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Kinetics of Aquation of $Cr(OH_2)_5CF_3^{2+}$ in Acidic Medium

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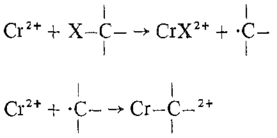
An investigation of the kinetic stability of the pentaaquotrifluoromethylchromium(III) complex in an aqueous medium is described. Initially the primary products of aquation are $Cr(H_2O)_6^{3+}$, HF, and CO. The initial rate of aquation of this complex is described by the differential rate law $-d \ln [(H_2O)_5CrCF_3^{2+}]/dt = k_0 + k_1[H^+]$ where $k_0 = 3.3 \times 10^{-8}$ sec^{-1} and $k_1 = 8.6 \times 10^{-8}$ M^{-1} sec^{-1} at 298°K. This rate of aquation is *ca.* five orders of magnitude slower than the rate of aquation of $(H_2O)_5CrCH_3^{2+}$.[2] A mechanism is proposed in which the activated complex contains a solvent molecule and in which the chromium–carbon and a carbon–fluorine bond are broken in a concerted manner. The overall rate of disappearance of complex was found to accelerate with time. This acceleration is ascribed to the aquation of a species, $(H_2O)_4CrFCF_3^+$, existing in equilibrium with the original chromium complex and the fluoride produced during aquation.

Introduction

Anet prepared the first organochromium(III) complex, pentaaquobenzylchromium(III) ion, by the reduction of benzyl chloride with chromium(II).[3] Since then, a number of organochromium(III) complexes[4,5] have been prepared using this same general reaction which involves the abstraction of a halo atom from an organic halide by Cr(II), followed by the rapid reaction of the organic radical with another Cr(II).



$$Cr^{2+} + X\!-\!\overset{|}{\underset{|}{C}}\!- \rightarrow CrX^{2+} + \cdot\overset{|}{\underset{|}{C}}\!-$$

$$Cr^{2+} + \cdot\overset{|}{\underset{|}{C}}\!- \rightarrow Cr\!-\!\overset{|}{\underset{|}{C}}\!-^{2+}$$

The dihalomethyl- and monohalomethylchromium(III) ions (halo = Cl, Br, and I) have been prepared in this fashion by reduction of the corresponding haloform or dihalomethane.[5] No fluoroorganochromium(III) complexes have been prepared by this route because the initial abstraction of the fluoro atom would involve breaking the strong C–F bond. We have avoided this difficulty and synthesized pentaaquotrifluoromethylchromium(III) ion by reduction of CF_3I with Cr(II). In this system the iodine atom is preferentially removed and the $\cdot CF_3$ radical reacts with another Cr(II).

The $Cr(OH_2)_5CF_3^{2+}$ ion is relatively inert to aquation in aqueous acid solutions compared to other organochromium(III) complexes. For example, the acid dependent rate constant for aquation of $Cr(OH_2)_5CH_3^{2+}$ is 5.2×10^{-3} M^{-1} sec^{-1} at 298°K;[2] the same parameter for $Cr(OH_2)_5CF_3^{2+}$ is 8.6×10^{-8} M^{-1} sec^{-1}. This inertness of the trifluoro species distinguishes it from the other trihalo analogs, since no organochromium(III) species have been isolated after reaction of Cr(II) with carbon tetrachloride[6] or carbon tetrabromide[5] presumably due to the rapid aquation of the complexes.

Experimental Section

Reagents. Iodotrifluoromethane (PCR) was used without further purification, as were reagent grade perchloric acid and sodium fluoride. $NaClO_4$ 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 solution.[7] All solutions were prepared using H_2O which had been deionized and then distilled using an all-glass still (Corning Model 1-a).

Analysis. Total chromium content was determined by using H_2O_2 in base as oxidant and measuring chromium as chromate ion (CrO_4^{2-}, ϵ_{372} 4815).[8] Carbon present in gaseous compounds was determined by absorption of CO_2 on an Ascarite tube after catalytic (CuO) combustion at 930°. (Control experiments were run to ensure that complete combustion occurred under these conditions.) Formic acid analyses were made by reduction of HCO_2H to H_2CO with Mg[9] and subsequent spectrophotometric determination of H_2CO with chromotropic acid.[10] Fluoride content was measured by titration with standard $La(NO_3)_3$ solutions using a specific fluoride ion electrode[11] (Orion, Model 94-09) after the pH was adjusted to 6 by NaOH.

