is regarded as very well established, especially when one considers that CrF^{2+} was quantitatively produced in the superficially similar reaction of $CrC(CH_3)_2OH^{2+}$ and Hg^{2+} which occurs 100–800 times faster than eq 23 and 24.

Even low concentrations of Cr^{2+} have been shown to exert a perturbing effect on the rate of both reactions, particularly on eq 24. Hence we first consider kinetic studies in which $Co(NH_3)_5F^{2+}$ was present during the Hg^{2+} reactions to scavenge all the Cr^{2+} remaining from the preparation or (in the case of $CrCH(CH_3)OC_2H_5^{2+}$) formed from homolysis of the isolated complex. The value of k_{obsd}, after minor correction for accompanying slow homolysis,[30] varied directly with the quotient $[Hg^{2+}]/[H^+]$, the rate constants being independent of $[Co(NH_3)_5F^{2+}]_0$. The rate law is thus given by eq 25 with $b_{Hg(Co)}$

$$-d[CrCH(CH_3)OR'^{2+}]/dt = b_{Hg(Co)}[CrCH(CH_3)OR'^{2+}][Hg^{2+}]/[H^+] \qquad (25)$$

$= 3.78 \pm 0.06\ s^{-1}$ for (α-hydroxyethyl)chromium(2+) ion ($R' = H$) and $0.318 \pm 0.002\ s^{-1}$ for (α-ethoxyethyl)chromium(2+) ion ($R' = C_2H_5$). The plots of $k_{obsd}/[Hg^{2+}]$ vs. $1/[H^+]$ are shown in Figure 3. Approximate activation parameters were determined for both reactions from the kinetic data at 24.7 and 5.1 °C. The value of ΔH^* is 75 kJ/mol for both complexes and ΔS^* (J/mol K) is ~21 ($CrCH(CH_3)OH^{2+}$) and ~0 ($CrCH(CH_3)OC_2H_5^{2+}$).

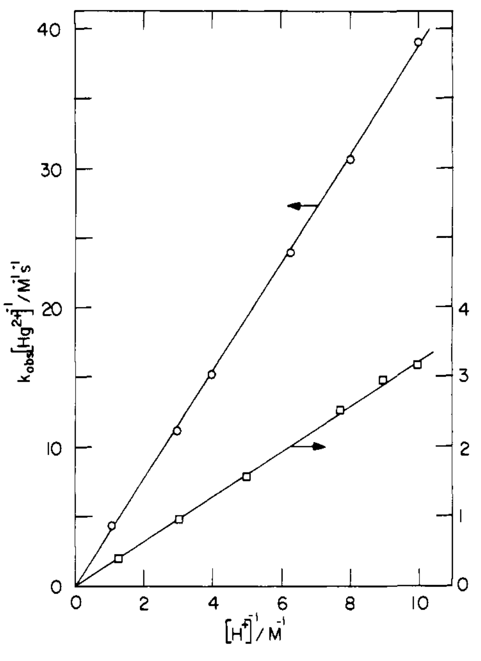

Figure 3. Plots of $k_{obsd}/[Hg^{2+}]$ vs. $1/[H^+]$ for the reaction between Hg^{2+} and $CrCH(CH_3)OH^{2+}$ (circles) and $CrCH(CH_3)OC_2H_5^{2+}$ (squares), illustrating the fit to the rate expression of eq 25.

A one-electron oxidation–reduction reaction can be ruled out since Cr^{2+} is definitely not a product or intermediate. On the other hand, the inverse $[H^+]$ dependence together with the quite appreciable rate of reaction of these species which have quite a sterically hindered α-carbon certainly disfavors a mechanism such as the S_E2 process with attack of Hg^{2+} directly at this position. In addition to that, a reaction by an S_E2 mechanism would be expected to show a large negative ΔS^*, quite different from our findings.

