Inorg. Chem. **1980**, *19*, 233-235

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Alkyl(1,4,8,12-tetraazacyclopentadecane)chromium(III) Complexes: Kinetics of Reactions with Mercury(II) and Methylmercury(II) Ions[1]

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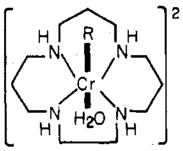
Received May 17, 1979

Kinetic data have been obtained on the reactions of R-Cr([15]aneN$_4$)(H$_2$O)$^{2+}$ complexes with mercury (II) and methylmercury(II) ions in aqueous perchloric acid. The reactions all follow a second-order rate expression, first order with respect to organochromium concentration and first order in the concentration of the mercury (II) electrophile. The reaction rates vary widely with the structure of R, decreasing sharply with increased steric bulk. The rates are also some 10^2–10^3 higher for Hg^{2+} than for CH_3Hg^+. The reactions are proposed to proceed by the S_E2 mechanism.

Introduction

A new class of σ-bonded alkyls of chromium(III) was recently described,[2] complexes in which the metal is bound in the planar tetradentate macrocycle 1,4,8,12-tetraazacyclopentadecane, also known as [15]aneN$_4$. These cationic complexes have six-coordinate trans structures, the position trans to the alkyl group being very labile and, generally, occupied by a molecule of water from the solvent.



[R-Cr([15]aneN$_4$)(H$_2$O)]$^{2+}$

These complexes react with electrophiles, including mercury(II) ion, Hg^{2+}, organomercury(II) ions, RHg^+, and molecular halogens. In this respect they are similar to other metal alkyls including the families of compounds such as $(H_2O)_5Cr\text{-}R^{2+}$ and R-Co^{III}(N$_4$ chelate)B. The reactions occurring with mercury(II) compounds are

$$\text{R-Cr([15]aneN}_4\text{)H}_2\text{O}^{2+} \xrightarrow{Hg^{2+}} \text{RHg}^+ + (\text{H}_2\text{O})_2\text{Cr([15]aneN}_4)^{3+} \quad (1)$$

$$\text{R-Cr([15]aneN}_4\text{)H}_2\text{O}^{2+} \xrightarrow{CH_3Hg^+} \text{CH}_3\text{HgR} + (\text{H}_2\text{O})_2\text{Cr([15]aneN}_4)^{3+} \quad (2)$$

A systematic kinetic study of electrophilic dealkylation reactions of organochromium compounds has only recently been completed for the pentaaquo series.[3] It is of some interest to explore the generality of the trends established in that study, to provide comparison of reactivity between electrophilic cleavage reactions of R-Cr^{III} and the well-studied R-Co^{III} analogues[4,5] and to determine the nature and magnitude of any effects attributable to the chelate structure. We have thus undertaken a study of the kinetics of reaction of this new series of compounds with Hg^{2+} and CH_3Hg^+, the processes shown in eq 1 and 2.

In the present study the R-Cr([15]aneN$_4$)H$_2$O^{2+} cations investigated included species in which R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, i-C_3H_7, c-C_6H_{11}, 1-adamantyl, and benzyl. The rates of reaction with Hg^{2+} have been measured at 25 °C for all R's listed and at other temperatures for many of these R groups, along with rates for R = CH_3, C_2H_5, and CH_2Ph with CH_3Hg^+ as well.

