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Stoichiometry and Kinetics of Aquation of $(H_2O)_5CrCH_2X^{2+}$ Ions (X = Cl, Br, I) in Acidic Solutions

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Mechanistic studies of the aquation of pentaaquo(halomethyl)chromium(III) ions (halo: chloro, bromo, iodo) have been made at 1.0 M ionic strength ($NaClO_4$–$HClO_4$) solution with hydrogen ion concentrations of 0.02–1.0 M in the absence of oxygen and light. The products of aquation of the chloro and bromo complexes are $Cr(OH_2)_6^{3+}$, halide ion, and methanol. Iodomethane is a major, if not the only, direct organic product from the aquation of $(H_2O)_5CrCH_2I^{2+}$ ion. The observed rates all follow the equation $-d \ln [\text{complex}]/dt = k[\text{complex}]$ where, at 298 K, $k = 5.6 \times 10^{-7}$ s^{-1} ($\Delta H^{\ddagger} = 26.1$ kcal/mol, $\Delta S^{\ddagger} = 8.6$ eu) for $CrCH_2Cl^{2+}$, $k = 2.4 \times 10^{-6}$ s^{-1} ($\Delta H^{\ddagger} = 24.3$ kcal/mol, $\Delta S^{\ddagger} = -2.7$ eu) for $CrCH_2Br^{2+}$, and $k = 4.5 \times 10^{-7}$ ($\Delta H^{\ddagger} = 25.4$ kcal/mol, $\Delta S^{\ddagger} = -2.4$ eu) for $CrCH_2I^{2+}$. A mechanism involving a carbanion-type transition state is proposed for $CrCH_2I^{2+}$. A mechanism for the chloro and bromo complexes is proposed which involves formation of a methanol–chromium intermediate, $(H_2O)_5CrCH_2OH^{2+}$, by eliminating HX after an S_N2 attack of H_2O at the carbon.

Introduction

The first aquoorganochromium(III) species containing a chromium–carbon σ bond was isolated by Anet and Leblanc.[1] They reported that the reduction of benzyl chloride by chromium(II) perchlorate solutions gave $(H_2O)_5CrCH_2C_6H_5^{2+}$ as one of the products. Since this first work, a number of similar organochromium(III) compounds have been reported.[2,3]

The great preponderance of work in organo–transition metal chemistry has centered mainly on compounds or complexes which contain π-bonding olefins, acetylenes, and cyclopentadienyls, whose other ligands usually include CO or phosphines, and whose metal has a relatively low valency and often an unusual configuration. By contrast, the aquoorganochromium(III) complexes are considered to contain σ-bonded carbanions, the other ligands are water, the metal has a relatively high valency (3+), and the complexes have a regular octahedral stereochemistry. These are, of course, the properties that enable them to be treated as coordination complexes. The development of a better understanding of the chemistry of pentaaquoorganochromium(III) complexes can therefore serve the useful purpose of helping link together organometallic chemistry and classical coordination chemistry. σ bonds between transition metals and carbon are often very reactive, and hydrolysis reactions are especially rapid. In contrast, the complexes of this study, $(H_2O)_5CrCH_2X^{2+}$ (X = Cl, Br, I), and also the complexes, $(H_2O)_5CrCHX_2^{2+}$ (X = Cl, Br, I), described in the following paper[4] are quite inert in acidic aqueous media. Typical half-lives for aquation of these complexes in 1 M $HClO_4$ solution at 25 °C range from 12 to 20 days.

Several mechanistic studies regarding decomposition of σ-bonded aquoorganochromium(III) species in acidic media have been reported, indicating that reaction can occur by different pathways depending on the organic moiety bonded to chromium metal. Homolytic cleavage leading to Cr^{2+} and a radical has been proposed[5] for the hydrolysis of (4-pyridylmethyl)pentaaquochromium(III) ion. An H_2O-assisted heterolytic cleavage of the Cr–C bond has been suggested in species containing aliphatic anions derived from simple alcohols and ethers.[6] The final organic products have an H in place of Cr(III). A solvent-assisted mechanism was also proposed[7] for decomposition of $(H_2O)_5CrCF_3^{2+}$, in which Cr–C and C–F bonds were broken in a concerted fashion. The difluorocarbenoid intermediates thus formed react rapidly to form carbon monoxide which is the only organic product observed. It is perhaps surprising that the strong C–F bond is being broken in the transition state. The data of the present study of $(H_2O)_5CrCH_2X^{2+}$ ions also seem to be best interpreted as indicating that the rate-determining step of decomposition involves substitution of the halogen by water rather than cleavage of the Cr–C bond.

