Kinetics and Mechanism of the Reactions of Organochromium Complexes with Mercury(II) and Methylmercury(II) Ions[1]

John P. Leslie, II, and James H. Espenson*

Contribution from the Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received October 20, 1975*

Abstract: Kinetics studies have been carried out on a family of organochromium complexes of the general formula $(H_2O)_5CrR^{2+}$ for the groups R = CH_3, C_2H_5, n-C_3H_7, $CH_2C(CH_3)_3$, i-C_3H_7, CH_2Cl, CH_2Br, CF_3, and p-$CH_2C_6H_4Z$ (Z = H, CH_3, CN, CF_3, and Br). These cations react with Hg^{2+} forming RHg^+ and $Cr(H_2O)_6{}^{3+}$, and with CH_3Hg^+ forming CH_3HgR and $Cr(H_2O)_6{}^{3+}$. Reaction rates were evaluated as a function of concentration in water at 25.0°, and in a few instances in other solvents and at other temperatures. These reactions are believed to follow a bimolecular, electrophilic substitution mechanism.

Electrophilic dealkylation of organocobalt compounds such as cobaloximes[2] and cobalamins has in recent years received extensive study,[3-14] from the point of view of both kinetics and stereochemistry. In contrast to this we are aware of no systematic investigation of the mechanism of dealkylation of organochromium ions by Hg(II), despite this reaction being used by Anet and Leblanc in their original characterization of the benzylchromium ion.[15] Some further results were obtained by Dodd and Johnson, who observed that the monochloromethyl- and monobromomethylchromium ions, $[(H_2O)_5CrCH_2X]^{2+}$, react with mercuric nitrate to produce the corresponding organomercury cation and hexaaquochromium(III) ion.[16] Johnson and co-workers also carried out a detailed kinetic study of the electrophilic cleavage reactions of 2-, 3-, and 4-pyridinomethylchromium ions with hydrated ions and halo complexes of Hg(II) and Tl(III).[17]

In the present work we report the results of a study of the chemical kinetics of the chromium–carbon bond cleavage reactions of a family of $(H_2O)_5CrR^{2+}$ cations, in which the group R is a primary or secondary alkyl, a haloalkyl, or a benzyl substituent. The complexes studied react with mercuric ion and with a monoalkylmercuric ion such as CH_3Hg^+ as shown in reactions 1 and 2.

$$(H_2O)_5CrR^{2+} + Hg^{2+}{}_{aq} = RHg^+{}_{aq} + Cr(H_2O)_6{}^{3+} \quad (1)$$

$$(H_2O)_5CrR^{2+} + CH_3Hg^+{}_{aq} = RHgCH_3 + Cr(H_2O)_6{}^{3+} \quad (2)$$

A chief point of interest is the rate of the electrophilic reaction, and the kinetic manifestations of steric and electronic changes in the group R. A reaction which is closely related to reaction 1 is the analogous reaction with bromine and iodine:[18]

$$(H_2O)_5CrR^{2+} + X_{2aq} \rightarrow Cr(H_2O)_6{}^{3+} + RX + X^- \quad (3)$$

for which the data suggest an SE2 mechanism, apparently free of the complications which attend the reaction of organocobalt complexes and halogens.[9,19-22] The comparison of reactions 1 and 3 should afford further mechanistic insight.

Results

Characterizations. Many of the organochromium complexes used in this work are previously reported compounds, which we characterized chiefly by their electronic spectra as summarized in the Experimental Section. The two complexes containing the secondary alkyl groups i-C_3H_7 and sec-C_4H_9 are original to this work. Their compositions were assumed from the alkyl hydroperoxides used in their preparations. For the isopropyl complex, this was confirmed by the positive NMR identification of i-C_3H_7HgCl resulting from reaction of $CrCH(CH_3)_2{}^{2+}$ with mercuric ion. Furthermore, the kinetic data for this complex were quite different from those of the primary alkyls. The t-C_4H_9 complex was not completely characterized.[23]

NMR determinations were used to confirm the organomercury products (RHgCl or RHgR′) of seven of the reactions of CrR^{2+} with Hg^{2+}, CH_3Hg^+, or $C_6H_5Hg^+$. The NMR spectrum[24] of C_2H_5HgCl (from $CrC_2H_5{}^{2+}$ + Hg^{2+}) matched that reported,[25] and that of neopentylmercuric chloride (from $CrCH_2C(CH_3)_3{}^{2+}$ + Hg^{2+}) was identical with that of an authentic sample.[26] The identity of isopropylmercuric chloride (from Cr-i-$C_3H_7{}^{2+}$ + Hg^{2+}) was deduced from the splitting pattern (($(CD_3)_2CO$) δ 1.50 (d, 6.4, CH_3) and 2.25–2.85 (m, 1, CH_2). Benzylmercuric chloride (from $CrCH_2C_6H_5{}^{2+}$ + Hg^{2+}) was identified from the CH_2 chemical shift and coupling constant (($CDCl_3$) δ 3.23 (s, J_{Hg-H} = 253 Hz)) in exact agreement with an authentic sample,[27] and the NMR spectrum of chloromethylmercuric chloride agreed with that in the literature.[16] Benzylmethylmercury (from $CrCH_2C_6H_5{}^{2+}$ + CH_3Hg^+) was confirmed from its NMR spectrum (($CDCl_3$) δ 0.38 (s, H3), 2.30 (s, H2)) compared to reported[27,28] chemical shifts δ 0.34 and 2.28. Finally, the identity of $C_6H_5CH_2HgC_6H_5$ (from $CrCH_2C_6H_5{}^{2+}$ + $C_6H_5Hg^+$) was confirmed by the CH_2 chemical shift ($CDCl_3$) δ 2.45 compared to the reported δ 2.57.[27] On the basis of these results, which include alkyl, haloalkyl, and aralkyl derivatives, it was assumed that the remaining reactions occurred analogously.[29]