Mass spectrometric analyses were made using a Consolidated Electrodynamics Type 21-104 180° sector mass spectrometer. The sample solutions were evacuated and degassed on a vacuum line and the aquation took place under vacuum conditions. After the desired reaction time, the solution was frozen in an acetone–CO_2 mixture. The sample tube was then opened directly on the mass spectrometer for measurement. In other analyses the sample was frozen in liquid nitrogen and the noncondensable gases were transferred to a sample tube for later analysis by mass spectroscopy. This was followed by a second sampling when the solution was frozen in an acetone–CO_2 bath.

$Cr(OH_2)_5CF_3^{2+}$. Pentaaquotrifluoromethylchromium(III) ion was prepared by bubbling CF_3I gas (PCR) into Cr(II) solutions and then agitating the reaction vessel for periods up to 24 hr. The brownish-orange $Cr(OH_2)_5CF_3^{2+}$ ion was 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. The $Cr(OH_2)_5CF_3^{2+}$ ion was allowed to aquate completely under a N_2 atmosphere and analyses were made for Cr, C as gaseous products and in solutions, chromium–fluorine complexes, and free fluoride ion. The average of several independent experiments gave Cr:C:F ratios of 1.0:0.96:2.97. Spectral measurements were made on freshly prepared solutions using a Cary Model 14 spectrophotometer.

$Cr(OH_2)_4FCrCF_3^+$. Fluorotetraaquotrifluoromethylchromium(III) ion was prepared by adding NaF to solutions of $Cr(OH_2)_5CF_3^{2+}$, waiting until the solution changed color from brownish-orange to pink, and separating the resulting chromium species on a Dowex 50W-X8 resin column (Na^+ ion form) which was maintained at 0°. The pink $Cr(OH_2)_4FCF_3^+$ ion was eluted with 0.01 M $HClO_4$–0.09 M $NaClO_4$ solutions. The average of several independent analyses gave Cr:C:F ratios of 1.0:0.99:3.85. Spectral measurements were made on freshly prepared solutions.

Kinetics. The kinetics of aquation of $Cr(OH_2)_5CF_3^{2+}$ were followed by measuring the decrease in absorbance at 380, 486, and 500 nm.

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(1) (a) University of the Pacific; (b) University of California, Davis.

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

(3) F. A. L. Anet and E. LeBlanc, *J. Amer. Chem. Soc.*, 79, 2649 (1957).

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

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

(6) F. A. L. Anet, *Can. J. Chem.*, 37, 58 (1959).

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(9) A. Grant and W. Morton, *Anal. Chem.*, 20, 267 (1948).

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(11) J. J. Lingane, *Anal. Chem.*, 40, 935 (1968).

Aliquots were removed by syringe from thermostated vessels with gas-tight rubber serum caps; purified nitrogen gas was used as the inert atmosphere. Absorbancies were measured on a Gilford-modified Beckman DU spectrophotometer (error ≤±1% in absorbance) or a Cary Model 14.

Results

Spectra. Most species having a chromium-carbon σ bond exhibit low (10-20 M^{-1} cm^{-1}) molar absorbancy indices near 500 nm and relatively high (100-400 M^{-1} cm^{-1}) molar absorbancy indices near 400 nm.[2,5] The spectrum of $Cr(OH_2)_5CF_3{}^{2+}$ has absorption maxima at 500 and 380 nm but with molar absorbancy indices of 40 and 67 M^{-1} cm^{-1}, respectively. There is also a small shoulder near 620 nm. The spectrum of $Cr(H_2O)_5CF_3{}^{2+}$ and also that of $FCr(H_2O)_4CF_3{}^{+}$ are given in Figure 1. The latter species has maxima at 518 and 388 nm with molar absorbancy indices of 37 and 60 M^{-1} cm^{-1}, respectively. Due to aquation of the trifluoromethyl moiety and a labile equilibrium involving the fluoride the latter are approximate values.

