

# Kinetics and Mechanism of the Cleavage Reactions of Alkylchromium Cations with Bromine<sup>1</sup>

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**Abstract:** Alkylpentaquochromium cations  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  ( $\text{R} = \text{alkyl, haloalkyl, and 4-pyridinomethyl}$ ) undergo reaction with molecular bromine in aqueous perchloric acid solutions forming, in a reaction of 1:1 stoichiometry,  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Br}^-$ , and the alkyl bromide,  $\text{RBr}$ . The reaction follows a mixed-second-order rate expression which can be interpreted in terms of an  $\text{S}_\text{E}2$  reaction mechanism, with an "open" transition state because  $\text{Cr}(\text{H}_2\text{O})_5\text{Br}^{2+}$  is not a product. On the basis of the variation in the rate constants for the alkyl derivatives, it is suggested that the stereochemical course of the reaction corresponds to inversion of configuration at carbon.

Reaction of metal alkyls with bromine results in cleavage of the metal-carbon bond and formation of alkyl bromide. The reaction mechanisms of alkyltin and lead compounds<sup>2,3</sup> and of organomercurials<sup>4</sup> have been extensively studied, using both kinetic and stereochemical determinations as reviewed recently.<sup>2d,5,6</sup>

Far less attention has been paid to the reactions of transition metal alkyls with bromine, and we are aware of no systematic kinetic investigations, although stereochemistry has been determined for  $\text{RMn}(\text{CO})_5$  (retention<sup>7</sup>),  $\text{RFe}(\text{CO})_2(\text{C}_5\text{H}_5)$  (inversion<sup>8</sup>), and alkylbis(dimethylglyoximate)cobalt (inversion<sup>9,10a,11</sup>).

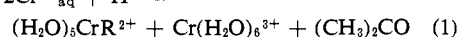
We report here the results of kinetic studies of the bromination reactions of the organochromium cations  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ . The compounds studied include the simple alkyls, haloalkyls, and 4-pyridinomethyl. In the course of this work several previously unknown alkylchromium compounds were prepared. Our interest is primarily to describe the rate behavior and particularly the rate dependence upon steric and electronic effects.

## Results

**Identification of the Organochromium Cations.** The previously known compounds were identified primarily on the basis of their characteristic uv-visible spectra in comparison with the spectra reported in the literature. This was the case for  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  with  $\text{R} = \text{CH}_2\text{Cl}$ ,<sup>12,13</sup>  $\text{CHCl}_2$ ,<sup>12,13</sup>  $\text{CH}_2\text{Br}$ ,<sup>12</sup>  $\text{CH}_2\text{I}$ ,<sup>12</sup>  $\text{CH}_3$ ,<sup>14-16</sup>

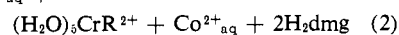
and  $4\text{-CH}_2\text{C}_5\text{H}_4\text{NH}^+$ .<sup>17</sup> In all of these cases the spectrum agreed with that reported; the individual spectra are presented in the thesis cited.<sup>1</sup>

The previously unknown complex  $(\text{H}_2\text{O})_5\text{CrCH}(\text{Cl})\text{-CH}_3^{2+}$  was prepared in a straightforward manner from the reaction of 1-bromo-1-chloroethane and  $\text{Cr}(\text{II})$  as suggested by earlier work.<sup>12,18</sup> The unsubstituted alkyl complexes, aside from the methyl, were also previously unknown. They were prepared from the appropriate hydroperoxide (eq 1). This reaction was originally



suggested by Kochi<sup>19</sup> for the synthesis of the methylchromium ion from *tert*-butyl hydroperoxide and was the basis of its first synthesis.<sup>14,15</sup> The reaction appears to be a general one, as it was successful for the three other unsubstituted alkyl derivatives. The method also produced a highly unstable compound presumed to be isopropylchromium ion which decomposed too rapidly for isolation and purification.

The methyl-, ethyl-, and propylchromium ions were also synthesized independently by an alkyl transfer reaction between the alkylcobaloxime and  $\text{Cr}^{2+}_{\text{aq}}$  (eq 2).<sup>16</sup>



These compounds were purified chromatographically, and their absorption spectra were determined (see Experimental Section). The compounds were further characterized by mass spectrometric determinations; ethane and neopentane, respectively, were the only volatile products of reaction of the ethyl- and neopentylchromium cations with acid, and ethyl and neopentyl bromides were the sole volatile products formed in their brominations.<sup>20</sup>

(12) D. Dodd and M. D. Johnson, *J. Chem. Soc. A*, 34 (1968).

(13) W. R. Bushey, Ph.D. Thesis, Iowa State University, 1972.

(14) W. Schmidt, J. H. Swinehart, and H. Taube, *J. Amer. Chem. Soc.*, **93**, 1117 (1971).

(15) M. Ardon K. Woolmington, and A. Pernick, *Inorg. Chem.*, **10**, 2812 (1971).

(16) J. H. Espenson and J. S. Shveima, *J. Amer. Chem. Soc.*, **95**, 4468 (1973).

(17) R. G. Coombes, M. D. Johnson, and N. Winterton, *J. Chem. Soc. A*, 7029 (1965).

(18) C. E. Castro and W. C. Kray, Jr., *J. Amer. Chem. Soc.*, **88** 4447 (1966).