The formation of $Cr(H_2O)_6{}^{3+}$ in both reactions 1 and 2 was confirmed by its electronic spectrum: λ 574 nm (ϵ 13.3), 408 (15.8). For the complex Cr-n-$C_3H_7{}^{2+}$ cation, the stoichiometry of each of the reactions was established quantitatively using a spectrophotometric method in 50% aqueous methanol (to avoid precipitation of the organomercurial at these higher concentrations; we regard the change of solvent as immaterial insofar as the stoichiometry is concerned). A fixed quantity of Cr-n-$C_3H_7{}^{2+}$ was added to each of several volumetric flasks followed by varying amounts of CH_3Hg^+ or Hg^{2+}. Immediately upon addition of the reagents and dilution to volume the absorbance at 393 nm, a maximum for Cr-n-$C_3H_7{}^{2+}$ (ϵ 380), was measured. The plots of absorbance vs. the mole ratio of mercury reactant to n-propylchromium are shown in Figure 1. In the case of CH_3Hg^+ the "break" occurs at a ratio 0.91 ± 0.03, supporting the 1:1 stoichiometry of reaction 2. The reaction of Hg^{2+} with Cr-n-$C_3H_7{}^{2+}$ shows a break at 0.48 ± 0.04, consistent with the $2CrR^{2+}{:}1Hg^{2+}$ stoichiometry expected from the *sum* of reactions 1 and 2.

Kinetic Determinations for Hg^{2+} Reactions. The kinetics of the reaction of a given organochromium cation with Hg^{2+} as

Table I. Summary of Kinetic Data[a] for Reactions of $(H_2O)_5CrR^{2+}$ with Hg^{2+}

R	Range of $10^3[Hg^{2+}]/M$	Range of $[H^+]$	$k_{Hg}/M^{-1}\ s^{-1}$
$-CH_3$	0.053	0.250	$(1.0 \pm 0.1) \times 10^7$
$-C_2H_5$	0.59-0.99	0.100-0.250	$(1.40 \pm 0.06) \times 10^5$
$-n\text{-}C_3H_7$	0.20-1.98	0.100-0.250	$(3.50 \pm 0.17) \times 10^4$
$-CH_2C(CH_3)_3$	1.32-5.94	0.250	$(4.9 \pm 0.2) \times 10^2$
$-i\text{-}C_3H_7$	0.95-6.32	0.250	1.56 ± 0.01
$-CH_2Cl$	21.2-47.6	0.135-0.250	$(5.90 \pm 0.15) \times 10^{-1}$
$-CH_2Br$	9.5-38.1	0.250-0.500	$(4.68 \pm 0.26) \times 10^{-1}$
$-CF_3$	370.	0.250	$<10^{-6}$ [b]
$-CH_2C_6H_5$	0.603-1.19	0.100-0.250	$(4.87 \pm 0.22) \times 10^4$
$-p\text{-}CH_2C_6H_4CH_3$	0.264-0.594	0.250	$(5.22 \pm 0.27) \times 10^4$
$-p\text{-}CH_2C_6H_4Br$	0.527-1.05	0.250	$(2.98 \pm 0.07) \times 10^4$
$-p\text{-}CH_2C_6H_4CF_3$	0.502-1.06	0.250	$(2.10 \pm 0.06) \times 10^4$
$-p\text{-}CH_2C_6H_4CN$	0.304-0.660	0.100-0.250	$(1.64 \pm 0.08) \times 10^4$
-2-pyridinomethyl	0.2-0.4	0.09-0.500	$(3.0 \pm 0.2) \times 10^1$ [c]
-3-pyridinomethyl	0.02-0.04	0.500	$(2.05 \pm 0.3) \times 10^2$ [c]
-4-pyridinomethyl	0.02-0.04	0.500	$(5.0 \pm 0.3) \times 10^2$ [c]

[a] At 25.0°, μ = 0.50 M ($LiClO_4$). [b] μ = 1.7 M. [c] From ref 17b.

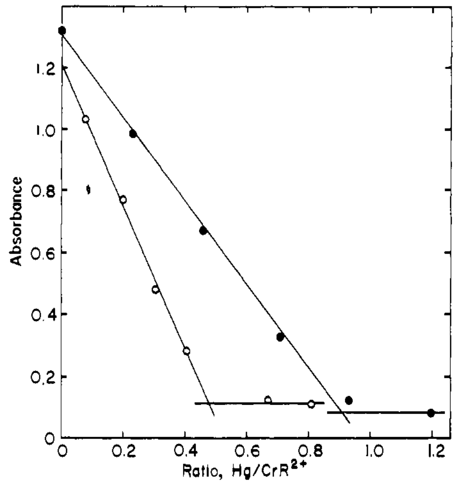

Figure 1. Spectrophotometric data obtained by the addition of varying quantities of Hg^{2+} (open circles) or CH_3Hg^+ (filled circles) to a given quantity of $Cr\text{-}n\text{-}C_3H_7^{2+}$.