Stoichiometry. Preliminary kinetic measurements of the aquation of $Cr(OH_2)_5CF_3{}^{2+}$ indicated that the rate accelerated as the reaction proceeded. The products of the reaction were therefore determined at various stages of the reaction at both 0.1 and 1.0 M $HClO_4$. Ionic strength was maintained at 1.0 M with $NaClO_4$ and $HClO_4$. Although, unlike some chromium-carbon complexes,[3] $Cr(H_2O)_5CF_3{}^{2+}$ appears to be inert to oxygen, all stoichiometric and kinetic experiments were performed in a nitrogen atmosphere.

The chromium products were identified, after separating the reaction mixture by ion-exchange chromatography, either by elemental analysis or by comparison of the uv-visible spectra with known compounds. Fluoride was determined by use of a specific fluoride ion electrode. Mass spectrometry was used to identify gaseous organic products, and glc was used for possible organic products in solution.

An analysis, after ~10% completion of the reaction, showed the primary reaction products to be $Cr(OH_2)_6{}^{3+}$, HF (the predominate fluoride species would be HF since the pH is 2), carbon monoxide, and trace amounts of formic acid. Fluoroform was not found as a product using mass spectroscopy. The initial stoichiometry in both 0.1 and 1.0 M $HClO_4$ can be represented by the equation

$$CrCF_3{}^{2+} + H_3O^+ = Cr^{3+} + 3HF + CO$$

As the aquation proceeded toward completion pentaaquofluorochromium(III) ion, CrF^{2+}, appeared in the reaction mixture, although CO remained the dominant carbon-containing product. (The green CrF^{2+} ion was eluted before $CrCF_3{}^{2+}$ by 1 M $HClO_4$.) In experiments with low [H^+], chromium species of charge +1 which were eluted with 0.1 M $HClO_4$ were also formed.

It is important to consider whether CrF^{2+} results from a reaction between the initial products Cr^{3+} and HF[12] or is produced directly during the aquation of $CrCF_3{}^{2+}$. The amounts of the various chromium species were followed with time at 55.2° for [H^+] = 0.05 M, and the data are presented in Table I. For comparison, Cr^{+3} and HF were allowed to approach equilibrium under similar conditions ([HF] = 3[Cr^{3+}] since 3HF's are produced by each $CrCF_3{}^{2+}$ in the initial aquation). The products of the anation reaction were followed as a function of time and the results are also presented in Table I. It is obvious that the ratio of [CrF^{2+}]/[Cr^{3+}] is much higher during the aquation of $CrCF_3{}^{2+}$ than in the anation of Cr^{3+}. This indicates that all the CrF^{2+} found in the aquation of $CrCF_3{}^{2+}$ cannot result from initial formation of Cr^{3+} and HF followed by subsequent anation. This conclusion is also supported by calculations using the literature value for the rate constant for formation of CrF^{2+}.[12]

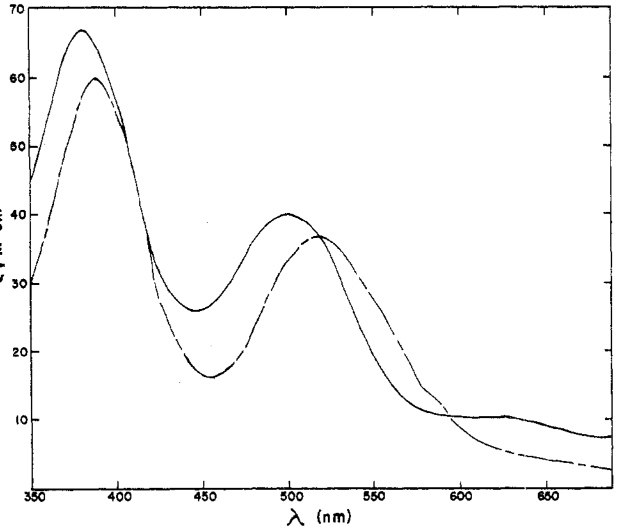

Figure 1: Visible spectra of $Cr(OH_2)_5CF_3{}^{2+}$ (——) and $Cr(OH_2)_4FCF_3{}^{+}$ (—— - ——).