Experimental Section

Materials. The organochromium complexes were prepared by reaction[2] of $(H_2O)_2Cr^{II}$([15]aneN$_4$)$^{2+}$ with a large excess of the desired alkyl bromide or iodide in weakly acidic solution, typically pH 5, under a strictly oxygen-free atmosphere of purified nitrogen. In a typical preparation 0.10 g (0.47 mmol) of [15]aneN$_4$ was dissolved in ~10 cm^3 of a solution and deaerated with Cr^{2+}-scrubbed nitrogen for at least 30 min. A slight deficiency of chromium(II) chloride[6] solution, 0.8 cm^3 of a 0.54 M solution, was added. Several minutes are required for complete conversion to the royal purple of the chromium(II) chelate, following which the neat deaerated alkyl halide, ~1 cm^3 (~10 mmol), was injected by syringe. The solution was vigorously stirred under nitrogen for some 20 min (or longer, depending on the particular halide used and its rate of reaction[2]). The solution was extracted with two 15-cm^3 portions of carbon tetrachloride or ether to remove unreacted alkyl halide and placed on a column of Sephadex C-25 cation exchange resin in the Na^+ form. The column, 8 × 1.6 cm, was equipped with a jacket through which water at 0 °C was circulated. The main solution species at pH 5 are Br(or I)Cr([15]aneN$_4$)(OH)$^+$ and R-Cr([15]aneN$_4$)(H$_2$O)$^{2+}$, with lesser and variable amounts of [(H$_2$O)Cr([15]aneN$_4$)(OH)$^{2+}$]. (The low temperature is needed not to stabilize the organochromium complex but to retard aquation of the halide complex and thus assist in the separations.) The column is eluted with sodium perchlorate at pH ~5 to avoid protonation of the halo-hydroxo complex which hinders its separation from the desired dipositive organochromium species. The halide complex is eluted first with 0.1 M sodium perchlorate, and then the organochromium cation with 0.2–0.4 M sodium perchlorate. These solutions can be stored, if desired, for several months at −10 °C. For air-sensitive complexes such as the mildly sensitive secondary alkyls and the more air-sensitive benzyl, the column and eluents were deaerated and the products collected and stored under nitrogen.

The 1-adamantyl complex was prepared by this method except that, for reasons of solubility, 4:1 v/v THF–H$_2$O was used as solvent and the reaction run for 40 min. The THF was removed by flash evaporation at room temperature and the complex chromatographed as usual after filtration of the precipitated excess 1-adamantyl bromide.

Solutions of mercury(II) perchlorate were prepared by boiling the oxide in a slight excess of perchloric acid or from the commercially available hydrated salt. *Caution*: One solution prepared from the oxide, orginally passed through a retentive paper filter, deposited a very small quantity of an unidentified, fine white residue over a period of some months. This residue (but not the solution) was very shock sensitive, and detonated violently as it was being rinsed with water from the reagent bottle from which the solution had just been decanted. Solutions of methylmercury(II) ion were prepared by dissolving methylmercuric acetate in dilute perchloric acid. These solutions were standardized as described previously.[3]

Other reagents and analyses have been described.[3] The organochromium complexes have characteristic absorption spectra,[1,2] which were used for analysis of the solutions as well as for monitoring the progress of the reactions.

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Table I. Summary of Kinetic Data[a,b] for Reactions of Mercury(II) Ion with R-Cr([15]aneN$_4$)(H$_2$O^{2+})

R	10^3[Hg^{2+}]/M	k_{Hg}/M^{-1} s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J mol^{-1} K^{-1}
$-CH_3$	0.047	$(3.1 \pm 0.2) \times 10^6$		
$-CH_2CH_3$	1.2–11.7	$(2.53 \pm 0.03) \times 10^3$	30.2 ± 1.2	-77 ± 4
$-n\text{-}C_3H_7$	1.2–11.7	$(8.21 \pm 0.04) \times 10^1$	48.8 ± 1.5	-45 ± 5
$-n\text{-}C_4H_9$	2.3–11.7	$(4.88 \pm 0.17) \times 10^1$	33.5 ± 2.1	-100 ± 7
$-n\text{-}C_5H_{11}$	4.5–11.7	$(4.33 \pm 0.20) \times 10^1$	29.7 ± 1.2	-114 ± 4
$-CH_2C_6H_5$	1.17–11.7	$(1.14 \pm 0.03) \times 10^3$	33.4 ± 1.6	-75 ± 5
$-i\text{-}C_3H_7$[c]	216–432	$(4.3 \pm 0.4) \times 10^{-3}$		
$-c\text{-}C_6H_{11}$[c]	216–432	$(1.6 \pm 0.4) \times 10^{-3}$		
-1-adamantyl[c]	216–432	$(3.1 \pm 0.1) \times 10^{-3}$		

[a] 25.0 °C. [b] At $\mu = 0.50$ M, [H$^+$] = 0.25 M, except as noted. [c] [H$^+$] = 0.17 M, $\mu = 1.46$ M, maintained with Ba(ClO$_4$)$_2$.

Kinetics. The rates of faster reactions were determined by stopped-flow spectrophotometry using a Durrum D110 instrument equipped with a Kel-F mixing block and a 2-cm optical path. Slower reactions were monitored by using a Cary Model 14 spectrophotometer.