(19) J. K. Kochi, *Rec. Chem. Progr.*, **27**, 207 (1966).

(20) (a) The results confirm that the neopentyl radical (which is formed as an intermediate in reaction 1) does not rearrange to a more stable radical prior to reaction with  $\text{Cr}^{2+}$ , which is consistent with the high rates reported<sup>20b</sup> for the latter reactions. (b) H. Cohen and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 320 (1972).

(1) Based in part on the M.S. Thesis of D. A. W., Iowa State University, May 1973.

(2) (a) M. Gielen and J. Nasielski, *Bull. Soc. Chim. Belg.*, **71**, 60 (1962); (b) M. Gielen, J. Nasielski, J. E. Dubois, and P. Fresnet, *ibid.*, **73**, 293 (1964); (c) M. Gielen and J. Nasielski, *Recl. Trav. Chim. Pays-Bas*, **82**, 228 (1963); (d) M. Gielen, *Accounts Chem. Res.*, **6**, 198 (1973).

(3) F. R. Jensen and D. D. Davis, *J. Amer. Chem. Soc.*, **93**, 4048 (1971).

(4) (a) F. R. Jensen and L. H. Gale, *J. Amer. Chem. Soc.*, **82**, 148 (1960); (b) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *ibid.*, **82**, 2466 (1960).

(5) D. S. Matteson, *Organometal. Chem. Rev., Sect. A*, **4**, 263 (1969).

(6) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, pp 75-99.

(7) R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1970).

(8) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971).

(9) F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, **93**, 5283 (1971).

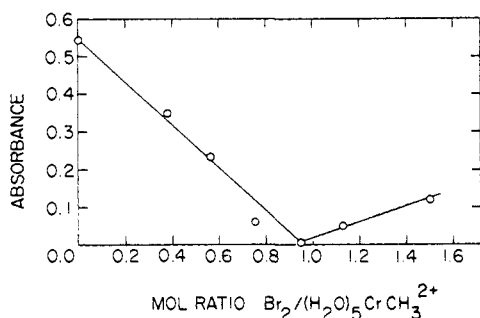
(10) (a) S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972); (b) S. N. Anderson, D. H. Ballard, and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 331 (1972).

(11) The reaction proves to be quite complex, however, and may well involve prior oxidation to an unstable alkylcobalt(IV), the latter compound then undergoing nucleophilic displacement of R by  $\text{Br}^-$ , a process undoubtedly occurring with inversion.<sup>10</sup>

**Table I.** Kinetic Data for the Reactions of Various Alkylchromium(III) Cations  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  with Bromine in Aqueous Perchloric Acid at  $25.0^\circ$  and  $\mu = 1.00 M$ 

R	Range of initial concn		Av $k_2$ , <sup>a</sup> $M^{-1} \text{sec}^{-1}$ (no.)
	$[\text{Br}_2]$ , M	$[\text{CrR}^{2+}]$ , M	
$-\text{CH}_3$	$1.4\text{--}2.5 \times 10^{-4}$	$1.1\text{--}2.5 \times 10^{-4}$	$(2.1 \pm 0.2) \times 10^6$ (3)
$-\text{C}_2\text{H}_5$	$0.3\text{--}7.3 \times 10^{-4}$	$2.8\text{--}40 \times 10^{-6}$	$(4.9 \pm 0.5) \times 10^6$ (6)
$-n\text{-C}_3\text{H}_7$	$1.4\text{--}1.6 \times 10^{-4}$	$1.2 \times 10^{-5}$	$(6.2 \pm 0.1) \times 10^6$ (2)
$-\text{CH}_2\text{C}(\text{CH}_3)_3$	$0.5\text{--}4.1 \times 10^{-4}$	$3.7\text{--}5.0 \times 10^{-5}$	$(9.9 \pm 0.6) \times 10^5$ (5)
$-\text{CH}(\text{Cl})\text{CH}_3$	$1.1\text{--}4.1 \times 10^{-3}$	$2.0\text{--}2.9 \times 10^{-4}$	$6.8 \pm 0.3$ (3)
$-\text{CH}_2\text{Cl}$	$1.0\text{--}29 \times 10^{-3}$	$0.77\text{--}33 \times 10^{-4}$	$1.06 \pm 0.06$ (22)
$-\text{CH}_2\text{Br}$	$0.1\text{--}31 \times 10^{-3}$	$1.0\text{--}5.4 \times 10^{-3}$	$(3.5 \pm 0.3) \times 10^{-1}$ (6)
$-\text{CH}_2\text{I}$	$0.41\text{--}3.6 \times 10^{-4}$	$1.4\text{--}6.7 \times 10^{-3}$	$7.13 \pm 0.06$ (6)
$-\text{CHCl}_2$	$1.7 \times 10^{-2}$	$1.7 \times 10^{-3}$	$< 3 \times 10^{-3}$
$-4\text{-CH}_2\text{C}_3\text{H}_5\text{NH}^+$	$2.5\text{--}8.5 \times 10^{-3}$	$2.6 \times 10^{-4}$	$(1.1 \pm 0.3) \times 10^3$ (2)

<sup>a</sup> The mean value of  $k_2$  cited together with the average deviation from the mean in the number of determinations given in parentheses.