Table I. Chromium(III) Products as a Function of Time During Aquation of [$(H_2O)_5CrCF_3{}^{2+}$] Ion and the Reaction of Fluoride with $Cr(OH_2)_6{}^{3+}$ [e]

	$(H_2O)_5CrCF_3{}^{2+}$ [a]				$Cr(OH_2)_6{}^{3+}$ + HF[b]		
Time, hr	$Cr\text{-}CF_3{}^{2+}$ [c]	CrF^{2+} [c]	Cr^{3+} [c]	+1 charged species[c,d]	Cr^{3+} [c]	CrF^{2+} [c]	$CrF_2{}^{+}$ [c]
24	68.8	18.3	10.7	2	95.0	5.0	
50	34.1	35.1	17.0	13.8	93.0	7.0	
72	15.4	48.2	16.8	19.7	87.6	12.0	0.4
144		61.9	17.8	20.3	78.2	19.0	3.0
∞		60.4	24.3	15.3	25.0	61.2	14.1

[a] Initial concentration: [$Cr(OH_2)_5CF_3{}^{2+}$] = 1.15 × 10^{-2} M. [b] Initial concentration: [$Cr(OH_2)_6{}^{3+}$] = 1.27 × 10^{-2}, [F^-] = 3.80 × 10^{-2} M. [c] Reported as per cent of total chromium. [d] It is believed that the +1 charged complex is a mixture of $FCrCF_3$ and CrF_2. At ∞ it is CrF_2. [e] Temperature = 55.2°, 0.05 M $HClO_4$, 0.95 M $NaClO_4$.

$FCr(OH_2)_4CF_3$. An examination of Table I shows that considerable amounts of a +1 charged chromium species are formed during the aquation of $CrCF_3{}^{2+}$. In fact, the percentage of +1 species builds up to intermediate values which are higher than the final, equilibrium one. The primary +1 species present after the reaction is complete is $CrF_2{}^{+}$. Aliquots were taken of the reaction mixture ([H^+] = 0.05 M) and diluted to ~0.02 M electrolyte concentration with ice-cold water; the resultant solution was passed through a refrigerated cation-exchange column in the Na^+-ion form. A small pink band was eluted before the green $CrF_2{}^{+}$ by using 0.01 M $HClO_4$-0.09 M $NaClO_4$ as the eluting agent. This pink +1 chromium species contains carbon and was identified as $FCr(OH_2)_4CF_3{}^{+}$ because it exhibited the same uv-visible spectrum as solutions of $FCr(OH_2)_4CF_3{}^{+}$ prepared independently.

Kinetics. The kinetics of aquation of $CrCF_3{}^{2+}$ were followed by measuring the decrease in absorbancy at several wavelengths. Since the stoichiometric experiments indicated that CrF^{2+}, Cr^{3+}, and HF were products, one of the wavelengths chosen was 486 nm, an isosbestic point for CrF^{2+} and Cr^{3+}. Plots of ln $(A_t - A_\infty)$ *vs.* time at this wavelength for

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(12) T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965).

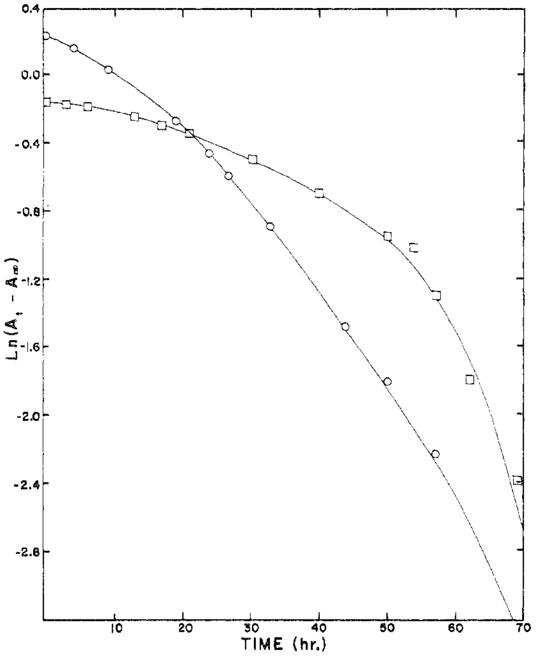

Figure 2. Plot of ln $(A_t - A_\infty)$ *vs.* time for the aquation of $Cr(OH_2)_5CF_3^{2+}$; λ 486 nm, an isosbestic point for Cr^{3+} and CrF^{2+}, (○) $[H^+] = 1\ M$; (□) $[H^+] = 0.1\ M$.