The conditions for the kinetics determinations were a temperature of 25.0 °C and 0.25 M perchloric acid; ionic strength was adjusted to 0.50 M by addition of lithium perchlorate. (These are the same experimental conditions as in the earlier work[3] concerning (H$_2$O)$_5$Cr–R^{2+}). For very slow reactions a higher concentration of mercury(II) was required, and the ionic strength, set at 1.46 M by the highest value of [Hg^{2+}], was maintained by addition of barium perchlorate.

Pseudo-first-order conditions were realized by use of a large excess of the mercury(II) reagent. Rate constants were evaluated from the stopped-flow data using a PDP-15 computer interfaced to a Biomation transient recorder which stored 1000 points from each kinetic run. The program[7] is one in which the rate constant and the final absorbance reading were adjusted to their optimal least-squares values. Kinetic data from slower reactions were treated by graphical methods. Plots of log ($D_t - D_\infty$) against time were used, where D_t and D_∞ are the respective absorbance readings at time t and at completion of the reaction. In some cases the reaction was followed to completion to obtain D_∞; in others a value was obtained by extrapolation using the Kezdy–Swinbourne method.[8]

Results

The reactions under investigation and their stoichiometry had previously been used[2] as one means of characterizing the new group of organochromium(III) complexes, R–Cr([15]aneN$_4$)(H$_2$O)$^{2+}$. In addition to the determinations earlier[2] additional spectrophotometric titrations of CH$_3$Cr([15]aneN$_4$)(H$_2$O)$^{2+}$ with Hg^{2+} and with CH$_3$Hg$^+$ were run. The "break point" in the former case occurs at a ratio of 1:1.96, consistent with the successive occurrence of reactions 1 and 2. In the titration with CH$_3$Hg$^+$ the break point occurs at 1:0.9, consistent with reaction 2. Other results have been summarized.[2]

The kinetic data for reactions of Hg^{2+} with R–Cr([15]aneN$_4$)(H$_2$O)$^{2+}$ complexes were obtained with a large excess of Hg^{2+}. Since the rate constants for Hg^{2+} reactions are generally ≥10^2 times greater than for CH$_3$Hg$^+$ reactions, only reaction 1 occurs to an appreciable extent under these conditions. Consistent with this, the kinetic data in each run followed pseudo-first-order kinetics, and the rate constants so obtained (designated k_{obs}) were directly proportional to the mean concentration of mercury(II) ion. The rate expression is thus as shown in eq 3. Kinetic data for reactions run at 25.0 °C are summarized in Table I. Several of the reactions were

$$-d[R\text{–}Cr([15]aneN_4)(H_2O)^{2+}]/dt = k_{Hg}[Hg^{2+}][R\text{–}Cr([15]aneN_4)(H_2O)^{2+}] \quad (3)$$

also studied at other temperatures, and the variations of k_{Hg} with temperature were correlated by the Eyring equation of activated complex theory. The resulting values of the activation parameters $\Delta H^‡$ and $\Delta S^‡$ are also given in Table I.

Table II. Summary of Kinetic Data[a] for Reactions of Methylmercury(II) Ion with R-Cr([15]aneN$_4$)(H$_2$O)$^{2+}$

R	10^3[CH$_3$Hg$^+$]/M	k_{CH_3Hg}/M^{-1} s^{-1}
$-CH_3$	1.04–8.93	$(1.63 \pm 0.02) \times 10^3$
$-CH_2CH_3$	0.94–7.43	9.9 ± 0.4
$-CH_2CH_3$[b]		8.2[b]
$-CH_2C_6H_5$	0.94–6.57	5.2 ± 0.1

[a] At 25.0 °C, [H$^+$] = 0.250 M, $\mu = 0.50$ M. [b] The reactant electrophile is CH$_3$CH$_2$Hg$^+$.