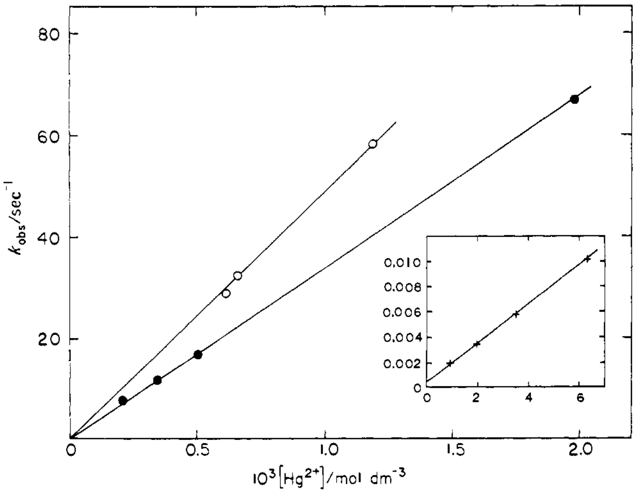

Figure 2. Plots of the pseudo-first-order rate constants vs. $[Hg^{2+}]$ for the reactions of Hg^{2+} with $Cr\text{-}n\text{-}C_3H_7^{2+}$ (filled circles) and $CrCH_2C_6H_5^{2+}$ (open circles). Inset: reaction of Hg^{2+} with $Cr\text{-}i\text{-}C_3H_7^{2+}$ showing nonzero intercept corresponding to acidolysis.

in eq 1 can be studied with virtually no interference from the simultaneous or subsequent occurrence of the secondary reaction of CrR^{2+} with HgR^+, eq 2. This is so for two reasons: the rate constant for a given organochromium cation with Hg^{2+} is at least 10^2 times larger than that with HgR^+, and the reaction rate determinations were made using excess Hg^{2+}, usually greater than or equal to a tenfold excess, thus rendering the second-stage reaction insignificant.

The pseudo-first-order rate plots constituted good straight lines to at least 80% completion. The values of k_{obsd} computed from the slopes of such plots show a linear dependence upon $[Hg^{2+}]$ as depicted in Figure 2 for the complexes $Cr\text{-}n\text{-}C_3H_7^{2+}$ and $CrCH_2C_6H_5^{2+}$. These data are evidently in accord with the rate expression

$$-d[CrR^{2+}]/dt = k_{Hg}[CrR^{2+}][Hg^{2+}] \qquad (4)$$

Table I summarizes the kinetic data for reaction 1, the value of k_{Hg} being determined from the slope of k_{obsd} vs. $[Hg^{2+}]$ by the method of least squares. The rate constant for each reaction was determined at 0.250 M H^+ with lithium perchlorate used to maintain an ionic strength of 0.50 M. In addition, for several of the complexes kinetic data were obtained at varying $[H^+]$, 0.1-0.5 M; the rate constants proved independent of $[H^+]$ in this range. The lack of appreciable reactivity of $CrCF_3^{2+}$ is noteworthy.

The neopentyl complex underwent acidolysis rather more rapidly than the other complexes, so that its isolation from the preparative solution—the reaction of Cr^{2+} and $(CH_3)_3\text{-}CH_2C(CH_3)_2OOH$—by ion exchange chromatography was not successful. In this case, therefore, the kinetics were conducted utilizing the unpurified reaction solution. The correctness of this method was to some extent verified by comparing the kinetic data for the reaction of $Cr\text{-}n\text{-}C_3H_7^{2+}$ obtained for the purified complex ($3.5 \times 10^4\ M^{-1}\ s^{-1}$) with that obtained from an unpurified preparative sample (3.4×10^4).

The primary alkyl complexes do not react with oxygen within the time they undergo decomposition by acidolysis, and their reactions with Hg^{2+} were also independent of whether oxygen was excluded from the run. The benzyl derivatives, which slowly react with oxygen,[30] were studied under inert atmosphere conditions. The complex $Cr\text{-}i\text{-}C_3H_7^{2+}$ proved to undergo acidolysis (or other decomposition reactions) more rapidly in the presence of oxygen than in its absence: $3 \times 10^{-3}\ s^{-1}$ compared to $\sim 3 \times 10^{-4}\ s^{-1}$ (25 °, 0.250 M H^+, μ = 0.50). For this complex, whose reaction with Hg^{2+} occurs relatively slowly, the plot of k_{obsd} vs. $[Hg^{2+}]$ had a nonzero intercept ($(4 \pm 1) \times 10^{-4}\ s^{-1}$), which we interpret to represent the concurrent, mercury-independent acidolysis.

Kinetic Determinations for CH_3Hg^+ Reactions. The reaction

Table II. Summary of Kinetic Data[a] for Reactions of $(H_2O)_5CrR^{2+}$ with CH_3Hg^+

R	Range of $10^3[CH_3Hg^+]/M$	Range of $[H^+]/M$	$k_{CH_3Hg}/M^{-1}\ s^{-1}$
$-CH_3$	0.424-1.06	0.250[b]	$(1.0 \pm 0.02) \times 10^4$ [b]
$-C_2H_5$	1.06-2.12	0.100-0.250	$(1.99 \pm 0.04) \times 10^2$
$-n-C_3H_7$	0.976-4.10	0.100-0.250	$(1.21 \pm 0.08) \times 10^2$
$-CH_2C(CH_3)_3$	1.78-6.24	0.100-0.400	5.8 ± 0.6[c]
$-CH_2Cl$	14-19	0.25	$\sim 6 \times 10^{-4}$ [d]
$-CH_2C_6H_5$	0.462-9.90	0.100-0.500	$(9.8 \pm 0.1) \times 10^1$
$-p-CH_2C_6H_4CH_3$	0.422-4.92	0.250	$(1.21 \pm 0.05) \times 10^2$
$-p-CH_2C_6H_4Br$	1.03	0.250	$(5.68 \pm 0.18) \times 10^1$
$-p-CH_2C_6H_4CF_3$	1.03	0.250	$(3.47 \pm 0.08) \times 10^1$
$-p-CH_2C_6H_4CN$	0.80-1.72	0.250	$(2.39 \pm 0.04) \times 10^1$

[a] At 25.0°, $\mu = 0.50$ M ($LiClO_4$). [b] Varies with $[H^+]$, see text. [c] Evaluated as described in the text. [d] Room temperature, k ±20%.