solutions with 1.0 and 0.1 *M* $HClO_4$ are shown in Figure 2. The plots show curvature, the reaction becoming faster toward the end with more curvature for the lower $[H^+]$. A possible interpretation of the curvature is that the rate is dependent on $[CrCF_3^{2+}]^{1/2}$.[13] In order to test this, rate constants were obtained by evaluating the initial slopes of ln $(A_t - A_\infty)$ *vs.* time plots for a number of different initial concentrations of $CrCF_3^{2+}$ and at several wavelengths. These rate constants agreed within an estimated experimental uncertainty of 5% for initial $[CrCF_3^{2+}]$ ranging from 2.1×10^{-4} to 3.3×10^{-3} *M* at both 1.0 and 0.1 *M* $[H^+]$. These observations are consistent with a first-order dependence on $[CrCF_3^{2+}]$ rather than half-order.

Initial Rates. The rate constants, k_{obsd}, were evaluated by determining the limiting initial slope and the results are summarized in Table II. The rate constants show dependence on $[H^+]$ and a plot of k_{obsd} *vs.* $[H^+]$ is shown in Figure 3. The linearity of this plot indicates that the rate law for the initial part of the aquation is

$$-d[CrCF_3^{2+}]/dt = (k_0 + k_1[H^+])[CrCF_3^{2+}]$$

The values of the rate constants calculated at 25° are $k_0 = 3.3 \times 10^{-8}$ sec^{-1} and $k_1 = 8.6 \times 10^{-8}\ M^{-1}$ sec^{-1}; for the acid-independent path $\Delta H^\ddagger = 24.9 \pm 2$ kcal/mol and $\Delta S^\ddagger = -9 \pm 6$ eu and for the acid-dependent path $\Delta H^\ddagger = 22.9 \pm 4$ kcal/mol and $\Delta S^\ddagger = -14 \pm 8$ eu.

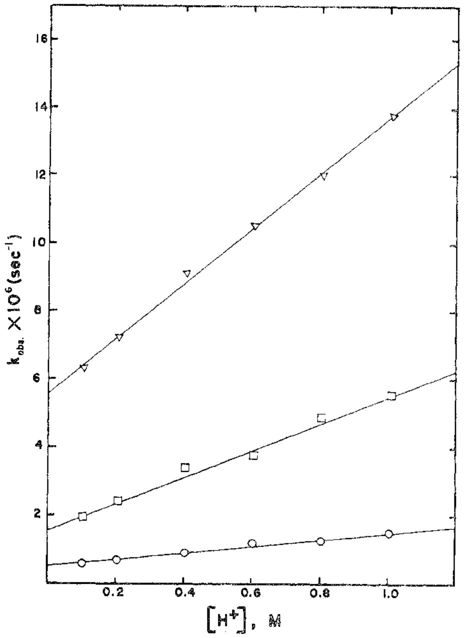

Figure 3: Dependence of the initial rate constant, k_{obsd}, for the aquation of $Cr(OH_2)_5CF_3^{2+}$ on $[H^+]$: (▽) 64.8°; (□) 55.2°; (○) 45.0°

Table II. Initial Rate Coefficients[a] for the Aquation of $[(H_2O)_5CrCF_3]^{2+}$ Ion as a Function of Temperature and Hydrogen Ion Concentration[b,c]

	$k_{obsd} \times 10^6$ sec^{-1} at			
$[H^+]$	35°	45°	55.2°	64.8°
0.1	0.23	0.6	1.9	6.3
0.2		0.7	2.4	7.2
0.4		0.9	3.4	9.1
0.6		1.1	3.7	10.5
0.8		1.3	4.9	12.0
1.0	0.53	1.5	5.5	13.8

[a] Estimated error ±5%. [b] Ionic strength was maintained at 1.0 *M* with $NaClO_4$ and $HClO_4$. [c] $-d[(H_2O)_5CrCF_3]^{2+}/dt = k_{obsd}[(H_2O)_5CrCF_3]^{2+}$.