The rate of reaction of the methylmercury(II) ion with a given organochromium complex is much lower than that of mercury(II) ion. In fact, the rates are so inconveniently low in most instances that only a limited number of compounds were examined. Again, the kinetic data were obtained under pseudo-first-order conditions. Variation of k_{obsd} with [CH$_3$Hg$^+$] was found to be in accord with the rate expression of eq 4, and the data are summarized in Table II.

$$-d[R\text{–}Cr([15]aneN_4)(H_2O)^{2+}]/dt = k_{CH_3Hg}[CH_3Hg^+][R\text{–}Cr([15]aneN_4)(H_2O)^{2+}] \quad (4)$$

Interpretation and Discussion

In earlier publications concerning electrophilic dealkylation, we have examined some of the general features of these reactions.[3,4] It thus suffices here to summarize our interpretations of the findings on these new systems. The second-order rate laws of eq 3 and 4 lend support to bimolecular electrophilic substitution (S$_E$2 mechanism). As was also found with members of the series (H$_2$O)$_5$Cr–R^{2+}, CH$_3$Hg$^+$ reacts some 10^2–10^3 times more slowly than Hg^{2+} with a given organochromium complex. This is typical of other electrophilic reactions of these species and can be taken as but a measure of the relative electrophilic strengths of Hg^{2+} and CH$_3$Hg$^+$.

In one run in which CH$_3$CH$_2$Hg$^+$ was used in place of CH$_3$Hg$^+$ the rate of reaction was very nearly the same, 8.2 vs. 9.9 M^{-1} s^{-1} (Table II). This confirms our earlier findings[3] that the rates of reactions of various R′Hg$^+$ species with (H$_2$O)$_5$Cr–CH$_2$C$_6$H$_5$$^{2+}$ and (H$_2$O)$_5$Cr–CH$_3$$^{2+}$ are not greatly affected by a change in the reactant species R′Hg$^+$.

The values of k_{Hg} (Table I) are markedly dependent on the nature of the alkyl group, R. In all, the rates span a range of 10^9. Primary alkyls as a group react much more readily than the secondary alkyls. The exact magnitude of the effect is not simply given, as it depends on the specific identity of the group R; also, different ionic strengths were used for the two sets of compounds. This striking difference in rate, some 10^4–10^9 rate reduction from primary to secondary alkyls, is also typical of the effects seen in related reactions of Hg^{2+}, those with (H$_2$O)$_4$Cr–R^{2+} [3] and with R–Co(dmgH)$_2$(H$_2$O).[4,9] Moreover, they are similar to the corresponding changes in

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the reactions[4] of $Br_2(aq)$ with $(H_2O)_5Cr{-}R^{2+}$.

Only for the alkylcobaloximes has a stereochemical determination proved feasible,[4a] since it is only here that a chiral organometallic complex can be made. We believe that in the chromium complexes the reaction probably proceeds with the same stereochemistry, namely, inversion of configuration at the α-carbon; aside from similar changes in reactivity with changes in R, however, direct evidence is lacking.

The 1-adamantyl complex, which is one of the more stable of the present group toward acidolysis or other decomposition, also reacts with mercury(II) ion. Its rate constant is comparable to that found for the secondary alkyls, yet it cannot react by an inversion process. It is thus questionable whether the 1-adamantyl complex follows the same mechanism; its rate is directly proportional to $[Hg^{2+}]$, however, and if direct attack at the α-carbon occurs, the process cannot involve inversion.

Another trend apparent from Table I is the marked change in rate among the primary alkyls. Models show that the α-carbon becomes more shielded with chain length, at least up to some three or four carbon atoms; beyond that, little increased shielding of the chromium–carbon bond toward attack by mercury(II) ion is noted.

The activation parameters given in Table I show rather wide ranges, considering the relatively narrow spread in values of k_{Hg} at 25 °C. The differences are well beyond experimental error, and it may be that variations in $\Delta S^{\ddagger}$ arise from different degrees of solvent participation in the transition state and not from any fundamental changes of mechanism.

It is of interest to compare the reactivity of $R{-}Cr([15]aneN_4)(H_2O)^{2+}$ and $(H_2O)_5Cr{-}R^{2+}$ [3] toward Hg^{2+}. At least two factors appear to govern the differences. First, the saturated macrocyclic ligand adds considerable steric bulk around the chromium–carbon bond, the site of reactivity. This steric bulk could cause a lowering of rate if the mechanism does involve, as suggested, attack of Hg^{2+} at the α-carbon leading to inversion of configuration at this carbon. In addition, replacement of four water molecules by the stronger-field nitrogen donor ligand will serve to increase the electron density on chromium and, in turn, on the α-carbon atom of R. These factors act in opposite direction, the former expected to lower the reactivity of the 15-aneN$_4$ complex, the latter to increase it, relative to the aquo complex. The data[3] actually show that the pentaaquo complex is always the more rapidly reacting, by factors ranging from ~ 3 ($R = CH_3$) to $\sim 4 \times 10^2$ ($R = n\text{-}C_3H_7$ and $i\text{-}C_3H_7$). We conclude that a compromise between the opposing influences is at work, with the steric factor always the dominant consideration, the more so the greater the further steric barrier posed by the group R.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Science, Chemical Sciences Division.