**Figure 1.** A plot showing the spectrophotometric titration of  $(\text{H}_2\text{O})_5\text{CrCH}_3^{2+}$  with  $\text{Br}_2$  at  $\lambda$  260 nm; the initial concentration of methylchromium ion in each solution was  $4.36 \times 10^{-5} M$ , and the optical path length was 5.00 cm.

**Stoichiometry.** The bromination of the alkylchromium complexes occurred according to the reaction shown in eq 3. The experiments used to establish this



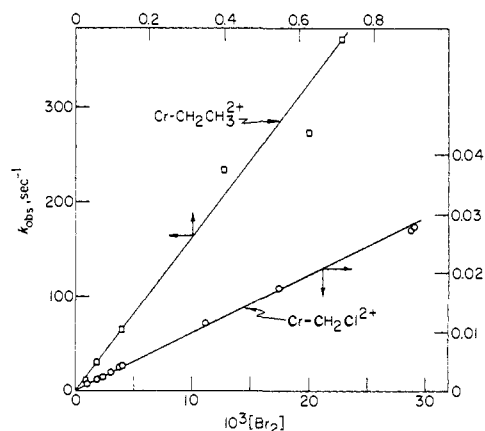
result were as follows. The 1:1 consumption of reactants was confirmed for the reaction of  $\text{CrCH}_2\text{Cl}^{2+}$  by an iodometric titration of the excess  $\text{Br}_2$  remaining after reaction with an approximate twofold excess of  $\text{Br}_2$ . In three determinations,  $1.05 \pm 0.03$  mol of  $\text{Br}_2$  was consumed per mole of  $\text{CrCH}_2\text{Cl}^{2+}$  taken. The stoichiometry of the reaction of the methylchromium complex was determined spectrophotometrically at  $\lambda$  260 nm, where both  $\text{CrCH}_3^{2+}$  (present only in solutions containing insufficient  $\text{Br}_2$ ) and  $\text{Br}_3^-$  (present only in solutions containing excess  $\text{Br}_2$ ) absorb. As shown in Figure 1, the reaction ratio  $\Delta[\text{Br}_2]/\Delta[\text{CrCH}_3^{2+}]$  was 0.94.

The Cr(III) product of the bromination was determined to be  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and not  $\text{Cr}(\text{H}_2\text{O})_5\text{Br}^{2+}$  by the absence of the latter complex when the product solution was chromatographed on Dowex 50W-X8 cation-exchange resin after first removing the excess bromine in a vigorous stream of nitrogen.<sup>21, 22</sup>

The stoichiometry of reaction 3 was further verified in the case of  $\text{R} = \text{CH}_2\text{Cl}$  by analysis of the free bromide

(21) The possibility remained that the thermodynamically unstable bromo complex ( $\text{Cr}^{3+} + \text{Br}^- = \text{CrBr}^{2+}$ ,  $K = 2 \times 10^{-3} M^{-1}$ ) had decomposed during the reaction (owing to the presence of a catalyst, perhaps, as the dissociation normally occurs very slowly<sup>22</sup>). This was ruled out, however, by performing the reaction of  $\text{CrCH}_2\text{Cl}^{2+}$  and  $\text{Br}_2$  in solutions to which had been added, prior to initiation of the bromination reaction, a known quantity of the authentic bromo complex. The products of the reaction were chromatographed as before, and the added  $\text{CrBr}^{2+}$  was recovered quantitatively ( $\geq 96\%$  recovery of the added  $\text{CrBr}^{2+}$ ).

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



**Figure 2.** Plots showing the linear variation of the pseudo-first-order rate constant with the average concentration of bromine for the reactions of  $\text{CrCH}_2\text{Cl}^{2+}$  (circles, right ordinate and lower abscissa scales) and  $\text{CrC}_2\text{H}_5^{2+}$  (squares, left ordinate and upper abscissa scales).

ion produced; in four determinations,  $0.90 \pm 0.05$  mol of  $\text{Br}^-$  was produced per mol of  $\text{CrCH}_2\text{Cl}^{2+}$ .

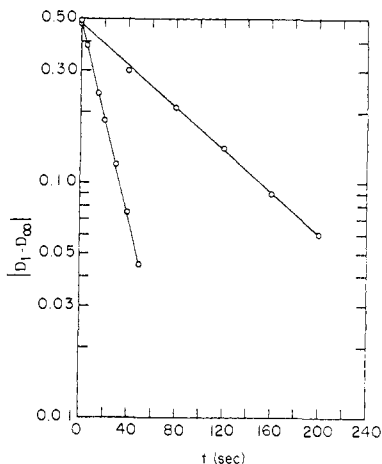
In every case examined (except  $\text{R} = \text{CH}_2\text{I}$  which will be discussed later) the observed mass spectrum of the volatile reaction products agreed closely with the published mass spectrum of the expected alkyl bromide.<sup>23</sup> The quantitative stoichiometry of  $\text{RBr}$  production, on the other hand, was assumed but not verified.