Experimental Section

Reagents. Reagent grade dichloro-, dibromo-, and diiodomethanes were used without further purification, as was reagent grade perchloric acid. $NaClO_4$ was prepared by the neutralization of Na_2CO_3 (Baker Analyzed reagent) with $HClO_4$. Stock solutions of $NaClO_4$ were analyzed by passing an aliquot through a cation-exchange column in the H^+ form and titrating the liberated acid with standardized base. Cr(II) solutions were prepared by dissolving electrolytic grade Cr metal (>99.999% pure, Apache Chemicals) in deoxygenated $HClO_4$.[8] All solutions were prepared by using H_2O which had been deionized and then distilled by using an all-glass still (Belco Glass, Inc.). Inert atmospheres were maintained by nitrogen or argon which had been purified by passing it over a column of BTS catalyst (B.A.S.F. Colors and Chemicals, Inc.).

Analysis. Total chromium content was determined by using H_2O_2 in base as the oxidant and measuring chromium as chromate ion (CrO_4^{2-}, ϵ_{372} 4815).[9] Halide ion analyses were done by the Volhard method after blanks were run to show that $Cr(OH_2)_6^{3+}$ and methanol did not interfere with the analysis. Methanol was analyzed by oxidation to carbon dioxide with a Ce(IV)–Cr(VI) oxidizing solution using a modification of the procedure described by Ferraris and King.[10] It was found that halide ion and $Cr(OH_2)_6^{3+}$ react with the oxidizing solution. Therefore, the amount of standardized $AgNO_3$ solution necessary to precipitate the halide ion was added to an aliquot of the sample. The mixture was then poured onto a short cation-exchange column which removed $Cr(OH_2)_6^{3+}$ and filtered out the AgX precipitate. The column was rinsed with enough water (25 mL) to remove the methanol from the column. The eluate was diluted to volume in a volumetric flask, and then an aliquot was taken and mixed with a 2.5- to 4-fold excess of oxidizing solution. After the oxidation of methanol to CO_2 had taken place (5 h), the excess oxidant was titrated with standardized ferrous sulfate by using ferroin as the indicator. Blanks were run on doubly distilled water which had been passed through a cation-exchange column containing $Cr(OH_2)_6^{3+}$ and AgX. The average amount of the oxidizing solution that reacted with the blanks was subtracted from the amount that reacted with the samples. The accuracy of this method was ±5%, as judged from analogous samples made from chromatographic grade methanol.

$Cr(OH_2)_5CH_2X^{2+}$. Pentaaquo(halomethyl)chromium(III) ions were prepared by modification of literature methods.[11] Chromium(II) solutions were mixed with the appropriate dihalomethane, CH_2X_2, with acetone as the cosolvent to maintain homogeneous solutions. The iodomethyl complex was formed in 15–20 min, but the chloromethyl complex needed several days. The brownish orange complex ions were separated from the reaction mixture on a Dowex 50W-X8 (Bio-Rad Laboratories) ion-exchange column using $NaClO_4$–$HClO_4$ solutions ($I = 1.00$ M) as eluting agents. Care was taken to wash the column with enough 0.1 M $HClO_4$ solution to remove all halide ions prior to elution of the desired complex. The positions of absorbance maxima agree with those reported by Dodd and Johnson,[11] but the molar absorptivities were generally higher. The complexes and their λ_{max} (nm) and ϵ_{max} (M^{-1} cm^{-1}) values are as follows. $CrCH_2Cl^{2+}$: 517, 23; 391, 225; 258, 3605. $CrCH_2Br^{2+}$: 397, 229; 520, 25. $CrCH_2I^{2+}$: 524, 34; 396, 322; 296, 3400; 264, 3350.