Registry No. $CH_3Cr([15]aneN_4)(H_2O)^{2+}$, 70832-96-1; $CH_3CH_2Cr([15]aneN_4)(H_2O)^{2+}$, 70832-97-2; $n\text{-}C_3H_7Cr([15]aneN_4)(H_2O)^{2+}$, 70832-98-3; $n\text{-}C_4H_9Cr([15]aneN_4)(H_2O)^{2+}$, 70832-99-4; $n\text{-}C_5H_{11}Cr([15]aneN_4)(H_2O)^{2+}$, 71818-69-4; $C_6H_5CH_2Cr([15]aneN_4)(H_2O)^{2+}$, 70833-03-3; $i\text{-}C_3H_7Cr([15]aneN_4)(H_2O)^{2+}$, 70833-00-0; $c\text{-}C_6H_{11}Cr([15]aneN_4)(H_2O)^{2+}$, 70833-01-1; (1-adamantyl)$Cr([15]aneN_4)(H_2O)^{2+}$, 70833-02-2; Hg^{2+}, 14302-87-5; CH_3Hg^+, 22967-92-6; $(H_2O)_2Cr([15]aneN_4)^{3+}$, 70832-95-0.

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Preparation, Reactions, and Reaction Mechanisms of a Family of Difunctional Complexes of Bis(benzylchromium) Cations[1]

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Received May 8, 1979

Six new dimetallic organochromium cations, each containing two benzylchromium-like units per molecule, were prepared from selected dibromides and chromium(II). These tetrapositive complexes (and certain related monochromium analogues) were isolated and purified by ion-exchange chromatography in aqueous solution. The complexes were characterized by their UV–visible absorption spectra and by the stoichiometry and composition of the products obtained from reactions with chloropentaamminecobalt(III) ion, with sodium carbonate, and with mercury(II) chloride. These complexes react with oxidizing agents such as iron(III) ion, copper(II) ion, and halopentaamminecobalt(III) ion in reactions that are first order in the concentration of organochromium ion, but independent of the identity as well as the concentration of oxidizing agent (except for iron(III) ion which shows, for some complexes, a small contribution of an Fe^{3+}-dependent pathway). These data, and comparisons with mononuclear, substituted benzylchromium cations, suggest that the rate-limiting step is unimolecular homolysis of a chromium–carbon bond. The dichromium cations produce only polymer. The monochromium cation $[p\text{-}CrCH_2C_6H_4CH_2OH]^{2+}$ also polymerizes upon oxidation and has $k_h = 1.66 \times 10^{-3}\ s^{-1}$ at 25 °C, consistent with other rates and leading to a Hammett substituent constant for $p\text{-}CH_2OH$ of $\sigma_p = +0.19$. The mechanism of homolysis and of the polymerization initiation step are discussed in light of the kinetic data which give no evidence of a biphasic or stepwise loss of the benzylchromium absorption bands used to monitor the reaction rate.

Introduction

Benzylic halides are sufficiently reactive toward chromium(II) that a halogen abstraction reaction occurs in aqueous or semiaqueous media. The radical so formed combines with a second chromium(II) ion in a rapid reaction, leading to the formation of the cationic organometallic benzyl(pentaaquo)chromium(III) ion.[2,3] These reactions occur as follows (omitting coordinated water or other solvent molecules; all the chromium ions are six-coordinate):

$$PhCH_2X + Cr^{2+} \xrightarrow{k_1} CrBr^{2+} + PhCH_2\cdot \quad (1)$$

$$PhCH_2\cdot + Cr^{2+} \xrightarrow{\text{fast}} CrCH_2Ph^{2+} \quad (2)$$

$$\text{net}\quad PhCH_2X + 2Cr^{2+} = CrBr^{2+} + CrCH_2Ph^{2+} \quad (3)$$

By analogy, if the benzylic halide were one containing two aralkyl halide ($ArCH_2X$) functional groups, it is to be expected that a tetrapositive dichromium complex will be formed provided an excess of chromium(II) is used in the reaction. For the sake of a brief notation for a number of such complexes,

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