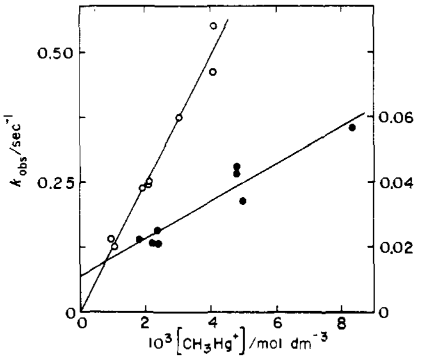

Figure 3. Plots of the pseudo-first-order rate constants vs. $[CH_3Hg^+]$ for the reactions of CH_3Hg^+ with $Cr-n-C_3H_7^{2+}$ (open circles, left ordinate scale) and with $CrCH_2C(CH_3)_3^{2+}$ (filled circles, right ordinate scale).

rates were determined by conventional or stopped-flow spectrophotometry, as appropriate to the rate of a given run. Pseudo-first-order plots were linear, and values of k_{obsd} thereby obtained show a linear variation with $[CH_3Hg^+]$ as depicted in Figure 3 for two typical complexes. All of these plots went through the origin, consistent with the rate law in eq 5. Values of the rate constants are summarized in Table II.

$$-d[CrR^{2+}]/dt = k_{CH_3Hg}[CrR^{2+}][CH_3Hg^+] \quad (5)$$

An exception to this general pattern is found for R = neopentyl, in which case the acidolysis provides an alternative, concurrent pathway for disappearance of the organochromium cation at a rate independent of $[CH_3Hg^+]$. The intercept of k_{obsd} vs. $[CH_3Hg^+]$ for the neopentyl complex is $(1.1 \pm 0.2) \times 10^{-2}\ s^{-1}$ (25.0°, $[H^+] = 0.250$ M, $\mu = 0.500$ M) in only fair agreement with a rate constant of $(0.4 \pm 0.1) \times 10^{-2}\ s^{-1}$ for the acidolysis process under the same conditions. (The latter reaction is independent of $[H^+]$ and of the presence of oxygen.) The kinetic data for the neopentyl complex were obtained on unpurified preparative solutions owing to its rapid acidolysis. The procedure was checked using the reaction of $Cr-n-C_3H_7^{2+}$ with CH_3Hg^+ which in one run had $k_{CH_3Hg} = 1.0 \times 10^2\ M^{-1}\ s^{-1}$ compared to the average rate constant $(1.21 \pm 0.08) \times 10^2\ M^{-1}\ s^{-1}$ using the purified complex.

Among all the reactions studied, only that of $CrCH_3^{2+}$ with CH_3Hg^+ shows a variation with $[H^+]$, increasing as $[H^+]$ decreases; values of $10^{-4}k_{CH_3Hg}$ at different $[H^+]$ at $\mu = 0.50$ M and 25.0°, are as follows: 1.06 ± 0.02 at 0.40 M, 1.14 ± 0.02 at 0.250 M, 1.58 ± 0.09 at 0.100 M and 3.16 ± 0.26 at 0.020 M. A treatment of the form $k = a + b[H^+]^{-1}$ yields the parameters $a = 9 \times 10^3\ M^{-1}\ s^{-1}$ and $b = 5.8 \times 10^2\ s^{-1}$.

Variations of Anion, Solvent, and Electrophile. A cursory study was done to learn the magnitude of the rate effect caused by variation of certain other parameters.

The rate studies employed CH_3HgOAc for matters of practical convenience, but the rate constant for the reaction of CH_3HgClO_4 with $CrCH_2C_6H_5^{2+}$ is identical (96 $M^{-1}\ s^{-1}$ compared to 98 ± 1 for the latter). The predominant species of methylmercuric ion in solution is undoubtedly $CH_3HgOH_2^+$, and the choice of weakly-coordinating anion is immaterial. The solution of CH_3HgClO_4 may possibly contain small traces of Ag^+ from the preparative procedures, but addition of 10^{-4} M Ag^+, a level far in excess of that which might be present, caused no detectable variation in rate constant toward $CrCH_3^{2+}$: $1.1 \times 10^4\ M^{-1}\ s^{-1}$, regardless of the addition of Ag^+.

The kinetic studies employed strictly aqueous solutions, with one determination of the rate constant for the reaction of CH_3Hg^+ with $CrCH_2C_6H_5^{2+}$ carried out in 2:1 v/v THF-H_2O at 25.0° and 0.50 M ionic strength. The latter reaction had $k_{HgCH_3} = 29\ M^{-1}\ s^{-1}$ compared to 98 ± 1 in water.

In the course of preliminary studies of the CH_3Hg^+ reactions we asked whether the nature of the organomercurial had a marked rate effect. Three kinetic experiments supported the lack of a pronounced effect: (1) with $CrCH_2C_6H_5^{2+}$ in 2:1 v/v THF-H_2O at 25.0°, $\mu = 0.5$ M, $C_6H_5CH_2HgClO_4$ and CH_3Hg^+ gave $k_{RHg} = 29$ and 30 $M^{-1}\ s^{-1}$, respectively; (2) with $CrCH_2C_6H_5^{2+}$ in water at 25.0°, $\mu = 0.1$ M, C_6H_5HgOAc and CH_3HgOAc gave $k_{RHg} = 40$ and 65 $M^{-1}\ s^{-1}$, respectively; (3) with $CrCH_3^{2+}$ in water at 25.0° and $\mu = 0.50$ M, C_6H_5HgOAc and CH_3HgOAc gave $k_{RHg} = 1.6 \times 10^4$ and $1.1 \times 10^4\ M^{-1}\ s^{-1}$, respectively.