**Kinetic Determinations.** The reactions of alkylchromium compounds with aqueous bromine were studied in perchloric acid solutions having an ionic strength of 1.0 M maintained with lithium perchlorate. Most experiments were performed with a large excess of bromine; these data conformed closely to a pseudo-first-order rate expression. The pseudo-first-order rate constant  $k_{\text{obsd}}$  showed a linear dependence on  $[\text{Br}_2]$ , shown in Figure 2 for  $\text{R} = \text{CHCl}_2$  and  $\text{C}_2\text{H}_5$ . The data are in accord with the rate expression

$$-d[\text{CrR}^{2+}]/dt = k_2[\text{CrR}^{2+}][\text{Br}_2] \quad (4)$$

In reactions with comparable concentrations of reactants, including experiments with excess  $\text{CrR}^{2+}$ , the kinetic data were plotted as  $\log([\text{CrR}^{2+}]/[\text{Br}_2])$  vs. time. The concentration conditions for each reaction and the average rate constants at  $25.0^\circ$  are summarized in Table I. Although most measurements were made at  $[\text{H}^+] = 1.00 M$ , in the case of  $\text{CrCH}_2\text{Cl}^{2+}$ ,  $[\text{H}^+]$  was

(23) "Eight Peak Index of Mass Spectra," Vol. 2, Mass Spectrometry Data Centre, Reading, England, 1970, Table 3.



**Figure 3.** Pseudo-first-order rate plots for the reaction of  $\text{CrCH}_2\text{I}^{2+}$  and  $\text{Br}_2$  in the presence of added  $\text{Br}^-$ . The upper line corresponds to a run with initial stoichiometric concentrations of  $4.11 \times 10^{-5} F \text{ Br}_2$ ,  $5.6 \times 10^{-4} F \text{ Br}^-$ , and  $1.42 \times 10^{-3} M \text{ CrCH}_2\text{I}^{2+}$  and the lower line to  $1.78 \times 10^{-4} F \text{ Br}_2$ ,  $1.3 \times 10^{-4} F \text{ Br}^-$ , and  $3.37 \times 10^{-3} M \text{ CrCH}_2\text{I}^{2+}$ .

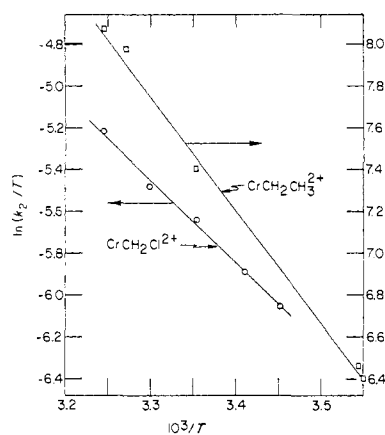
varied in the range 0.036–1.00  $M$ , without effect on the value of  $k_2$ . The medium in which the hydrocarbon complexes were studied consisted of both  $\text{HClO}_4$  and  $\text{LiClO}_4$  at  $\mu = 1.0 M$ , and  $k_2$  was insensitive to this variation in  $[\text{H}^+]$ .

The dichloromethyl complex reacts with  $\text{Br}_2$  only very slowly, if at all. A solution of this chromium complex,  $1.7 \times 10^{-3} M \text{ CrCHCl}_2^{2+}$ , was treated with a tenfold excess of  $\text{Br}_2$ . The spectrum was unchanged over a period of 30 min, giving an estimated upper limit of  $k_2 < 3 \times 10^{-3} M^{-1} \text{ sec}^{-1}$ .

Both the kinetics and stoichiometry of the reaction of  $\text{CrCH}_2\text{I}^{2+}$  with  $\text{Br}_2$  were complicated by the occurrence of a second reaction in the presence of excess bromine. The initial organic product was the expected  $\text{CH}_2\text{I}^+\text{Br}$  as determined mass spectrometrically, but samples taken from the reaction solution at later times gave evidence for  $\text{CH}_2\text{Br}_2$  as well. In the runs with excess bromine, the kinetic traces indicated the occurrence of a slower secondary reaction. To avoid this complication, the kinetic determinations were carried out in the presence of a tenfold excess of  $\text{CrCH}_2\text{I}^{2+}$  and in the presence of a low concentration of  $\text{Br}^-$ .<sup>24</sup> The pseudo-first-order rate plots under these circumstances were linear as shown in Figure 3, because the second reaction (presumably between  $\text{CH}_2\text{I}^+\text{Br}$  and  $\text{Br}_2$ ) was relatively much slower than the first at low  $[\text{Br}_2]$ .

**Activation Parameters.** The dependence of  $k_2$  upon temperature was determined for two complexes,  $\text{CrCH}_2\text{Cl}^{2+}$  and  $\text{CrCH}_2\text{CH}_3^{2+}$ . The data are shown in Figure 4, where each plotted point is the average of the rate constants at the temperature in question. In numerical analysis of the data, however, each individual rate determination was employed. For  $\text{CrCH}_2\text{Cl}^{2+}$

(24) Bromide ions were added to convert a very small part of the  $\text{Br}_2$  to  $\text{Br}_3^-$  ( $K \sim 16 M^{-1}$ ); the  $\text{Br}_2$  concentration was not diminished appreciably by  $\text{Br}_3^-$  formation, but the resulting absorbance of  $\text{Br}_3^-$  at  $\lambda 325 \text{ nm}$  can be used to follow the reaction. The concentration of  $\text{Br}^-$  was low enough that only a very small proportion of the  $\text{Br}_2$  was converted to  $\text{Br}_3^-$ . Also, since  $[\text{Br}^-]$  was large relative to  $[\text{Br}_2]$ ,  $[\text{Br}^-]$  remained nearly constant throughout the run. Similar experiments for  $\text{CrCH}_2\text{Cl}^{2+}$  and  $\text{CrCH}_2\text{Br}^{2+}$  established that in these reactions the addition of  $\text{Br}^-$  was without effect save a slight lowering of the rate by the amount expected if  $\text{Br}_2$  reacts and  $\text{Br}_3^-$  does not.