Kinetics. The kinetics of aquation of $(H_2O)_5CrCH_2X^{2+}$ ions were followed by measuring the decrease in absorbance at three different

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Table I. Products of the Aquation of $(H_2O)_5CrCH_2X^{2+}$ Ions[a]

	$[H^+]$, M	mmol	
		complex	X^-
$CrCH_2Cl^{2+}$	0.02	10.5	10.4
	0.10	9.6	9.7
	1.0	12.2	12.0
$CrCH_2Br^{2+}$	0.10	9.78	9.58
	1.0	14.0	14.0
	1.0	24.0	24.1
$CrCH_2I^{2+}$	0.10	25.0	12.7
	1.0	15.4	6.5

[a] Conditions: $I = 1.0$ M ($HClO_4$-$NaClO_4$); inert atmosphere; absence of light.

Table II. Products of the Aquation of $(H_2O)_5CrCH_2X^{2+}$ Ions[a]

	$[H^+]$, M	mmol	
		complex	CH_3OH
$CrCH_2Cl^{2+}$	0.02	9.04	9.00
	0.10	12.6	12.65
	1.0	7.64	7.55
$CrCH_2Br^{2+}$	0.10	10.8	10.6
	1.0	16.8	16.9
	1.0	7.47	7.36
$CrCH_2I^{2+}$	0.02	9.17	3.4
	0.10	12.5	2.4
	1.0	19.9	10.5

[a] Conditions: $I = 1.0$ M ($HClO_4$-$NaClO_4$); inert atmosphere; absence of light.

Table III. Rate Constants for the Aquation of $(H_2O)_5CrCH_2X^{2+}$ Ions[a] $[-d \ln [complex]/dt = k_0[complex]]$

	T, °C	$[H^+]$, M	10^5k_0, s^{-1}
$CrCH_2Cl^{2+}$	45	0.05	0.95 ± 0.08
	45	1.0	0.93 ± 0.05
	55	0.05	3.54 ± 0.15
	55	1.0	3.51 ± 0.10
	65	0.10	11.7 ± 0.3
	65	1.0	11.6 ± 0.2
$CrCH_2Br^{2+}$	35	0.10	1.05 ± 0.04
	35	1.0	0.95 ± 0.05
	45	0.10	3.30 ± 0.15
	45	1.0	3.0 ± 0.2
	55	0.10	11.9 ± 0.4
	55	1.0	11.5 ± 0.4
$CrCH_2I^{2+}$	45	0.10	0.76 ± 0.03
	45	1.0	0.77 ± 0.02
	55	0.10	2.50 ± 0.05
	55	1.0	2.51 ± 0.04
	70	0.1	14.0 ± 0.1
	70	1.0	14.0 ± 0.1

[a] Conditions: $I = 1.0$ M ($HClO_4$-$NaClO_4$); inert atmosphere; absence of light.

Table IV. Activation Parameters at 25 °C for Aquation of $(H_2O)_5CrCH_2X^{2+}$ Ions[a] $[-d \ln [complex]/dt = k[complex]]$

	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k, s^{-1}
$CrCH_2Cl^{2+}$	26.1 ± 0.2	8.6 ± 0.5	5.6×10^{-7}
$CrCH_2Br^{2+}$	24.3 ± 1.3	−2.7 ± 4.1	2.4×10^{-6}
$CrCH_2I^{2+}$	25.4 ± 0.2	−2.4 ± 0.7	4.5×10^{-7}

[a] Conditions: $I = 1$ M ($HClO_4$-$NaClO)_4$; absence of light and oxygen.

wavelengths. Aliquots were removed by syringe from thermostated vessels with gastight rubber serum caps; light was excluded from the vessels. Absorbencies were measured on a Gilford-modified Beckman DU spectrophotometer (error <±1% in absorbance) or a Cary Model 14.

Results

Stoichiometry. The stoichiometric measurements of the products of the $(H_2O)_5CrCH_2X^{2+}$ ions were made on solutions treated with similar conditions as the kinetic experiments. Although the complexes appear to be inert to oxygen, all stoichiometric and kinetic experiments were performed in a nitrogen atmosphere with light excluded.

The chromium product was identified as $Cr(OH_2)_6^{3+}$ by comparison of the final UV–vis spectrum of the reaction solution with an authentic sample. Also, careful experiments to detect other chromium products by ion-exchange separation of the aquated solutions were negative. Halide ion was identified by precipitation with silver nitrate and was quantitated by the Volhard method or by the use of specific halide ion electrodes. The results of the experiments are shown in Table I. The analyses with the chloromethyl and bromomethyl complexes indicated that one halide ion per complex is formed during aquation. However, the experiments with the iodomethyl complex indicated that the I^-/Cr ratio was significantly less than 1. Furthermore, this ratio increased with increasing temperature of the aquation and also increased if the aquated solution was kept at elevated temperatures for a longer time.