The second experiment also provides a limited measure of ionic strength effects: k_{CH_3Hg} is 65 at $\mu = 0.1$ M and 98 at $\mu = 0.5$ M (25.0°, aqueous solution).

Effects of Temperature and Electronic Substituents. For three of the reactions investigated, rate constants were evaluated at different temperatures. These data and the corresponding activation parameters are given in Table III.

Both k_{Hg} and k_{CH_3Hg} show a mild variation with the substituent in the series of para substituted benzylchromium cations. The correlation we make of these data takes the form of a linear-free-energy relation according to the Hammett equation. Figure 4 depicts the plots of log k vs. the substituent parameter σ. Values[31] of the reaction constant are k_{Hg}, $\rho = -0.62 \pm 0.05$; k_{CH_3Hg}, $\rho = -0.85 \pm 0.05$.

Interpretation and Discussion

The experimental observations bearing on the reaction can be succinctly summarized as follows: (1) the respective mercury products of reactions 1 and 2 are RHg^+ and $RHgCH_3$,[29] (2) the rates are first order in $[CrR^{2+}]$ and first order in $[Hg^{2+}]$ or $[CH_3Hg^+]$; (3) the rates are independent of $[H^+]$, with the sole exception of $CH_3Hg^+ + CrCH_3^{2+}$; (4) for a given CrR^{2+} complex, $k_{Hg} \geqslant 10^2 k_{CH_3Hg}$, (5) the reaction rates of various organomercurial cations with a given CrR^{2+} complex

Table III. Temperature Effects and Activation Parameters

Reaction	$Cr\text{-}n\text{-}C_3H_7^{2+} + Hg^{2+}$	$Cr\text{-}n\text{-}C_3H_7^{2+} + CH_3Hg^+$	$CrCH_2Cl^{2+} + Hg^{2+}$
$k/M^{-1}\,s^{-1}$ (T/°C)	$(3.08 \pm 0.08) \times 10^4$ (17.7°) $(3.50 \pm 0.17) \times 10^4$ (25.0°) $(4.08 \pm 0.20) \times 10^4$ (29.9°)	$(0.78 \pm 0.01) \times 10^2$ (15.1°) $(1.21 \pm 0.08) \times 10^2$ (25.0°) $(1.73 \pm 0.05) \times 10^2$ (35.1°) $(2.35 \pm 0.05) \times 10^2$ (41.1°)	0.356 ± 0.009 (17.3°) 0.590 ± 0.015 (25.0°) 0.730 ± 0.014 (29.4°) 1.02 ± 0.02 (36.0°)
$\Delta H^{\ddagger}$/kJ mol^{-1}	13.8 ± 3.3	28.6 ± 2.4	39.8 ± 0.8
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	-111 ± 11	-109 ± 8	-116 ± 3

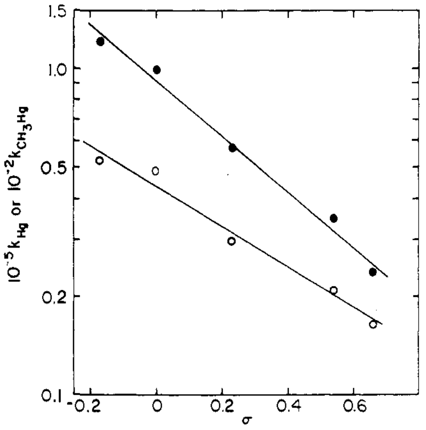

Figure 4. Plots of k_{Hg} (open circles) and k_{CH_3Hg} (filled circles) on a log scale vs. the Hammett substituent parameters σ_p.

are about the same; (6) Hg^{2+}, CH_3Hg^+, and Br_2 show parallel changes in reactivity toward variation of R in the series of CrR^{2+} complexes; (7) the rate is sharply lowered by addition of electronegative substituents to the α carbon atom, the most dramatic example being the nonreactive $CrCF_3^{2+}$, and is mildly decreased by electron withdrawing substituents in the benzylchromium complexes; (8) the rate decreases with steric bulk of the alkyl substituent, particularly so for the secondary isopropyl complex.

The observations suggest an electrophilic reaction, with formal carbanion transfer from chromium to mercury. The small negative reaction constants resulting from the Hammett correlation suggest that little additional "free carbanion character" develops in the transition state, compared to the ground state. The first-order rate dependence upon [electrophile] eliminates a unimolecular SE1 mechanism for which the heterolysis of CrR^{2+} to form Cr^{3+} and RR^- would be the rate-limiting step. Even in the few reactions with a nonzero intercept in a plot of k_{obsd} vs. [Hg^{2+}] or [CH_3Hg^+], it was possible to demonstrate that this corresponds to the competing acidolysis of CrR^{2+} and not to a concurrent SE1 electrophilic reaction. The kinetic data support an SE2 (open) mechanism, as this term is defined by Abraham;[33] that is, there is in the transition state no bridging between the incoming mercury electrophile and a water molecule coordinated to the pentaaquo(organo)chromium complex.

The reactivity of $Hg^{2+}{}_{aq}$ compared to $CH_3HgOH_2^+$ is markedly higher, reflecting the greater electrophilic character of the former. Yet the change here is *far* less marked than in the analogous reactions of alkylcobalt complexes where RHg^+ is virtually unreactive despite facile reaction of Hg^{2+}.[5,8] Perhaps this difference is not fundamental: the overall reactivity of the RCr^{2+} complexes greatly exceeds that of the RCo(chelate) derivatives, for one thing, in addition to which the scale of reactivity is compressed for the more rapidly reacting chromium complexes. A second point of note is the lack of rate sensitivity to a change from CH_3Hg^+ to $PhHg^+$ or $PhCH_2Hg^+$ which suggests the essentially constant electrophilicity of these three.

