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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 $-\mathrm{d}\ln[\text{complex}]/\mathrm{d}t = k[\text{complex}]$, where $k = 4 \times 10^{-6}\ \mathrm{s}^{-1}$ ($\Delta H^{\ddagger} = 24.4$ kcal/mol, $\Delta S^{\ddagger} = 1.3 \pm 1.1$ eu) for $CrCHCl_2^{2+}$ at 298 K and $k = 1.4 \times 10^{-6}\ \mathrm{s}^{-1}$ ($\Delta H^{\ddagger} = 27.3$ kcal/mol, $\Delta S^{\ddagger} = 6.3 \pm 4.6$ 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 $k_0 = 8.5 \times 10^{-8}\ \mathrm{s}^{-1}$ ($\Delta H^{\ddagger} = 2.73$ kcal/mol, $\Delta S^{\ddagger} = 0.8 \pm 1.7$ eu) and $k_1 = 2.0 \times 10^{-9}\ \mathrm{s}^{-1}$ ($\Delta H^{\ddagger} = 28.9$ kcal/mol, $\Delta S^{\ddagger} = -3.2 \pm 3.4$ 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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Table I. Stoichiometries of the Aquation of $(H_2O)_5CrCHX_2{}^{2+}$ Ions

complex	$[H^+]$, M	mmol complex	mmol X^-	X^-/Cr
$CrCHCl_2{}^{2+}$	1.0[a]	0.552	1.135	2.06
$CrCHCl_2{}^{2+}$	0.1[a]	0.993	1.875	2.01
$CrCHCl_2{}^{2+}$	1.0[b]	0.192	0.386	2.01
$CrCHCl_2{}^{2+}$	0.1[b]	0.241	0.840	2.00
$CrCHBr_2{}^{2+}$	1.0[a]	0.550	1.131	2.05
$CrCHBr_2{}^{2+}$	1.0[b]	0.357	0.703	1.97
$CrCHBr_2{}^{2+}$	0.1[b]	0.930	1.856	1.98
$CrCHI_2{}^{2+}$	1.0[b]	0.140	0.275	1.98
$CrCHI_2{}^{2+}$	0.01[b]	0.316	0.626	1.98

[a] $HClO_4$–$NaClO_4$ solution. [b] CF_3SO_3H–CF_3SO_3Na solution.

First a number of experiments were run to determine the percentages of CO and HCO_2H as products from a specific complex under a given set of conditions. Then samples at the same conditions were degassed and allowed to aquate. A Toepler pump was used to push the gaseous products from the sample (liquid-nitrogen temperature) to a gas buret connected to a manometer. The reaction solution was put through several freeze–thaw cycles to be sure that all gas was transferred to the measuring gas buret. The total moles of gaseous products were calculated from the observed pressure and volume of the gases at room temperature.

Kinetic Measurements. The kinetics of aquation of $CrCHBr_2{}^{2+}$ and $CrCHCl_2{}^{2+}$ were followed by measuring decreases in absorbance at 370, 395, and 420 nm, while for $CrCHI_2{}^{2+}$ the wavelengths were 400, 410, and 430 nm. Aliquots were removed by syringe from thermostated dark vessels with gastight rubber septum caps; purified nitrogen gas was used as the inert atmosphere.[13] Absorbencies were measured on a Gilford-modified DU spectrophotometer (error $<\pm 1\%$ in absorbance) or a Cary Model 14. The reactions were followed to completion (10 half-lives). The data were treated by a linear least-squares computer program which calculated rate constants and displayed plots of absorbance vs. time and ln $(A_t - A_\infty)$ vs. time on a graphics terminal.