Methanol was identified as the major product of the aquation of the chloromethyl and bromomethyl complexes by gas chromatography and by a ceric ammonium nitrate spot test.[12] Quantitative determination of methanol was done by oxidation to CO_2 with a Ce(IV)–Cr(VI) oxidizing solution. The data are reported in Table II for all three complexes. Again, $CrCH_2Cl^{2+}$ and $CrCH_2Br^{2+}$ ions yield CH_3OH/Cr ratios very close to 1, while the $CrCH_2I^{2+}$ ion gave significantly lower values.

A major organic product for the aquation of $CrCH_2I^{2+}$ was found by gas chromatographic analysis to be methyl iodide. Furthermore experiments on methyl iodide indicate that it partially hydrolyzes to CH_3OH and I^- under the conditions of the study. The stoichiometries of the aquation reactions are therefore taken as

$$(H_2O)_5CrCH_2X^{2+} + 2H_2O \rightarrow Cr(OH_2)_6^{3+} + CH_3OH + X^- \qquad X = Cl, Br$$

$$(H_2O)_5CrCH_2I^{2+} \xrightarrow{H_3O^+} Cr(OH_2)_6^{3+} + CH_3I$$

The only organic product for the iodomethyl complex is shown as CH_3I. It is difficult to establish unequivocally that all the methanol that is found is formed by the hydrolysis of CH_3I rather than a portion resulting directly from the aquation of the complex.

Kinetics. The kinetics of the aquation reaction were followed spectrophotometrically, with measurements at three wavelengths. One of these wavelengths was at the maximum near 390 nm, and the other two wavelengths bracketed this maximum. The absorbance vs. time data were treated with a first-order equation. All three complexes exhibited good linearity over 95% of the reaction, confirming that the aquation is first order in complex. In addition there was no dependence of the rate constants on wavelength. The kinetic data are given in Table III. The rate constants at 25 °C show a surprising order. The bromomethyl complex aquates the fastest, while the chloromethyl and iodomethyl complexes have similar rates with the iodo rate slightly lower. Activation parameters for the reactions are given in Table IV.

Discussion

The rate constants for the aquation of the $CrCH_2X^{2+}$ ions fall within a narrow range. The relative values at 25 °C for $CrCH_2Cl^{2+}$:$CrCH_2Br^{2+}$:$CrCH_2I^{2+}$ are 1.3:5.3:1.0. The iodomethyl complex aquates the slowest and furthermore gives CH_3I as the product while the bromo and chloro complexes yield methanol.

Consider first possible mechanisms for the iodomethyl complex. The fact that CH_3I is formed argues that a carbanion

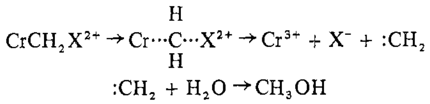
Scheme I

$$CrCH_2X^{2+} \rightarrow CrC^+H_2{}^{2+} + X^-$$

$$CrC^+H_2 \rightarrow Cr^{3+} + :CH_2 \xrightarrow{H_2O} CH_3OH \qquad (Ia)$$

$$CrC^+H_2 \xrightarrow{H_2O} CrCH_2OH^{2+} + H^+ \rightarrow Cr^{3+} + CH_3OH \qquad (Ib)$$

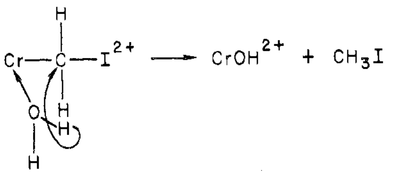
Scheme II



$$CrCH_2X^{2+} \rightarrow Cr\cdots\overset{H}{\underset{H}{C}}\cdots X^{2+} \rightarrow Cr^{3+} + X^- + :CH_2$$

$$:CH_2 + H_2O \rightarrow CH_3OH$$

type pathway is involved. A free carbanion would probably not be generated in acidic aqueous media so a solvent-assisted[6] mechanism may be active.



The hydroxy species, $CrOH^{2+}$, would quickly be protonated.

It is appropriate to note that Hine[13] in a series of papers established that for the halomethyl carbanions $^-CH_2X$, the iodo is the most stable and chloro the least stable. This is presumably due to delocalization of charge in the iodo case.