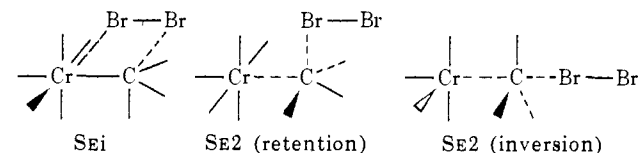
**Figure 4.** Temperature dependences for two reactions, shown as the variation of  $\ln(k_2/T)$  vs.  $1/T$  for  $\text{CrCH}_2\text{Cl}^{2+}$  (circles, left ordinate scale) and  $\text{CrC}_2\text{H}_5^{2+}$  (squares, right ordinate scale).

the activation parameters are  $\Delta H^\ddagger = 33.1 \pm 1.8 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -134 \pm 6 \text{ J mol}^{-1} \text{ }^\circ\text{K}^{-1}$ , with the uncertainty representing one standard deviation. The analogous values for  $\text{CrC}_2\text{H}_5^{2+}$  are  $44.8 \pm 3.3 \text{ kJ mol}^{-1}$  and  $15 \pm 11 \text{ J mol}^{-1} \text{ }^\circ\text{K}^{-1}$ .

### Interpretation and Discussion

**Mechanisms, Steric and Electronic Effects.** The net bromination reactions observed are formally, and perhaps mechanistically as well, electrophilic reactions. The strict adherence to a first-order dependence upon  $[\text{Br}_2]$  rules out an  $\text{S}_\text{E}1$  mechanism in which the rate-determining step would be homolysis of the alkylchromium cation,  $\text{CrR}^{2+} \rightleftharpoons \text{Cr}^{2+} + \text{R}\cdot$ . We consider three bimolecular mechanisms with the transition states depicted in Scheme I respectively  $\text{S}_\text{E}i$ ,  $\text{S}_\text{E}2$  (retention),

**Scheme I.** Possible Bimolecular Mechanisms for Electrophilic Bromination



and  $\text{S}_\text{E}2$  (inversion). The former has a “closed” structure, whereas the latter are open. The  $\text{S}_\text{E}i$  mechanism and other closed four-center configurations are ruled out by the unambiguous test that the products are the separate ions  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and  $\text{Br}^-$  rather than the kinetically stable bromo complex  $(\text{H}_2\text{O})_5\text{CrBr}^{2+}$ . The data appear to be in accord with the  $\text{S}_\text{E}2$  mechanism, but the question of the stereochemistry of the substitution process at the  $\alpha$ -carbon atom will be deferred to a later section.

The reaction is subject to rather pronounced electronic effects from halogen substitution. A marked rate increase is noted for  $\text{CrCH}_3^{2+}$  compared to  $\text{CrCH}_2\text{Cl}^{2+}$  (by a factor of  $2 \times 10^6$ ), for  $\text{CrCH}_2\text{Cl}^{2+}$  compared to  $\text{CrCHCl}_2^{2+}$  (by  $>3 \times 10^3$ ), and for  $\text{CrCH}_2\text{CH}_3^{2+}$  compared to  $\text{CrCH}(\text{Cl})\text{CH}_3^{2+}$  (by  $1.4 \times 10^5$ ). In each of these three examples, the comparison has been made between two complexes in which  $\text{Cl}$  was replaced by  $\text{H}$ , the latter invariably reacting the more rapidly. We argue that this, too, is consistent with the  $\text{S}_\text{E}2$  mechanism because halogen substitution provides a more positive  $\alpha$ -carbon atom, which would be less susceptible to electrophilic attack.

By way of contrast, steric alterations provide a much smaller effect. The replacement of H by the much larger CH<sub>3</sub> lowers the rate relatively little, as seen by comparison of CrCH<sub>3</sub><sup>2+</sup> and CrCH<sub>2</sub>CH<sub>3</sub><sup>2+</sup> (rate decreases by a factor of 4.3). The similar reactivity of the three CrCH<sub>2</sub>X<sup>2+</sup> (X = Cl, Br, I) cations suggests counterbalancing steric and electronic effects.