One possibility is that the reaction proceeds by a hydride abstraction from coordinated alcohol (or ether) by $HgOH^+$ like the reaction of free alcohols and ethers with Hg^{2+}.[16] A reaction proceeding by this mechanism should show a large deuterium isotope effect, and it does not; the rate constant for the reaction of $CrCD(CD_3)OC_2D_5^{2+}$ with Hg^{2+} in $H_2O/HClO_4$ was within the experimental error identical with the one obtained with $CrCH(CH_3)OC_2H_5^{2+}$. The product of the reaction is CD_3CDO, identified by its mass spectrum, confirming that no hydrogen exchange occurred in the ether part of the complex prior to or during the reaction with Hg^{2+}.

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(29) Correction of the observed amount of CrF^{2+} when the reaction is run in the presence of $Co(NH_3)_5F^{2+}$ for the CrF^{2+} produced by the residual excess of Cr^{2+} from the preparation of $CrCH(CH_3)OH^{2+}$ suggests that a small quantity of Cr^{2+} may be formed, but it is ≤15% of the Cr^{3+} formed during reaction 23.

(30) Actually the mercury-independent rate constant for $CrCH(CH_3)OC_2H_5^{2+}$ was $(4.19 \pm 0.06) \times 10^{-3}\ s^{-1}$, exactly a factor of 2 higher than the rate constant for homolysis as determined in the presence of other oxidants.[19] This suggests two fast reactions follow homolysis: $\cdot CH(CH_3)OC_2H_5 + Hg^{2+} + H_2O \rightarrow Hg^+ + CH_3CHO + C_2H_5OH + H^+$ and $CrCH(CH_3)OC_2H_5^{2+} + Hg^+ + H_2O \rightarrow Hg^0 + Cr^{2+} + CH_3CHO + C_2H_5OH + H^+$.

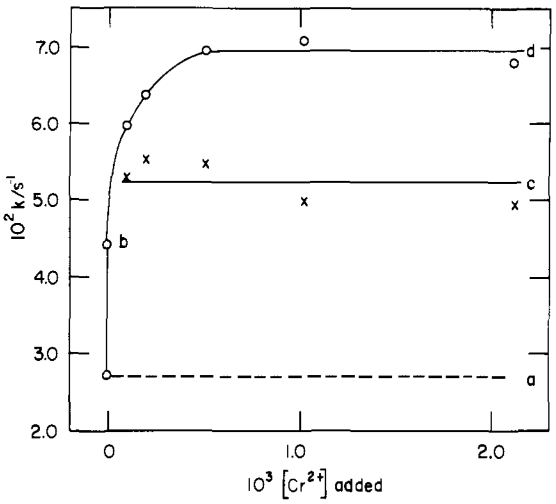
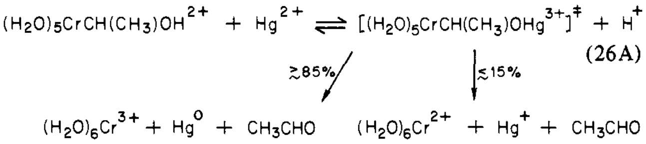


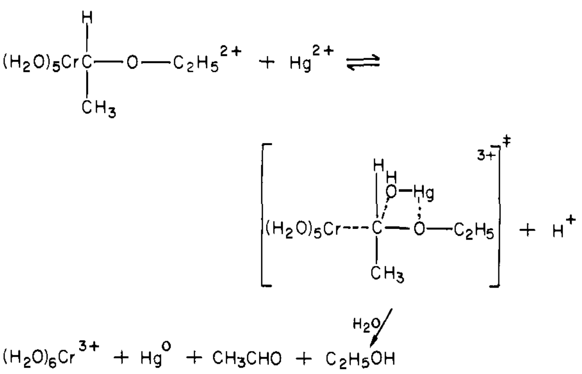
Figure 4. Dependence of first-order-rate constants for $CrCH(CH_3)OC_2H_5^{2+}$–Hg^{2+} reaction on [Cr^{2+}] (0.20 M H^+, 8 × 10^{-5} M $CrCH(CH_3)OC_2H_5^{2+}$, 1.48 × 10^{-2} M Hg^{2+}): (a) in the presence of 3 × 10^{-3} M $Co(NH_3)_5F^{2+}$; (b) no Cr^{2+} or $Co(NH_3)_5F^{2+}$ added; (c) from the slower part of the kinetic plots (see text); (d) from the faster part of the kinetic plots.[31]