Several mechanistic schemes can be proposed to explain the production of methanol by $CrCH_2Cl^{2+}$ and $CrCH_2Br^{2+}$ ions. One extreme would be a purely dissociative or S_N1 mechanism and the other an associative or S_N2 type (Scheme I).

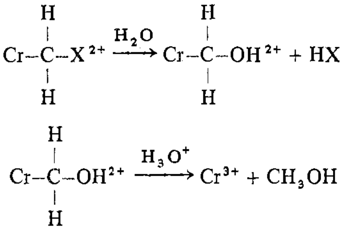
The first step in Scheme I involves an S_N1 loss of X^- to form a carbonium type intermediate, $CrC^+H_2{}^{2+}$. The empty p orbital of the C in this intermediate would be of the correct symmetry to overlap with filled t_{2g} orbitals of Cr(III) and might provide a means of stabilization. The order of rate of aquation ($CrCH_2Br^{2+} > CrCH_2Cl^{2+}$) is consistent with the order of the strength of the C–X bond. The carbonium intermediate could react in two possible ways [(Ia) and (Ib)] to produce methanol. In step Ia, $:CH_2$ is formed which rapidly reacts with water to form CH_3OH. In several experiments, 1-buten-4-ol was added to the sample (50:50 v/v) to see if the addition products of methylene to the double bond could be detected. No addition products were detected by gas chromatography, but this does not necessarily prove that $:CH_2$ is not an intermediate in the aquation since the reaction with water is rapid. In step Ib, water adds to $CrC^+H_2{}^{2+}$, producing a methanol–chromium(III) intermediate, $CrCH_2OH^{2+}$. It is known that $CrCH_2OH^{2+}$ aquates to form $Cr(OH_2)_6{}^{3+}$ and CH_3OH in acidic aqueous solution at rates much faster than those of the aquation of any of the halomethyl complexes.[6] Calculations using the appropriate rate constants indicate that the $CrCH_2OH^{2+}$ intermediate would never build up to a detectable concentration.

Another mechanistic pathway which is related to Scheme I involves a concerted breaking of a Cr–C and a C–X bond to form $:CH_2$ (Scheme II).

The data would not allow distinguishing between Scheme I and Scheme II.

The different stoichiometry of the iodomethyl complex in that CH_3I rather than methanol is formed and the fact that the iodomethyl complex aquates the slowest are relevant to the question of the mechanism of reaction of the chloro and bromo complexes. If the $CrCH_2Br^{2+}$ ions aquate via a dissociative type mechanism as in Schemes I and II in which a C–X bond is broken, it would seem reasonable to expect the $CrCH_2I^{2+}$ ion to react via the same pathway and at the fastest rate. We, therefore, take the stoichiometric and kinetic discrepancy of the iodomethyl complex as an argument against a dissociative mechanism for the chloromethyl and bromomethyl complexes. It should be noted that the deviation of the iodomethyl occurs both in the stoichiometry and in the rate of aquation. If the iodomethyl complex exhibited a change in stoichiometry but reacted at the fastest rate, then an argument could be made that there was a faster competing reaction which masked a dissociative pathway. This is not the case, however.

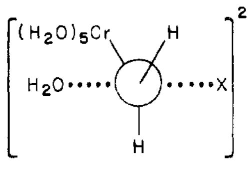
Scheme III



$$Cr\text{–}\overset{H}{\underset{H}{C}}\text{–}X^{2+} \xrightarrow{H_2O} Cr\text{–}\overset{H}{\underset{H}{C}}\text{–}OH^{2+} + HX$$

$$Cr\text{–}\overset{H}{\underset{H}{C}}\text{–}OH^{2+} \xrightarrow{H_3O^+} Cr^{3+} + CH_3OH$$