Results

Stoichiometry. The aquation reactions of the organochromium ions $Cr(OH_2)_5CHX_2{}^{2+}$ (X = Cl, Br, I) actually involves an oxidation–reduction. The carbon-containing products are CO and HCO_2H which have carbon in a formal +2 oxidation state in contrast to a formal 0 oxidation state for carbon in the original complexes. The product solutions in all cases exhibit UV–vis spectra which are consistent with $Cr(OH_2)_6{}^{3+}$, and ion-exchange chromatography yielded no evidence of other chromium products. Halide ion was determined as another product. Molecular hydrogen was also identified as a major component of the gaseous products. The results of the experiments designed to determine the stoichiometries of the aquation reactions are summarized in Tables I–III. In the initial part of this work the stoichiometric measurements and also the kinetic experiments were performed on 1.0 M ionic strength $HClO_4$–$NaClO_4$ solutions. With perchlorate present, the sum of millimoles of CO and HCO_2H agreed well with the moles of Cr, and the Cr:C ratios ranged from 1.0:0.96 to 1.0:1.0. The Cr:X^- ratios were also determined and ranged from 1.0:1.97 to 1.0:2.14 with the average (six experiments) 1.0:2.07 for the chloro complex. The moles of molecular hydrogen were determined by measuring the total moles of gaseous products with a gas buret and then subtracting the number of moles of CO. The carbon species undergo a two-electron oxidation, and correspondingly there would be 1 mol of H_2 produced/mol of original complex to achieve a balance, with the assumption that H^+ is the only species that is reduced. However, considerably fewer millimoles of H_2 were found; in a typical experiment in 1 M $HClO_4$ starting with 0.203 mmol of $(H_2O)_5CrCHCl_2{}^{2+}$, only 0.078 mmol of H_2 was found. Numerous experiments designed to explain the discrepancy by checking the accuracy of the method, by modifying equipment, and by purifying chemicals were unsuccessful. The stoichiometric measurements were eventually done in trifluoromethanesulfonic acid solutions rather than perchloric acid. With CF_3SO_3H, the measured millimoles of H_2 agreed well with the starting millimoles of complex, and the Cr:X ratio was very close to 2.0 in all cases (Table III). It was therefore concluded that perchlorate ion or impurities in the perchloric acid reacted with organochromium intermediates in a side reaction. (The rate constants were the same in both $HClO_4$ and CF_3SO_3H solutions so the side reaction must occur after the rate-determining step.)

Table II. Stoichiometries of the Aquation of $(H_2O)_5CrCHX_2{}^{2+}$ Ions

complex	$[H^+]$, M	mmol complex	mmol CO	mmol HCO_2H	C/Cr
$CrCHCl_2{}^{2+}$	1.0[a]	0.291	0.141	0.140	0.97
$CrCHCl_2{}^{2+}$	0.1[a]	0.473	0.252	0.214	0.98
$CrCHCl_2{}^{2+}$	1.0[b]	0.211	0.046	0.166	1.0
$CrCHCl_2{}^{2+}$	0.1[b]	0.254	0.058	0.190	0.98
$CrCHCl_2{}^{2+}$	0.01[b]	0.192	0.033	0.158	0.99
$CrCHBr_2{}^{2+}$	1.0[a]	0.129	0.091	0.032	0.95
$CrCHBr_2{}^{2+}$	0.1[a]	0.374	0.227	0.145	0.99
$CrCHBr_2{}^{2+}$	1.0[b]	0.178	0.030	0.145	0.98
$CrCHBr_2{}^{2+}$	0.1[b]	0.190	0.035	0.150	0.98
$CrCHI_2{}^{2+}$	1.0[a]	0.187	0.124	0.054	0.96
$CrCHI_2{}^{2+}$	1.0[b]	0.082	0.014		
$CrCHI_2{}^{2+}$	0.1[b]	0.208	0.042	0.168	1.01
$CrCHI_2{}^{2+}$	0.01[b]	0.252	0.058	0.188	0.98

[a] $HClO_4$–$NaClO_4$ solution. [b] CF_3SO_3H–CF_3SO_3Na solution.