Table IV presents the relative rate constants for reactions of aliphatic organochromium cations with the electrophiles Br_2, Hg^{2+}, and CH_3Hg^+. These data indicate the close similarity of these three reactions among themselves, and the rougher agreement between these three and two others, namely, $RCo(dmgH)_2H_2O + Hg^{2+}{}_{aq}$ and $RSn(CH_2C(CH_3)_3)_3 + Br_2$. The latter are two electrophilic reactions for which inversion of configuration has been established.[14a,34] In contrast to these, reactions where the steric course is known to be retention of configuration show a somewhat different pattern of reactivity. We therefore offer the *tentative* suggestion that reactions 1 and 2 proceed with inversion of configuration; the same suggestion was made previously for reaction of Cr^{2+} with Br_2.[18a] Examined in more detail, reaction of Hg^{2+} with CrR^{2+} shows more pronounced rate effects with steric bulk of R than do either of the reactions $CrR^{2+} + CH_3Hg^+$ or $CrR^{2+} + Br_2$. The latter is the least sterically dependent of the three. It seems reasonable that the rates are more subject to steric influence the greater the extent of solvation of the electrophile, which decreases in the order $Hg^{2+} > CH_3Hg^+ > Br_2$.

The values of $\Delta S^{\ddagger}$ for the three reactions studied at more than a single temperature were large, negative numbers, all ca. -110 J mol^{-1} K^{-1}. The large rate variations for the different reactions arise entirely from differences in $\Delta H^{\ddagger}$.

Experimental Section

Preparation of Alkyl Hydroperoxides. Of the compounds with the general formula $RC(CH_3)_2OOH$, only R = CH_3 is commercially available; the compounds with R = C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $(CH_3)_3CCH_2$, $sec\text{-}C_4H_9$, and $t\text{-}C_4H_9$ were prepared from the appropriate alcohol and hydrogen peroxide according to the general procedure of Milas and Sugenor[35] with but slight modification. A typical procedure[36] is the following preparation of 2,4,4-trimethylpentyl 2-hydroperoxide:water (3.1 cm^3) and concentrated sulfuric acid (3.5 cm^3, 0.06 mol) were added to a 100-cm^3 round-bottom flask and cooled to 0°. 2,4,4-Trimethyl-2-pentanol (10 cm^3, 0.06 mol) and hydrogen peroxide (ca. 6 cm^3 of a 50% solution, 0.08 mol) were added to the flask simultaneously and dropwise over a period of 45 min with vigorous stirring.[37] This mixture was left to react at 0° with stirring for ca. 6 h, after which the aqueous phase, separated by centrifugation, was discarded. The organic layer was washed twice with water, and proved by peroxide analysis (see below) to be 5.1 M $(CH_3)_3CCH_2C(CH_3)_2OOH$, compared to 6.2 M for the pure compound based on an estimated density of 0.9 g cm^{-3}. This material was used without further purification for the synthesis of the neopentylchromium(III) cation.

Proton NMR spectra of the hydroperoxides in $CDCl_3$ confirmed the assigned structures, but in every case were so close to that of the parent alcohol that they did not prove the absence of the latter materials, which is the most likely contaminant. Since these alcohols do not react with Cr^{2+} under the conditions employed, and since the ultimate RCr^{2+} complexes are purified chromatographically, removal from the hydroperoxide of the final traces of alcohol was deemed unnecessary.

The alcohols for the above preparations were the commercial reagent-grade compounds, except for R = neopentyl in which case the compound was prepared by the reaction of 4,4-dimethyl-2-pentanone (50 cm^3, 0.35 mol) and methyl magnesium bromide.

The alkyl hydroperoxides were determined by a modification of the method of Wagner et al.[38] wherein 1-3 mmol of the compound is

Table IV. Relative Rates for a Series of Electrophilic Substitution Reactions of Metal Alkyls

Reaction	Stereochemistry	Relative rates at 25°					Ref
		$-CH_3$	$-C_2H_5$	-*n*-C_3H_7	$-CH_2C(CH_3)_3$	$-CH(CH_3)_2$	
$CrR^{2+} + Hg^{2+}{}_{aq}$	–	71	1.00	0.25	3.5×10^{-3}	1.1×10^{-5}	*a*
$CrR^{2+} + CH_3Hg^{+}{}_{aq}$	–	50	1.00	0.61	2.9×10^{-2}	–	*a*
$CrR^{2+} + Br_{2\,aq}$	–	4.3	1.00	1.3	2.0×10^{-2}	–	*b*
$RCo(dmgH)_2H_2O + Hg^{2+}{}_{aq}$	Inversion	530	1.00	0.74	7.4×10^{-2}	$<5 \times 10^{-6}$	*c*
$RSn(CH_2C(CH_3)_3)_3 + Br_2$	Inversion	6.9	1.00	0.28	4.0×10^{-3}	5.2×10^{-2}	*d*
$RHgBr + HgBr_2$	Retention	2.4	1.00	–	0.78	–	*e*
$R_2Hg + HCl$	Retention	0.16	1.00	0.62	–	0.68	*f*
"SN2"	Inversion	33	1.00	0.04	10^{-6}	3×10^{-3}	*g*