We favor a mechanism analogous to the one proposed earlier for copper(II) and iron(III) oxidation of these complexes,[1,2] but now two electrons are transferred within the same transition state as shown in eq 26 and 27. A minor part (≲15%) of CrCH(CH$_3$)OH^{2+} reacts with Hg^{2+} via a one-electron transfer mechanism, as shown by the formation of small amounts of Cr^{2+} in the reaction.



(26A)

(26B)



(27A)

(27B)

The mechanism changes from a one-electron transfer ($CrC(CH_3)_2OH^{2+}$) through a predominantly ($CrCH(CH_3)OH^{2+}$) to exclusively ($CrCH(CH_3)OC_2H_5^{2+}$) two-electron transfer. Considering the energetics of the intermediates involved, the two-electron products (Cr^{3+} and Hg^0) appear to be more easily accessible than the one-electron products (Cr^{2+} and Hg^+). With the assumption that the standard reduction potentials of the organochromium ions parallel those of the corresponding free radicals, then $CrC(CH_3)_2OH^{2+}$ is the strongest reductant of the three and should thus be the most likely to react by a one-electron process.

We return now to two interrelated issues raised earlier in this discussion: (1) the reactions are affected by Cr^{2+} and (2) the effect of added $Co(NH_3)_5F^{2+}$ is not to participate directly in the reactions, but it is simply to remove Cr^{2+} rapidly. The effect[31] of Cr^{2+} (see also Figure 4) suggests that its effect is to cause additional formation of Hg^+ via eq 29, which occurs on a comparable time scale to eq 28 leading to an additional pathway for loss of CrROR′, eq 30.

Table I. Summary of the Kinetic Parameters for the Mercury(II) Reactions with α-Hydroxyalkyl and α-Alkoxyalkyl Complexes of Chromium(III)[a]

complex	k_{Hg}[b]	$k_{Hg(Co)}$[b,c]
$CrCH_2OH^{2+}$[d]	228 (7)	
$CrCH_2OCH_3^{2+}$[e]	90.5 (8)	
$CrC(CH_3)_2OH^{2+}$[f]	166 (14) + 467 (7)/[H^+]	86 (18) + 653 (12)/[H^+]
$CrCH(CH_3)OH^{2+}$[g-i]	4.11 (8)/[H^+]	3.78 (6)/[H^+]
$CrCH(CH_3)OC_2H_5^{2+}$[e,j]	0.535 (27)/[H^+]	0.318 (2)/[H^+]

[a] 24.8 °C, 1.0 M ionic strength. [b] Numbers in parentheses represent standard deviations. [c] In the presence of $Co(NH_3)_5F^{2+}$. [d] In 1 M aqueous methanol. [e] In water. [f] In 1 M 2-propanol. [g] k_{Hg} is identified as k_{13}. [h] In 1 M ethanol. [i] $k_{Hg(Co)}$ is identified as the rate constant for eq 23. [j] $k_{Hg(Co)}$ is identified as the rate constant for eq 24.

$$CrCH(CH_3)OC_2H_5^{2+} + 2Hg^{2+} + H_2O \xrightarrow{0.318/[H^+]} Cr^{3+} + Hg_2^{2+} + CH_3CHO + C_2H_5OH + H^+ \quad (28)$$

$$Cr^{2+} + Hg^{2+} \xrightarrow{\sim 1.47/[H^+]} Cr^{3+} + Hg^+ \quad (29)$$

$$CrCH(CH_3)OC_2H_5^{2+} + Hg^+ + H_2O \xrightarrow{\text{fast}} Cr^{2+} + Hg^0 + CH_3CHO + C_2H_5OH + H^+ \quad (30)$$