The comparison between CrCH<sub>2</sub>Cl<sup>2+</sup> and CrCH<sub>2</sub>-CH<sub>3</sub><sup>2+</sup> is an interesting one because the steric bulk of Cl and CH<sub>3</sub> are virtually identical.<sup>25</sup> The latter complex reacts more rapidly by a factor of 4.6 × 10<sup>5</sup>, all of which can be attributed to electronic effects in this particular comparison. One way of expressing this result is to say that the relatively electron-donating methyl group provides a sufficiently higher electron density to the α-carbon atom as to impart a much higher rate. The reason for the significantly higher reactivity of the ethylchromium cation does *not* reside in the relative values of Δ*H*<sup>‡</sup>; the ethyl complex, in fact, has a significantly higher value of Δ*H*<sup>‡</sup>, a difference which would serve to reverse the observed reactivity order. The origin of the large rate difference is found in the very large difference in the Δ*S*<sup>‡</sup> value for these two reactions, the value for CrCH<sub>2</sub>CH<sub>3</sub><sup>2+</sup> being slightly positive and that for CrCH<sub>2</sub>Cl<sup>2+</sup> being a large negative number. The latter may be explained in terms of a relatively reactant-like transition state in which the halogen atom of the coordinated CH<sub>2</sub>Cl group is somewhat solvated by the positive end of the dipole of highly polar aqueous solvent molecules, although the overall 2+ charge on the complex suggests such solvation is relatively slight. In the transition state the effect of the developing charge separation (Cr<sup>3+</sup> and Br<sup>-</sup> are being formed) will serve to provide better solvation for the Cl atom of CH<sub>2</sub>Cl. The increasing interaction of solvent molecules in the transition state as compared to the ground state should provide a considerable entropy decrease. In contrast, this effect should be lacking for CH<sub>2</sub>CH<sub>3</sub>.

**Stereochemistry.** The question of whether these reactions occur with inversion or retention of configuration at the α-carbon is an important and interesting one, certainly one which is central to a complete formulation of the reaction mechanism.

Because the present data refer to kinetic determinations only and direct stereochemical studies have not yet been carried out, we feel that this subject must be approached cautiously and that the following be regarded as an inference of stereochemistry only and not as a nearly conclusive demonstration.

The electrophilic cleavage reactions of molecular halogens are known to occur with both retention and inversion.<sup>7-10</sup> The factors responsible for a given stereochemical course are diverse. The stereochemistry must depend upon whether the transition state is open or closed and upon whether the metal center has readily accessible, empty low-lying orbitals.<sup>9</sup> The availability of the latter would preclude a closed transition state, and favor the SE2 mechanism.

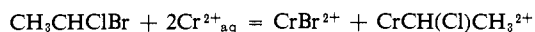
Following the arguments of Jensen and Davis,<sup>3</sup> we shall attempt to infer the stereochemistry by comparing the relative reactivity of several of the alkyl compounds to their reactivity in comparison with SE2 reactions of known stereochemistry: (1) HCl and HgR<sub>2</sub><sup>26</sup> (reten-

tion<sup>27</sup>) and (2) bromine and RSnR'<sub>3</sub>, with R' = neopentyl<sup>2</sup> (inversion<sup>28</sup>).

The rate variations for the SE2 inversion process,<sup>3,29</sup> although not quantitatively the same as shown by the reaction of Br<sub>2</sub> + CrR<sup>2+</sup>, do exhibit the same general rate tendencies, from which we infer that the probable steric course of this reaction is inversion of configuration.

## Experimental Section

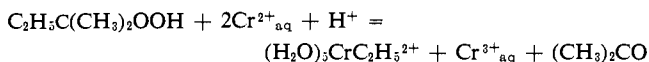
**Materials.** The known haloalkylchromium cations were prepared as described in the literature,<sup>12,13</sup> and the details will be given for a typical complex, CrCH(Cl)CH<sub>3</sub><sup>2+</sup>, the only haloalkyl derivative of those studied here which was not previously known. The reaction was



About 10 ml of water was flushed with a stream of oxygen-free N<sub>2</sub> for about 30 min, after which 0.3 ml of 1-bromo-1-chloroethane and 3 mmol of Cr(ClO<sub>4</sub>)<sub>2</sub> were added. The reaction mixture was stirred vigorously under nitrogen for 1 hr; then the aqueous phase was transferred to a column (50 × 1 cm) of Dowex 50W-X2 cation-exchange resin. The column was rinsed with water; then the chromium complexes were eluted with 0.5 *F* HClO<sub>4</sub>. The green CrBr<sup>2+</sup> elutes first followed by the reddish CrCH(Cl)CH<sub>3</sub><sup>2+</sup>; the best fractions of the latter were retained. The complex had an absorption spectrum with maxima at λ 530 nm (ε 16.4 M<sup>-1</sup> cm<sup>-1</sup>), 394 (172), and 270 (1990).

The methyl complex was prepared by the reaction of *tert*-butyl hydroperoxide and Cr(II),<sup>14,15,19</sup> but the desired methylchromium complex was eluted from Dowex 50W-X2 resin with 0.5 *F* LiClO<sub>4</sub>, rather than with HClO<sub>4</sub>.<sup>16,30</sup>

The ethylchromium cation was prepared from the reaction of *tert*-amyl hydroperoxide and Cr(II)