Table III. Stoichiometries of the Aquation of $(H_2O)_5CrCHX_2{}^{2+}$ Ions

complex	$[H^+]$, M	mmol complex	mmol total gas	mmol CO[d]	H_2/Cr
$CrCHCl_2{}^{2+}$	1.0[a]	0.345	0.196	0.042	0.45
$CrCHCl_2{}^{2+}$	0.1[a]	0.203	0.102	0.024	0.38
$CrCHCl_2{}^{2+}$	1.0[c]	0.467	0.410	0.056	0.76
$CrCHCl_2{}^{2+}$	1.0[b]	0.192	0.221	0.023	1.03
$CrCHCl_2{}^{2+}$	1.0[b]	0.214	0.250	0.035	1.00
$CrCHCl_2{}^{2+}$	0.1[b]	0.231	0.265	0.040	0.97
$CrCHBr_2{}^{2+}$	1.0[a]	0.282	0.178	0.050	0.45
$CrCHBr_2{}^{2+}$	1.0[b]	0.178	0.190	0.030	0.90
$CrCHBr_2{}^{2+}$	0.1[b]	0.135	0.150	0.023	0.94
$CrCHI_2{}^{2+}$	1.0[a]	0.128	0.074	0.023	0.40
$CrCHI_2{}^{2+}$	1.0[b]	0.082	0.093	0.014	0.96
$CrCHI_2{}^{2+}$	0.01[b]	0.190	0.218	0.028	1.00
$CrCDCl_2{}^{2+}$	1.0[b]	0.201	0.240	0.036	1.01

[a] $HClO_4$–$NaClO_4$ solution. [b] CF_3SO_3H–CF_3SO_3Na solution. [c] HBF_4. [d] Calculated from percentages of CO in organic product (Table II).

The reaction in CF_3SO_3H solution is written as

$$2(H_2O)_5CrCHX_2{}^{2+} + 5H_2O \rightarrow 2(H_2O)_6Cr^{3+} + CO + HCO_2H + 2H_2 + 4X^- + 2H^+$$

Perhaps a better way of expressing the stoichiometry is

$$(H_2O)_5CrCHX_2{}^{2+} \xrightarrow[F_3SO_3H-CF_3SO_3^-]{\text{aqueous}} (H_2O)_6Cr^{3+} + [CO, HCO_2H] + H_2 + 2X^-$$

Kinetics. The rates of the reactions were measured by following changes in absorbance at several wavelengths as a function of time. Pseudo-first-order kinetics were observed for all the complexes under all conditions investigated. The first-order plots of ln $(A_t - A_\infty)$ vs. time (computer-graphics display) were linear over 95% of the reaction. Results of the kinetics experiments are summarized in Table IV. The chloro and bromo complexes, $CrCHCl_2{}^{2+}$ and $CrCHBr_2{}^{2+}$, did not exhibit a hydrogen ion dependence in the range of 0.01–1.0

Table IV. Kinetics of the Aquation of $(H_2O)_5CrCHX_2^{2+}$ and $(H_2O)_5CrCDX_2^{2+}$ Ions