Another mechanism which would lead to formation of methanol involves an associative step in which a water molecule displaces a halide ion (Scheme III). In this scheme a methanol–chromium(III) species, $CrCH_2OH^{2+}$, is formed which rapidly reacts to form the final products. The same question arises as to why the iodomethyl complex has a change in stoichiometry and reverses the rate trend of the chloromethyl and bromomethyl complexes. It is important to consider results of studies of the hydrolysis of the methyl halides.[14] The relative rates at 373 K in water for CH_3Cl:CH_3Br:CH_3I are 1:12:4. The explanation for this deviation from normal order of halide reactivity is that more effective solvation of smaller anions in water opposes the trend in carbon–halogen bond strengths. For the bromide and iodide the higher solvation of bromide outweighs the higher strength of the C–Br bond. The accepted conclusion considering all the data is that hydrolysis of the methyl halides is probably an S_N2 reaction in which bond making is more important than bond breaking, and the rates are therefore less sensitive to the carbon–halogen bond strengths.[14] It seems reasonable to come to similar conclusions regarding the reactions of the $CrCH_2X^{2+}$ complexes. For these species there are additional steric hindrances not present in the methyl halides. In the associative step, a water molecule must presumably approach from the back side of the halide ion leaving group. The pentaaquochromium(III) moiety may restrict to some extent the ease of approach, and the iodomethyl complex would exhibit the largest degree of steric hindrance. Another way of considering the situation would be to look at relative stabilities of transition states for the $CrCH_2X^{2+}$ complexes. An S_N2 type mechanism would require a trigonal-bipyramidal type transition state.



The iodomethyl complex should exhibit the greatest degree of nonbonded interaction which raises the energy of the transition state. Another pathway involving rupture of the Cr–C bond will become dominant if its energy of activation is lower than that of the bimolecular substitution process.

Registry No. $(H_2O)_5CrCH_2Cl^{2+}$, 17477-09-7; $(H_2O)_5CrCH_2Br^{2+}$, 17477-12-2; $(H_2O)_5CrCH_2I^{2+}$, 17477-14-4.

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Stoichiometry and Kinetics of Aquation of $(H_2O)_5CrCHX_2^{2+}$ Ions (X = Cl, Br, I) in Acidic Solutions

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Mechanistic studies of the aquation of pentaaquo(dihalomethyl)chromium(III) ions (halo: chloro, bromo, iodo) have been made at hydrogen ion concentrations of 0.02–1.0 M in the absence of oxygen and light. For $(H_2O)_5CrCHCl_2^{2+}$ and $(H_2O)_5CrCHBr_2^{2+}$ the observed rate follows the equation $-d \ln [\text{complex}]/dt = k[\text{complex}]$, where $k = 4 \times 10^{-6}\ s^{-1}$ ($\Delta H^‡ = 24.4$ kcal/mol, $\Delta S^‡ = 1.3 \pm 1.1$ eu) for $CrCHCl_2^{2+}$ at 298 K and $k = 1.4 \times 10^{-6}\ s^{-1}$ ($\Delta H^‡ = 27.3$ kcal/mol, $\Delta S^‡ = 6.3 \pm 4.6$ eu) for $CrCHBr_2^{2+}$ at 298 K. The iodo complex showed a mild inverse hydrogen ion dependence, and the rate law has the form $(k_0 + k_1[H^+]^{-1})[CrCHI_2^{2+}]$ where $k_0 = 8.5 \times 10^{-8}\ s^{-1}$ ($\Delta H^‡ = 2.73$ kcal/mol, $\Delta S^‡ = 0.8 \pm 1.7$ eu) and $k_1 = 2.0 \times 10^{-9}\ s^{-1}$ ($\Delta H^‡ = 28.9$ kcal/mol, $\Delta S^‡ = -3.2 \pm 3.4$ eu) at 298 K. The products of aquation are $Cr(OH_2)_6^{3+}$, halide ion, CO, HCO_2H, and H_2. For deuterated complexes, $CrCDX_2^{2+}$, HD is the major hydrogen product and no kinetic isotope effect is detected ($k_H/k_D \approx 1$). A mechanism is proposed in which a chromium–formyl intermediate, $(H_2O)_5CrCOH^{2+}$, is formed by eliminating two halide ions by an S_N2 attack of H_2O at the carbon.