An aqueous solution of the hydroperoxide was prepared by neutralizing the crystalline sodium hydroperoxide<sup>31</sup> by slow, dropwise addition of cold 70% perchloric acid. Typically 15 ml of the neutral aqueous solution of *tert*-amyl hydroperoxide was flushed thoroughly with nitrogen and then treated with 8 ml of 1 *F* chromium(II) perchlorate; the reaction appeared to be complete within seconds. The solution was placed on a column of Dowex 50W-X2 (50 × 1 cm) cooled by circulating water at 0° through a jacket. The column was washed with 50 ml of 0.1 *F* LiClO<sub>4</sub>, and the desired ethylchromium complex was eluted with 0.5 *F* LiClO<sub>4</sub>. The yellow complex (H<sub>2</sub>O)<sub>5</sub>CrC<sub>2</sub>H<sub>5</sub><sup>2+</sup> elutes just before the blue-purple Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>. The absorption spectrum of CrC<sub>2</sub>H<sub>5</sub><sup>2+</sup> has maxima at λ 562 (10.3), 394 (258), and 275 (1440). The same complex isolated from the reaction of ethylcobaloxime and Cr<sup>2+</sup> as in eq 2 had maxima at 394 (266) and 275 (1620); a smaller maximum was

(26) R. E. Dessy, G. F. Reynolds, and J.-Y. Kim, *J. Amer. Chem. Soc.*, **81**, 2683 (1959).

(27) L. H. Gale, J. Landgrebe, and F. R. Jensen, *Chem. Ind. (London)*, 118 (1960).

(28) The kinetics and stereochemistry have also been examined in acetic acid.<sup>28</sup> The conclusion reached by these workers was that the reaction of the cyclopropyl derivative proceeds with retention of configuration. Other workers, however, have found that the reaction of Sn(CH<sub>3</sub>)<sub>2</sub>(1-methyl-2,2-diphenylcyclopropyl) with Br<sub>2</sub> is accompanied by racemization.<sup>29</sup> Stereochemical generalizations based on results applicable to cyclopropyl systems may not be correct, however, in view of the very high resistance with which cyclopropyl derivatives undergo inversion of configuration.<sup>3</sup>

(29) K. Sisido, T. Miyanisi, and T. Isida, *J. Organometal. Chem.*, **23**, 117 (1970).

(30) Because CrCH<sub>3</sub><sup>2+</sup> undergoes rather rapid decomposition at high [H<sup>+</sup>],<sup>14</sup> elution with HClO<sub>4</sub> as employed in the previous isolation of this complex<sup>15</sup> yields a product already partially decomposed. Consequently the LiClO<sub>4</sub>-eluted material used here has molar absorptivities somewhat higher than those reported earlier:<sup>16</sup> λ<sub>max</sub> 550 nm (ε 12.0 M<sup>-1</sup> cm<sup>-1</sup>), 392 (243), and 258 (2680) as compared to 550 (9.6), 392 (196), and 258 (2160).<sup>15</sup>

(31) N. A. Milas and D. M. Sugenor, *J. Amer. Chem. Soc.*, **68**, 205 (1946).

(25) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, New York, N. Y., 1960, p 260.

also seen at  $\sim 525$  nm, but the position of this weak absorption is difficult to locate.

A similar procedure was used for the neopentylchromium cation, preparing the hydroperoxide from 2,4,4-trimethyl-2-pentanol and hydrogen peroxide. The alcohol was prepared from 2,4,4-trimethyl-2-pentanone and  $\text{CH}_3\text{MgBr}$ , followed by hydrolysis in an ice-sulfuric acid mixture. The neopentylchromium complex was isolated as described for the ethyl derivative; absorption maxima were seen at 387 (204) and 289 (840).

Solutions of  $\text{Cr}(\text{ClO}_4)_2$  were prepared under nitrogen by reduction of  $\text{Cr}(\text{ClO}_4)_3$  with amalgamated zinc.

The chromium concentrations were analyzed spectrophotometrically after oxidation to chromate in alkaline peroxide; at  $\lambda$  372 nm,  $\epsilon = 4830 \text{ M}^{-1} \text{ cm}^{-1}$ . The concentration of  $\text{Br}_2$  in stock solutions was determined spectrophotometrically and by volumetric analysis. The molar absorptivity of  $\text{Br}_2$  at 452 nm is

$103 \text{ M}^{-1} \text{ cm}^{-1}$  and provides a convenient analysis.<sup>32</sup> Solutions were also analyzed by adding aliquots to an excess of sodium iodide and titrating the liberated iodine with sodium thiosulfate.

**Kinetic and Stoichiometric Measurements.** The slower reactions were followed using a Cary Model 12 or 14 spectrophotometer, the latter equipped with a 0–0.1 absorbance scale. The faster reactions were studied using a Durrum stopped-flow spectrophotometer.

The mass spectra<sup>33</sup> of the volatile products were obtained on samples from experiments carried out in which the reactants were contained in a two-bulb assembly.

(32) M. R. Jaffe, D. P. Fay, M. Cefola, and N. Sutin, *J. Amer. Chem. Soc.*, **93**, 2878 (1971).

(33) We are indebted to Mr. G. D. Flesch of the Ames Laboratory for his help in making these measurements.