complex	$[H^+]$, M	T, °C	10^5k, s^{-1}
$CrCHCl_2^{2+}$	1.0^a	65	58.4 ± 0.4
$CrCHCl_2^{2+}$	1.0^a	55	20.2 ± 0.2
$CrCHCl_2^{2+}$	0.5^a	55	20.0 ± 0.2
$CrCHCl_2^{2+}$	0.1^a	55	20.3 ± 0.3
$CrCHCl_2^{2+}$	0.02^a	55	20.6 ± 0.4
$CrCHCl_2^{2+}$	1.0^b	55	20.0 ± 0.1
$CrCHCl_2^{2+}$	0.1^b	55	20.1 ± 0.1
$CrCHCl_2^{2+}$	1.0^a	45	5.9 ± 0.1
$CrCHCl_2^{2+}$	0.1^a	45	6.0 ± 0.1
$CrCHCl_2^{2+}$	1.0^a	35	1.60 ± 0.02
$CrCHCl_2^{2+}$	1.0^b	35	1.58 ± 0.02
$CrCDCl_2^{2+}$	1.0^a	55	20.5 ± 0.4
$CrCHBr_2^{2+}$	1.0^a	65	39.5 ± 0.2
$CrCHBr_2^{2+}$	1.0^a	55	11.0 ± 0.1
$CrCHBr_2^{2+}$	1.0^b	55	11.1 ± 0.1
$CrCHBr_2^{2+}$	0.1^a	55	11.0 ± 0.1
$CrCHBr_2^{2+}$	0.1^b	55	10.8 ± 0.2
$CrCHBr_2^{2+}$	1.0^a	45	2.26 ± 0.04
$CrCHBr_2^{2+}$	0.1^a	45	2.25 ± 0.04
$CrCHBr_2^{2+}$	1.0^b	35	0.73 ± 0.02
$CrCDBr_2^{2+}$	1.0^a	55	11.0 ± 0.1
$CrCHI_2^{2+}$	1.0^a	85	23.4 ± 0.1
$CrCHI_2^{2+}$	0.5^a	85	24.2 ± 0.1
$CrCHI_2^{2+}$	0.1^a	85	30.4 ± 0.1
$CrCHI_2^{2+}$	0.05^a	85	36.5 ± 0.3
$CrCHI_2^{2+}$	0.02^a	85	56.5 ± 0.5
$CrCHI_2^{2+}$	0.1^a	75	7.55 ± 0.04
$CrCHI_2^{2+}$	0.1^a	75	9.91 ± 0.03
$CrCHI_2^{2+}$	0.02	75	20.3 ± 0.3
$CrCHI_2^{2+}$	1.0^a	65	2.08 ± 0.05
$CrCHI_2^{2+}$	0.1^a	65	2.75 ± 0.03
$CrCHI_2^{2+}$	0.02^a	65	5.10 ± 0.12
$CrCHI_2^{2+}$	1.0^b	65	2.20 ± 0.2
$CrCDI_2^{2+}$	1.0^a	65	2.1 ± 0.1

[a] $HClO_4$–$NaClO_4$ solution. [b] CF_3SO_3H–CF_3SO_3Na solution.

Table V. Activation Parameters for Aquation of $(H_2O)_5CrCHX_2^{2+}$ Ions

complex	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k,[a] s^{-1}
$(H_2O)_5CrCHCl_2^{2+}$	24.4 ± 1.5	1.2 ± 1.1	4.1×10^{-6}
$(H_2O)_5CrCHBr_2^{2+}$	27.3 ± 1.5	6.3 ± 4.6	1.4×10^{-6}
$(H_2O)_5CrCHI_2^{2+}$ (k_1)	28.9 ± 1.2	−3.2 ± 3.4	2.0×10^{-9} [b]
$(H_2O)_5CrCHI_2^{2+}$ (k_0)	27.3 ± 1.6	0.8 ± 1.7	8.5×10^{-8} [c]

[a] 25 °C. [b] Inverse H^+ dependent. [c] H^+ independent.

M H^+. The iodo complex, $CrCHI_2^{2+}$, did have a mild inverse hydrogen ion dependence. Plots of k_{obsd} vs. $[H^+]^{-1}$ were linear for all temperatures and the rate law is

$$-d[CrCHI_2^{2+}]/dt = (k_0 + k_1[H^+]^{-1})[CrCHI_2^{2+}]$$

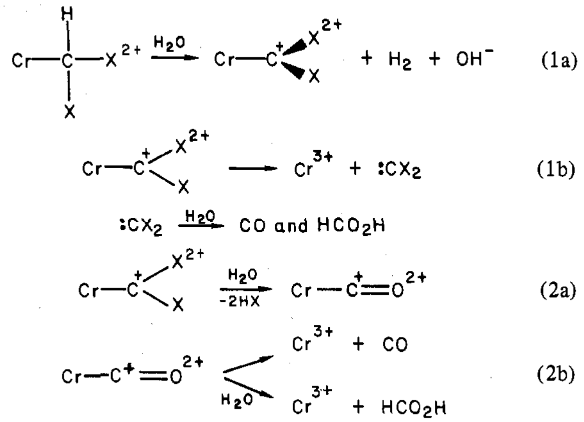
Activation parameters for the three complexes were determined from the temperature dependence of the values for the rate constants. The values are summarized in Table V.