[a] This work. [b] Reference 18a. [c] References 5, 14a. [d] Data from ref 9, rates quoted relative to $C_2H_5Sn(CH_2C(CH_3)_3)_3$ for which $k = 1.15$ $M^{-1}\,s^{-1}$ at 45° in 0.366 M NaBr in methanol. [e] Data from E. D. Hughes and H. C. Volger, *J. Chem. Soc.*, 2359 (1961), and E. D. Hughes, C. K. Ingold, F. G. Thorpe, and H. C. Volger, *ibid.*, 1133 (1961), rates quoted relative to $C_2H_5HgBr + HgBr_2$ for which $k = 5.4 \times 10^{-5}$ $M^{-1}\,s^{-1}$ in ethanol at 100°. [f] Data from R. E. Dessy, G. F. Reynolds, and J.-Y. Kim, *J. Am. Chem. Soc.*, **81**, 2683 (1959), rates quoted in 10:1 Me_2SO/dioxane at 50° relative to $Hg(C_2H_5)_2$ for which $k = 8.2 \times 10^{-4}$ $M^{-1}\,s^{-1}$. [g] The data for "typical" SN2 substitution from A. Streitweiser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962, p 13.

added to isopropyl alcohol (40 cm^3) and acetic acid (2 cm^3). The solution is heated to boiling, sodium iodide (2 g) added, and the mixture refluxed for 5 min. After cooling to room temperature, the solution is titrated with aqueous sodium thiosulfate to the disappearance of the iodine coloration.

Preparation of Organochromium Complexes. The general reaction used to prepare the alkyl complexes, $CrC_nH_{2n+1}{}^{2+}$, is given in eq 6, and the general reaction used for benzyl and haloalkyl complexes in eq 7.

$$C_nH_{2n+1}C(CH_3)_2OOH + 2Cr^{2+} = Cr^{3+} + CrC_nH_{2n+1}{}^{2+} + (CH_3)_2CO \quad (6)$$

$$RBr + 2Cr^{2+} = CrBr^{2+} + CrR^{2+} \quad (7)$$

Reaction 6 was first used by Kochi[39] for the preparation of $CrCH_2C_6H_5{}^{2+}$, and later by others[40] for $CrCH_3{}^{2+}$. Espenson and Williams[18a] have described the preparation of several other primary alkyl chromium cations by the same reaction, but the conditions were not optimally adjusted. The following preparations yielded[41] CrR^{2+} complexes, isolated and purified by cation exchange chromatography. In addition, in this work two secondary and one tertiary alkyl complex were prepared for the first time.

The general procedure is to carry out the reaction in ca. 50 cm^3 of thoroughly deoxygenated aqueous 0.01 M perchloric acid, reacting 0.6-1 mmol of the hydroperoxide with ca. 3 mmol of $Cr(ClO_4)_2$. The reaction is virtually complete upon mixing, and the excess Cr^{2+} was oxidized by bubbling the solution with oxygen for 10 min. The reaction solution was then passed through a 15 × 1 cm column of Dowex 50W-X8, 100-200 mesh, cation exchange resin in the lithium ion form that was chilled by the circulation of ice water through a condenser-type jacket. The column was washed with 50-200 cm^3 of cold water, and the pale yellow or orange organochromium complex eluted with 0.5 F lithium perchlorate. The ion exchange separation was often carried out with a slight positive pressure of nitrogen applied to the column to speed the passage of solution. The above procedure was successful for R = CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, and *sec*-C_4H_9, which were typically obtained as ca. 50 cm^3 of 3×10^{-3} M CrR^{2+}, collected, and stored at 0° to minimize acidolysis. (The isopropyl and *sec*-butyl derivatives were, in addition, mildly oxygen sensitive, and were stored and utilized under nitrogen, although oxygen was briefly introduced to oxidize the excess Cr^{2+} prior to separation.) The acidolysis of the neopentylchromium cation proceeds relatively rapidly (contrary to a previous report;[18a] the half-life towards acidolysis is roughly 15 min at 0° in 0.5 F $LiClO_4$, and may be accelerated by the ion exchange resin). Its reactions were studied using the reaction solution itself, without benefit of ion exchange separation, under the assumption that Cr(III) and organic by-products are innocuous in the reactions studied. This point was verified independently by the reproducibility of kinetic data for the *n*-propylchromium cation with and without the separation and purification step.

Reaction 7 for the preparation of haloalkyl and benzyl complexes has been widely utilized;[15-18,30,39,42] the precise procedures used for the preparation and separations are given elsewhere.[1]

Table V. Uv-Visible Spectra of Organochromium Complexes $(H_2O)_5CrR^{2+}$ in Aqueous Solution

R	λ_{max}/nm (ϵ/$M^{-1}\,cm^{-1}$)		
$-CH_3$[a]	550 (12.0)	392 (246)	258 (2400)
$-C_2H_5$	560 (8.5)	394 (390)	275 (2400)
-*n*-C_3H_7	550 (8.3)	393 (380)	276 (2650)
$-CH_2C(CH_3)_3$		405 (ca. 200)	283
-*i*-C_3H_7	557 (10.0)	399 (366)	290 (1800)
-*sec*-C_4H_9	—	400 (370)	283 (1775)
-*t*-C_4H_9	—	407	310
$-CH_2Cl$	517 (23.7)	393 (225)	260 (3560)
$-CH_2Br$[b]	520 (28.9)	397 (255)	266 (3280)
$-CF_3$	490 (43.2)	380 (77.6)	220 (5500)
$-CH_2C_6H_3$[c]	355 (2200)	297 (6970)	274 (7670)

[a] From J. S. Shveima and J. H. Espenson, *J. Am. Chem. Soc.*, **95,** 4468 (1973). [b] Reference 18a. [c] Reference 43.