## Coordination Chemistry of Sodium and Potassium Complexation with Macrocyclic Polyethers

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**Abstract:** Isolation and paper chromatographic solution studies of  $\text{MX}$  (where  $\text{M}^+ = \text{Na}^+$  or  $\text{K}^+$ ;  $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , or  $\text{NCS}^-$ ) complexes with macrocyclic polyethers (general abbreviation R), benzo-15-crown-5 (I), dibenzo-18-crown-6 (II), dibenzo-24-crown-8 (III), and dibenzo-30-crown-10 (IV), were carried out. Competitive isolation of R–MX complexes from ethanol has been investigated for  $\text{X}^- = \text{I}^-$  and  $\text{NCS}^-$ . Based essentially on information from ir spectra and X-ray molecular structure, the structures of most of these complexes are discussed. Isolation of the R–ML (where  $\text{L}^-$  is an organic anion obtained by the deprotonation of 2-nitrophenol (H1), 4-nitrophenol (H2), 2,4-dinitrophenol (H3), 2,4,6-trinitrophenol (H4), 2-hydroxybenzoic acid (H6), 2,6-dihydroxybenzoic acid (H6), 2-nitrobenzoic acid (H7), or 2-aminobenzoic acid (H8)) complexes is also reported. Potassium complexes of the types  $[(\text{I})_2\text{-K}]^+\text{L}^-$ ,  $[(\text{I})_2\text{-K}]^+[\text{L},\text{aq}]^-$ ,  $[(\text{I})_2\text{-K}]^+[\text{L},\text{HL}]^-$ , and  $[(\text{I})_2\text{-K}]^+[\text{L},(\text{HL})_2]^-$  are isolated. The relevance of such conjugated anions to natural systems is discussed.

Macrocyclic polyethers (Figure 1, general abbreviation R) are polydentate ligands of flexible conformation which interact with alkali metal ions to form lipid-soluble cations.<sup>1,2</sup> The metal–ligand interactions are of the ion-dipole type and basically controlled by the fit of the metal ion into the “hole” of R. Different workers have measured these forces in diverse media spectrophotometrically,<sup>3–5</sup> calorimetrically,<sup>6</sup> and electrometrically.<sup>7,8</sup>

From different R and alkali metal salts (MX), 1:1, 3:2, and 2:1 (R:MX) complexes have been isolated using stoichiometric and excess R,<sup>1,2</sup> and single crystal X-ray structural analysis in many cases has been accomplished by Truter, *et al.*,<sup>9–13</sup> Dunitz, *et al.*,<sup>14</sup> and Groth.<sup>15</sup>

(1) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

(2) C. J. Pedersen, *J. Amer. Chem. Soc.*, **92**, 386 (1970).

(3) P. B. Chock, *Proc. Nat. Acad. Sci. U. S. A.*, **69**, 1939 (1972).

(4) K. H. Wong, G. Konizer, and J. Smid, *J. Amer. Chem. Soc.*, **92**, 666 (1970).

(5) A. T. Tsatsas, R. W. Stearns, and M. R. William, *J. Amer. Chem. Soc.*, **94**, 5247 (1972).

(6) R. M. Izatt, J. H. Rattig, D. P. Nelson, B. L. Heymore, and J. J. Christensen, *Science*, **164**, 443 (1969); *J. Amer. Chem. Soc.*, **93**, 1619 (1971).

(7) S. G. A. McLaughlin, G. Szabo, G. Eisenman, and S. Ciani, Abstracts, 14th Annual Meeting of the Biophysical Society, Baltimore, Md., Feb 1970.

(8) H. K. Frensdorff, *J. Amer. Chem. Soc.*, **93**, 600 (1971).

(9) M. A. Bush and M. R. Truter, *Chem. Commun.*, 1439 (1970).

(10) D. E. Fenton, M. Mercer, and M. R. Truter, *BBA (Biochim. Biophys. Acta) Chem. Commun.*, **48**, 10 (1972).

The late Professor Sir Ronald Nyholm, however, realized the importance of detailed chemical investigations of R–MX complexes to see whether by using R as the models for the transport mediators of the cell membrane it is possible to find out the role played by the coordination chemistry of sodium and potassium in the preferential uptake of potassium over sodium in natural systems. This led us to undertake the preliminary isolation studies<sup>16</sup> of the complexes using R of different size and flexibility (I–IV, Figure 1) with MX ( $\text{M}^+ = \text{Na}^+$  or  $\text{K}^+$  and  $\text{X}^- = \text{Br}^-$ ,  $\text{I}^-$ , or  $\text{CNS}^-$ ) and ML (where  $\text{L}^-$  is a chelating organic anion obtained from the deprotonation of any of 2-nitrophenol (H1), 2,4-dinitrophenol (H3), 2-hydroxybenzoic acid (H5), and 2-nitrobenzoic acid (H7)).

In the present investigations the range of experiments has been extended to include  $\text{Cl}^-$  for  $\text{X}^-$  and anions of 4-nitrophenol (H2), 2,4,6-trinitrophenol (H4), 2,6-dihydroxybenzoic acid (H6), and 2-aminobenzoic acid (H8) for  $\text{L}^-$ . Synthesis of complexes from media con-

(11) D. E. Fenton, M. Mercer, N. S. Poonia, and M. R. Truter, *J. Chem. Soc., Chem. Commun.*, 66 (1972).

(12) P. R. Mallinson and M. R. Truter, *J. Chem. Soc.*, 1818 (1972).

(13) D. Bright and M. R. Truter, *J. Chem. Soc.*, 1544 (1970).

(14) Quoted by M. R. Truter, *Struct. Bonding (Berlin)*, 1973.

(15) P. Groth, *Acta Chem. Scand.*, **25**, 3189 (1971).

(16) N. S. Poonia and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, 2062 (1973).