The sequence would be completed as before (eq 14 and 15). With the steady-state approximation for [Hg^+], the rate law is given by eq 31 in which the second term in parenthesis corresponds to the Cr^{2+}-catalyzed path.

$$\frac{-d[CrROR'^{2+}]}{dt} = \left(k_{28} + \frac{k_{29}k_{30}[Cr^{2+}]}{k_{30}[CrROR'^{2+}] + k_{14}[Cr^{2+}]}\right)[Hg^{2+}][CrROR'^{2+}] \quad (31)$$

The two limiting conditions are realized at the following: (a) high [Cr^{2+}], where the rate constant is $k_{28} + (k_{29}k_{30})/k_{14}$, independent of [$Cr^{2+}$] (plateau in Figure 4), and (b) [Cr^{2+}] = 0, i.e., in the presence of $Co(NH_3)_5F^{2+}$, where the rate constant reduces to k_{28}.

Similar observations[32] were made in the case of $CrCH(CH_3)OH^{2+}$, although the effect of Cr^{2+} is much smaller. Here the rate constant of the uncatalyzed reaction (eq 26) is higher than k_{29}, and only a minor contribution from the catalyzed pathway can be expected. For the same reason no catalysis by Cr^{2+} was observed in the reaction of $CrC(CH_3)_2OH^{2+}$ with Hg^{2+},

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(31) When Cr^{2+} is added to the reaction of $CrCH(CH_3)OC_2H_5^{2+}$ with Hg^{2+}, the following patterns are noted. If the amount of Cr^{2+} exceeds 10^{-4} M (0.20 M H^+, 1.47 × 10^{-2} M Hg^{2+}, 8 × 10^{-5} M $CrCH(CH_3)OC_2H_5^{2+}$), first-order plots become curved in such a way that initial parts give higher "rate constants" which show a dependence on [Cr^{2+}]. The rate constant evaluated from the latter portion of the reaction amounts to 0.053 s^{-1}, independent of [Cr^{2+}] under the conditions cited. The dependence of the initial portion of the reaction on [Cr^{2+}] becomes less pronounced as [Cr^{2+}] is raised and finally reaches a point (at ~5 × 10^{-4} M Cr^{2+}) after which additional Cr^{2+} has no effect on the rate of the reaction (Figure 4). At this point the rate "constant" evaluated from the initial part of the plot amounts to $k_{obsd} = 0.070$ s^{-1}, compared to $k_{obsd} = 0.027$ s^{-1} from experiments in which all Cr^{2+} was scavenged by $Co(NH_3)_5F^{2+}$. The amount of the reaction which proceeds by the faster rate correlates well with the amount of added Cr^{2+}. Also the time scale for the faster reaction is the same as the time scale for the Hg^{2+}–Cr^{2+} reaction under identical conditions. All these observations strongly imply that Hg^{2+}–Cr^{2+} reaction is the crucial one in catalyzing the decomposition of $CrCH(CH_3)OC_2H_5^{2+}$, as discussed in the text.

(32) The omission of $Co(NH_3)_5F^{2+}$ in the reaction of $CrCH(CH_3)OH^{2+}$ with Hg^{2+} only slightly increases the rate constant ($k_{Hg(Co)} = 3.78/[H^+]$, $k_{Hg} = 4.11/[H^+]$). Addition of free Cr^{2+} (6 × 10^{-4}–2 × 10^{-3} M) further increases the rate constant ($k = 47.7$ M^{-1} s^{-1} at 0.10 M H^+) independent of [Cr^{2+}] in this concentration range.