The uv-visible absorption spectrum of each organochromium complex was obtained on one or more samples immediately following elution from the ion exchange resin.[36] The molar absorptivities (see Table V) were computed on the basis of a determination of total chromium as chromate at λ 372 nm (ϵ 4.83×10^3 $M^{-1}\,cm^{-1}$),[43] and although we regard them as values accurate to within 5%, the values are really lower limits in that the most likely systematic error is a lower absorbance caused by any partial acidolysis or imperfect separation from $Cr(H_2O)_6{}^{3+}$, a complex which absorbs less strongly than any of the organochromium derivatives.

Other Reagents. Solutions of mercuric perchlorate were prepared by boiling the oxide in a slight excess of perchloric acid. The solution was filtered then analyzed by Volhard titration with sodium thiocyanate. Solutions of methylmercuric perchlorate were prepared by reaction of methylmercuric chloride (1.89 g, 7.5 mmol) and silver perchlorate (6.75 mmol) in ethanol (150 cm^3)-water (15 cm^3). After stirring for 3 h, the solution was filtered to remove silver chloride and unreacted CH_3HgCl. Ethanol was removed under vacuum and the remaining solution made up to ca. 50 cm^3 with water, providing ca. 0.1 M CH_3HgClO_4. A similar procedure was used for benzylmercuric perchlorate solutions. The solutions of CH_3Hg^+ were analyzed spectrophotometrically using dithizone(diphenylsemicarbazone). The absorbance at λ 618 nm of dithizone in carbon tetrachloride is measured with and without extraction of the aqueous CH_3HgClO_4 solution.[44,45]

Chromium(II) perchlorate solutions in dilute perchloric acid were prepared by reduction of $Cr(ClO_4)_3$ with amalgamated zinc under an oxygen-free atmosphere of Cr^{2+}-scrubbed nitrogen. Hydrated $Cr(ClO_4)_3$ was prepared from the reaction of chromium trioxide and hydrogen peroxide in aqueous perchloric acid, recrystallizing the product twice.

Lithium perchlorate was prepared from the carbonate and perchloric acid, and was recrystallized twice. All other materials were the best commercial grade, and were used without purification.

Experimental Methods. Uv-visible spectra as well as rate constants for reactions of >10 s mean reaction time were determined using a Cary Model 14 recording spectrophotometer. For the kinetic determinations all reagents except the organochromium complex were added to a quartz cell of suitable optical path which, if required for the complex being studied, was purged of oxygen by bubbling the solution with Cr^{2+}-scrubbed nitrogen through a serum cap for at least 20 min. The cell was immersed to the filling neck in a constant temperature water bath and allowed to equilibrate for at least 20 min, at which time reaction was initiated by injection of a small aliquot of the thermostated CrR^{2+} stock solution. The reaction was monitored by recording a continuous tracing of absorbance at a single suitable wavelength in the region 258–420 nm vs. time.

The rates of faster reactions were determined using a Durrum stopped-flow spectrophotometer having a Kel-F mixing block and a 2-cm optical path.

A Varian A-60 spectrometer was used for proton NMR measurements. For identification of the RHg^+ and $RHgR'$ products, the organomercurial was extracted from the reaction solution into chloroform or carbon tetrachloride (after adding excess HCl in the case of RHg^+), the solvent evaporated under vacuum, and the residue redissolved in 1 cm^3 of an appropriate NMR solvent, usually $CDCl_3$ or CCl_4.

Kinetic Data. The very rapid reaction of Hg^{2+} and $CrCH_3{}^{2+}$ required the use of comparable concentrations of reagents, and most runs had only a two–threefold excess of Hg^{2+}. The kinetic data for these runs were treated according to eq 8

$$\ln\{1 + \Delta_0/[\mathrm{CrCH_3}^{2+}]_t\} = \ln\{[\mathrm{Hg}^{2+}]_0/[\mathrm{CrCH_3}^{2+}]_0\} + \Delta_0 k_2 t \qquad (8)$$

where $\Delta_0 = [\mathrm{Hg}^{2+}]_0 - [\mathrm{CrCH_3}^{2+}]_0$, by a plot of the left side vs. t. The absorbance (D) values were used to compute $[\mathrm{CrCH_3}^{2+}]_t$, which is given as $[\mathrm{CrCH_3}^{2+}]_0(D_t - D_\infty)/(D_0 - D_\infty)$.

In all of the other experiments the concentration of mercuric ion or of the methyl mercuric ion was at least tenfold higher than that of the organochromium cation. In these runs a pseudo-first-order rate constant was computed either from the slope of a plot of log $(D_t - D_\infty)$ vs. time or from a plot made according to the method of Swinbourne,[46] plotting D_t vs. $D_{t+\tau}$. In the latter method, eq 9, τ is chosen as a constant time interval of ca. 0.5–1 half-life, and the pseudo-first-order rate constant, k_{obsd}, is computed as ln (slope)/τ.

$$D_t = D_\infty[1 - \exp(k\tau)] + D_{t+\tau}\exp(k\tau) \qquad (9)$$

References and Notes

(1) (a) Based in part on the Ph.D. Thesis of J.P.L., Iowa State University, Oct 1975. (b) Work performed for U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

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(29) The reactions of $CrCH_2I^{2+}$ and $CrCHCl_2{}^{2+}$ with Hg^{2+} produce appreciable $Hg_2{}^{2+}$.[16] Reactions such as those of $CrCH_2Cl^{2+}$ and $CrCH_2Br^{2+}$ with Hg^{2+}, on the other hand, produce <1% $Hg_2{}^{2+}$. A convenient test for $Hg_2{}^{2+}$ production is realized by passing the product solution through a column of Dowex 50W-X8 ion exchange resin, eluting Hg^{2+} and RHg^+ with 1 F $HClO_4$, and then introducing 1 F HCl. The presence of $Hg_2{}^{2+}$ is indicated by a copious white precipitate at the top of the resin column.

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