Introduction

Studies in this laboratory on (halo-substituted methyl)-pentaaquochromium(III) ions establish that carbon–halogen bond rupture is an important feature in the pathways for decomposition of these species in acidic aqueous solution. Even C–F bonds are broken before or at the same time as Cr–C bonds in the aquation of $(H_2O)_5CrCF_3^{2+}$ ions.[1]

The series of ions $(H_2O)_5CrCH_2X^{2+}$ (X = Cl, Br)[2] aquate to form $(H_2O)_6Cr^{3+}$, X^-, and methanol.[3] Evidence seems to favor an S_N2 attack of water at the carbon center to eliminate halide ion in the rate-determining step. In this work we report the results of a study made on the series $(H_2O)_5CrCHX_2^{2+}$ ions (X = Cl, Br, I). Formaldehyde would be the expected product if these dihalomethyl species aquated in an analogous fashion as the (monohalomethyl)chromium(III) species. However, the observed products in the absence of oxygen and light are formic acid and carbon monoxide as well as halide ion and hexaaquochromium(III) ions. Thus the organic moiety undergoes a two-electron oxidation. Molecular hydrogen is also a product, and the presumed oxidizing agent is hydrogen ions. Studies with deuterated species, $CrCDX_2^{2+}$, were also done to further investigate the mechanism. A chromium–formyl intermediate $(H_2O)_5CrCOH^{2+}$ is postulated in a mechanism which best fits the results of this study.

Experimental Section

Reagents. All solutions were prepared by using water which had been passed through a Barnstead ion-exchange demineralizer and then distilled in a Corning Model 1-a distilling apparatus. Nitrogen or argon, used to maintain an inert atmosphere, was purified by passing it over a column of BTS catalyst (B.A.S.F. Colors and Chemicals, Inc.) and then bubbling through concentrated H_2SO_4. Reagent grade perchloric acid and formic acid were used without further purification. $NaClO_4$ was prepared by the neutralization of Na_2CO_3 (Baker Analyzed reagent) with $HClO_4$. Stock solutions of $NaClO_4$ were analyzed by passing an aliquot through a cation-exchange column in the H^+ form and titrating the liberated acid with standard base. Cr(II) solutions were prepared by dissolving electrolytic grade Cr metal (>99.999% pure, Apache Chemicals) in deoxygenated perchloric acid solutions.[4] Trifluoromethanesulfonic acid (3M Corp.) was doubly distilled under vacuum by using an all-glass still[5] (Teflon sleeves were used instead of grease). Chloroform, bromoform, and iodoform were used without further purification. Deuteriochloroform (Aldrich) and deuteriobromoform (K & K) were checked for purity by NMR. Deuterioiodoform was prepared by the haloform reaction using acetone-d_6 (Aldrich) and deuterium oxide (K & K). No hydrogen resonance peak was found with NMR.

$Cr(OH_2)_5CHX_2^{2+}$ (X = Cl, Br, I),[6] pentaaquo(dihalomethyl)-chromium(III) ions, were prepared by reaction of the appropriate haloform with Cr(II) solutions. The reddish orange complexes were separated from the reaction mixture by ion-exchange techniques. The wavelengths of maxima and molar absorbencies of the complexes are as follows [λ_{max} (nm), ϵ_{max} ($M^{-1}\ cm^{-1}$)]. $CrCHCl_2^{2+}$: 514, 37.9; 396, 160; 266, 4120. $CrCHBr_2^{2+}$: 521, 46.8; 401, 179; 280, 4637. $CrCHI_2^{2+}$: 538, 65.9; 415, 330; 324, 3098; 281, 4067. These values are in good agreement with values reported previously.[7-9] The spectra of the deuterated complexes were essentially identical with those of the H compounds.

Stoichiometric Measurements. These experiments were designed to determine the final products of the aquation reactions. All measurements were made under conditions similar to those of the kinetic experiments, i.e., 1.0 M ionic strength and absence of light and oxygen. The chromium product was identified as $Cr(OH_2)_6^{3+}$ by comparison of UV–visible spectra with an authentic sample. Halide determinations were made by the Volhard method. Formic acid was identified as one of the carbon-containing products by GC. Quantitative measurements of formic acid were done colorimetrically with chromotropic acid[10] after reduction to formaldehyde with magnesium metal.[11] The gaseous products were identified as hydrogen and carbon monoxide by gas-phase IR and mass spectrometric studies. Solutions of the complexes were degassed by at least six freeze–thaw cycles. After aquation of the degassed solution, the gaseous products were expanded at liquid nitrogen temperature into an evacuated IR cell or into a gas sample tube for later analysis by mass spectroscopy.[12] Carbon monoxide was quantitated by absorption of CO_2 on an Ascarite tube after catalytic (CuO) combustion at 830 °C. (Control experiments were run to ensure that complete combustion occurred under these conditions.) The amount of hydrogen was determined by difference after the total moles of gaseous products were measured with a gas buret.

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