Table II. Summary of Stoichiometry, Products, and Mechanisms for Reactions of $CrROH^{2+}$ and $CrROR'^{2+}$ with Hg^{2+}

		products[a]		
system: Hg^{2+} +	stoichiometry	immediate	eventual	mechanism
$CrCH_2OH^{2+}$ [b]	2:1 (eq 3)	Cr^{3+}, ($HgCH_2OH^+$)	Cr^{3+}, Hg_2^{2+}, HCHO	S_E2
$CrCH_2OCH_3^{2+}$ [b]	2:1 (eq 4)	Cr^{3+}, $HgCH_2OCH_3^+$	Cr^{3+}, Hg_2^{2+}, HCHO, CH_3OH	S_E2
$CrC(CH_3)_2OH^{2+}$	2:1 (eq 11)	Cr^{2+}, (Hg^+), $(CH_3)_2CO$	Cr^{3+}, Hg_2^{2+}, $(CH_3)_2CO$	1-e ET[e]
$CrC(CH_3)_2OH^{2+}$ + $Co(NH_3)_5F^{2+}$	1:1:1 (eq 12)	Cr^{2+}, (Hg^+), $(CH_3)_2CO$	CrF^{2+}, Hg_2^{2+}, $(CH_3)_2CO$	
$CrCH(CH_3)OH^{2+}$ [c]	1:1 (eq 23)	(Cr^{3+} + Hg^0, >85%),[d] CH_3CHO	Cr^{3+}, Hg_2^{2+}, CH_3CHO	2-e ET (⩾85%)
$CrCH(CH_3)OC_2H_5^{2+}$ [c]	1:1 (eq 24)	Cr^{3+}, (Hg^0, $HOCH(CH_3)OC_2H_5$)	Cr^{3+}, Hg_2^{2+}, CH_3CHO, C_2H_5OH	2-e ET

[a] Products inferred but not detected are given in parentheses. [b] No effect of $Co(NH_3)_5F^{2+}$. [c] Addition of $Co(NH_3)_5F^{2+}$ alters the rate because it eliminates the effect of Cr^{2+} via eq 29 and 30 (see Figure 4 and ref 31). [d] Up to 15% may proceed by 1-e ET producing Cr^{2+} + Hg^+ initially. [e] Key: e, electron; ET, electron transfer.

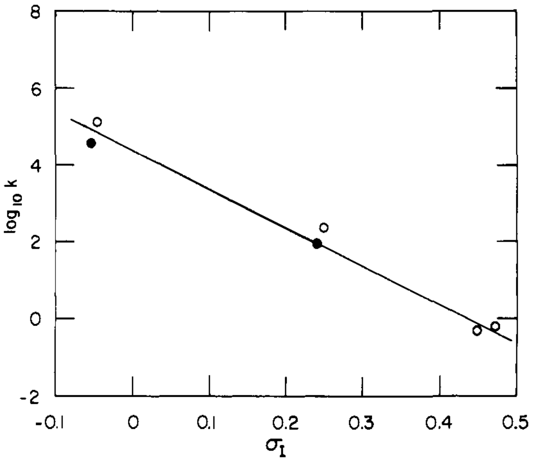

Figure 5. Correlation of inductive effects in S_E2 reactions of organochromium cations with Hg^{2+} showing a plot of log k vs. the inductive parameter σ_I for two series of compounds, $CrCH_2X^{2+}$ having approximately constant steric requirements with X = CH_3, OH, Br, and Cl (open circles) and X = CH_2CH_3 and OCH_3 (filled circles).

where k_{13} exceeds k_{29} by more than 2 orders of magnitude.

Summary and Concluding Remarks

(α-Hydroxyalkyl)- and (α-alkoxyalkyl)chromium complexes studied in this work react with Hg^{2+} by several mechanisms as summarized in Table II. (Hydroxymethyl)chromium(2+) and (methoxymethyl)chromium(2+) react by an electrophilic substitution mechanism. The unstable organomercurials produced readily decompose in acidic aqueous solution. It is instructive to compare these results to those[12] for S_E2 reactions of alkyls since we contend that they occur by the same mechanism. The activation parameters for reactions of Hg^{2+} with $CrCH_2OCH_3^{2+}$ and $CrCH_2Cl^{2+}$ ($\Delta H^{\ddagger}$ = 39.8 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −116 J mol^{-1} K^{-1})[11] are in good agreement, the somewhat greater reactivity of the former (90.5 vs. 0.59 M^{-1} s^{-1}) arising entirely from the $\Delta S^{\ddagger}$ term.