Deuterated Complexes. The deuterated complexes, $CrCDX_2^{2+}$, were synthesized from Cr(II) solutions and the appropriate deuterated haloform, CDX_3. Stoichiometric and kinetic measurements were made with these complexes under similar conditions to those used for the hydrogen species. Mass spectral experiments indicated that greater than 90% of the molecular hydrogen product from the deuterated complexes was HD. Kinetic measurements were performed for all three complexes, $CrCDX_2^{2+}$, under a range of temperature and acid concentrations. In all cases, the rate constants for the deuterio and hydro species were the same within experimental error (±4%) (Table IV).

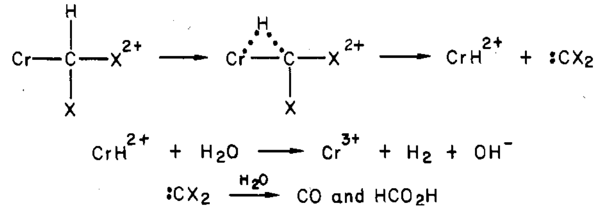
Discussion

The aquation of $(H_2O)_5CrCHX_2^{2+}$ ions actually involves an oxidation–reduction reaction. A mechanism for the reaction should be consistent with the following experimental criteria: (1) stoichiometry, (2) rate laws, (3) the order of the values for the rate constants for the three complexes ($CrCHCl_2^{2+}$ > $CrCH_2Br_2^{2+}$ > $CrCHI_2^{2+}$), (4) observation of HD as the major hydrogen product of the reactions involving the deuterated complexes, and (5) absence of a kinetic isotope effect in the deuterated complexes.

Scheme I



Scheme II



The stoichiometry of the reactions, i.e., the production of CO and HCO_2H, suggests the possibility of a dihalocarbene, $:CX_2$, intermediate since it is known that $:CX_2$ on hydrolysis gives CO and HCO_2H products.[14] Several mechanisms can be devised which yield dihalocarbene intermediates: Schemes I and II.

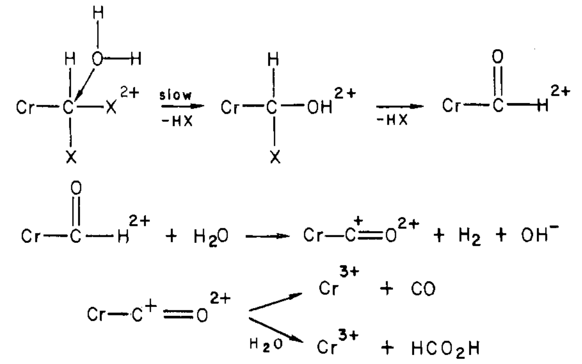
In Scheme I a hydride ion is lost to produce H_2 and a carbonium ion, $CrC^+X_2^{2+}$, intermediate. The empty p orbital of $CrC^+X_2^{2+}$ has the correct symmetry to overlap with the filled t_{2g} orbital of Cr(III) and might provide a means of stabilization. The carbonium ion intermediate could react by two different pathways. In steps 1a and 1b, free dihalocarbene is generated which then forms the final products. In steps 2a and 2b, the carbonium ion reacts with water, losing 2 HX to form an acyl carbonium ion, $CrC^+{=}O^{2+}$. The acyl carbonium ion could then undergo heterolytic cleavage to form CO or react with water to form HCO_2H. Acyl carbonium ions of the type $RC^+{=}O$ have extra stability due to resonance and have been reported to be stable in solution.[15] The OH^- produced in the first step in Scheme I would be neutralized rapidly in the acidic solution.

In Scheme II a dihalocarbene is formed by hydride transfer to the chromium center concerted with breaking the Cr–C bond. It has been shown by Light and Zeiss[16] that $Cr(CD_3)_3$ undergoes fragmentation by α metal hydride elimination and the authors suggest that a methyl group when bonded to chromium may exist in tautomeric form $CrCD_3 \rightleftharpoons DCrCD_2$.