There are now enough data at hand to attempt a correlation of inductive effects. Consider first two series of complexes $Cr-CH_2-X^{2+}$: series A with X = CH_3 (k = 1.4 × 10^5 M^{-1} s^{-1}),[12] OH (2.26 × 10^2), Br (4.7 × 10^{-1}),[12] and Cl (5.9 × 10^{-1});[12] series B with X = CH_2CH_3 (3.5 × 10^4)[12] and OCH_3 (9.05 × 10^1). These series are ones in which the groups X have, at least approximately, the same steric requirements.[33] Figure 5 shows a plot of log k vs. σ_I, the latter inductive parameter being derived from Taft's constants for $\sigma(CH_2X)$ by the relationship $\sigma_I(X) = 0.45\sigma^*(CH_2X)$.[34,35] The two groups lie quite close to one another and can almost be considered to constitute one correlation and not two, although it is to be noted that series B is systematically lower than A. The slope of the line affords a value of the reaction constant $\rho = -10$ (or, if evaluated from log k vs. $\sigma^*(CH_2X)$, $\rho^* = -4.5$).

The exceptionally negative reaction constant[34,35] helps to confirm the S_E2 nature of the reaction and its strong sensitivity to electronic effects such that electron-releasing substituents strongly accelerate the rate, consistent with the change from a carbanion-like group R in the ground state to the pentacoordinate carbon in activated complex. These substituent effects are similar to those for substituted benzyl and phenyl derivatives in other electrophilic reactions[12,14b,15] of RCr^{2+} and $RCo(dmgH)_2B$, most notably p-$XC_6H_4Co(dmgH)_2H_2O$ + Hg^{2+}, for which a correlation by the Hammett relationship yields $\rho = -6.3$.[36]

(α-Hydroxyisopropyl)chromium(2+) reacts with Hg^{2+} in a predominantly acid-dependent one-electron redox reaction. The initial products of the reaction, Cr^{2+} and Hg^+, react further to form more stable products, Cr^{3+} and Hg^0. In some experiments Cr^{2+} was scavenged with $Co(NH_3)_5F^{2+}$ in which case Hg^+ reacts in two competitive reactions, eq 17 and 18.

(α-Hydroxyethyl)chromium(2+) and (α-ethoxyethyl)chromium(2+) react with Hg^{2+} in acid-dependent two-electron redox reactions. Cr^{2+} catalyzes both reactions through the formation of highly reactive Hg^+. The catalyzed path is much less pronounced for $CrCH(CH_3)OH^{2+}$ owing to its higher reactivity in the uncatalyzed reaction.

Mercury(II) is a more versatile reagent than Cu^{2+} and Fe^{3+},[1,2] and many aspects of its known reactivity in inorganic and organometallic chemistry have been found in this work: (1) electrophilic substitution ($CrCH_2OH^{2+}$ and $CrCH_2OCH_3^{2+}$); (2) one-electron redox chemistry, most probably through the transition state $[CrC(CH_3)_2OHg^{3+}]^{\ddagger}$; (3) two-electron redox chemistry through similar transition states, $[CrCH(CH_3)OHg^{3+}]^{\ddagger}$ and $[CrCH(CH_3)O(HgOH)C_2H_5^{3+}]^{\ddagger}$, which are available to mercury(II) due to its high acidity; (4) oxidation of free radicals ($\cdot CH(CH_3)OC_2H_5$) produced by homolysis. It is interesting to note that the change from electrophilic substitution to a redox process is rather sharp: $CrCH_2OH^{2+}$ reacts by an S_E2 reaction, while the next member of the series, $CrCH(CH_3)OH^{2+}$, reacts only by a redox reaction. An analogous situation is found in $CrCH_2OCH_3^{2+}$, $CrCH(CH_3)OC_2H_5^{2+}$ series. This is not totally unexpected in view of the known dramatic effects of steric hindrance on electrophilic substitutions by Hg^{2+} [12,13] and the apparent insensitivity[1,2] to steric effects of the rates of the redox reactions of these complexes with Cu^{2+} and Fe^{3+}.

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