Both Schemes I and II fit the observed stoichiometry and rate laws and yield HD for deuterated complexes. However, the rate-detemining step in each case involves breaking a C–H bond and should exhibit a kinetic isotope effect with the deuterated complexes.

A mechanism can be devised which has as a rate-determining step nucleophilic attack by a water molecule at the carbon center (Scheme III). Plausible arguments can be made

Scheme III



that this mechanism is consistent with all the experimental criteria. It gives the correct stoichiometry, including HD as a product of the deuterated complexes. This pathway would show a first-order rate dependence on the complexes. It would also have no kinetic isotope effect for the deuterated species since breaking the C–H bond occurs after the rate-determining step. The kinetic rates observed were in the order $CrCHCl_2^{2+} > CrCHBr_2^{2+} > CrCHI_2^{2+}$ which is the reverse of the bond strength order. However, it is the order of the steric hindrance to nucleophilic attack of H_2O on the carbon center.

The iodo complex, $(H_2O)_5CrCHI_2^{2+}$, was the only one which exhibited an inverse H^+ dependence. The inverse H^+ dependence could be due either to nucleophilic attack by OH^-, which is a better nucleophile than water, or to a conjugate-base mechanism. In the latter case, the pathway would involve a rapidly established equilibrium step

$$(H_2O)_5CrCHI_2^{2+} \rightleftharpoons (H_2O)_4OHCrCHI_2^{+} + H^+$$

producing a hydroxy species which is postulated to react more rapidly than the pentaaquo form. No choice can be made between these two explanations for the inverse H^+ path on the basis of the experimental evidence. It is also not clear why only the iodo complex should exhibit the inverse H^+ path. If the conjugate-base mechanism were operative, this might mean that there is some type of electronic effect that makes this path important in the iodo complex but not in the bromo or chloro. An alternate explanation would be that the hydroxy species form to a greater extent with the iodo complex. Current theories do not seem to be developed enough to judge these possibilities. If the inverse H^+ path is a result of nucleophilic attack by OH^-, then a somewhat simpler explanation can be developed. It has been established that the ratio of k_{OH^-}/k_{H_2O} decreases in nucleophilic substitution reactions for RX compounds in the sequence RI > RBr > RCl.[17] If the same is true for the $CrCHX_2^{2+}$ complexes, then the inverse path may not be observed for the bromo and chloro complexes.

In Scheme III, the chloro, bromo, and iodo complexes have an identical intermediate, $CrC(=O)H^{2+}$, which reacts to give the final products. This would imply that all three complexes would show the same ratio of CO to HCO_2H. This was found to be correct, within experimental error in CF_3SO_3H solutions. The average values of mmol of CO/mmol of HCO_2H in CF_3SO_3H–CF_3SO_3Na solutions are as follows: $CrCHCl_2^{2+}$, 0.22 ± 0.04; $CrCHBr_2^{2+}$, 0.22 ± 0.01; $CrCHI_2^{2+}$, 0.23 ± 0.05 (Table II). This result is further support for Scheme III.

Much current interest is focused on formylmetal compounds, MCOH, as possible intermediates in the catalytic transformation of mixtures of CO and H_2 (synthesis gas) to useful fuels such as methanol or alkanes. The well-known Fischer–Tropsch synthesis is an example. Of course any catalyst for the conversion of CO and H_2 to some compound must also catalyze the reverse process. The majority of the studies on transition-metal–formyl compounds and transition-metal complexes as catalysts for conversion of synthesis gas have been with metals in low oxidation states. The results of this study provide arguments for a chromium–formyl intermediate with Cr in the +3 oxidation state producing CO and H_2. This would suggest that attention should be given to higher oxidation metal complexes as potential Fischer–Tropsch type catalysts.

Registry No. $CrCHCl_2^{2+}$, 17477-10-0; $CrCHBr_2^{2+}$, 17477-11-1; $CrCHI_2^{2+}$, 17477-13-3; $CrCDCl_2^{2+}$, 71500-65-7; $CrCDBr_2^{2+}$, 71500-66-8; $CrCDI_2^{2+}$, 71500-67-9.

References and Notes

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