Product Catalysis. The downward curvature of the pseudo first-order plots of ln $(A_t - A_\infty)$ *vs.* time (Figure 2) for the aquation of $CrCF_3^{2+}$ are consistent with catalysis by a product of the reaction. To test this interpretation, the products of the initial reactions, CO, Cr^{3+}, and HF, were added to solutions of $CrCF_3^{2+}$ in order to determine their effect on the aquation reaction. Increased pressure of CO had no effect nor did added Cr^{3+}. Chromium(II) was also added since Schmidt and Swaddle[13] showed that some organochromium(III) complexes form chromium(II) by homolytic scission of the chromium-carbon bond. However, added Cr^{2+} did not appreciably affect the rate of the aquation reaction.

When NaF was added to a solution of $CrCF_3^{2+}$, at room temperature, in 0.1 *M* $HClO_4$, a color change from brownish-orange to pink occurred in less than 5 min. If the $[H^+]$ was increased the pink color faded to orange, and if more fluoride was then added the pink color reintensified. The reversibility of this reaction was confirmed by spectral measurements using the Cary 14. Once additional fluoride ion had been added the concentration of the different species could be varied by changing the $[H^+]$ concentration. A pink singly charged chromium complex which was subsequently identified as $FCr(OH_2)_4CF_3^+$ was isolated from the pink solution by ion-exchange techniques. A small amount of a zero-charged organochromium complex was formed under conditions of high fluoride and low H^+ concentrations.

The rate of disappearance of $CrCF_3^{2+}$ was increased by the addition of fluoride ion. Upon addition of the NaF, the solutions of $CrCF_3^{2+}$ showed an initial rapid change in absorbancy, followed by a slower decrease. The rapid initial change was attributed to the formation of $FCr(OH_2)_4CF_3^+$ ion, in the equilibrium described above. The slower change was associated with the breaking of the Cr-C bond in the chromium complexes.

Plots of ln $(A_t - A_\infty)$ *vs.* time (λ 486 nm, an isosbestic point for Cr^{3+} and CrF^{2+}) were linear at first and then showed

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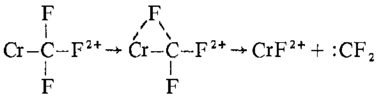
(13) A. R. Schmidt and T. W. Swaddle, *J. Chem. Soc. A*, 1927 (1970).

slight curvature as more fluoride ion was produced. The initial rate constants were determined as a function of fluoride ion. At 55.2°, 0.1 *M* $[H^+]$ ion, and an initial $(H_2O)_5CrCF_3^{2+}$ concentration of 6.28×10^{-3} *M*, k_{obsd} varied from 10.9×10^{-6} sec^{-1} at 1.26×10^{-2} *M* $[F^-]$ to 72.0×10^{-6} sec^{-1} at 3.42×10^{-2} *M* $[F^-]$. Under these conditions most of the fluoride is present as HF and the free fluoride ion concentration varied from 4.5×10^{-5} to 15.5×10^{-5} *M*. The rate increase shows more than a first-order dependence on fluoride as the rate increases *ca.* sevenfold for an ~2.7-fold increase in total fluoride or an ~3.5-fold increase in fluoride ion. Other experiments showed the rate dependence on fluoride to be more pronounced at lower $[H^+]$.

To avoid the complications of product catalysis it was decided to scavenge the fluoride ion produced in the aquation reaction. The Al^{3+} ion which has a large affinity for fluoride ion, $\log K_1 = 7.0$ and $\log \beta_6 = 27$,[14] was used as the scavenging ion. It was added as the perchlorate salt. In a solution of 2×10^{-2} *M* complex, 0.05 *M* $[H^+]$, and 0.40 *M* $[Al^{3+}]$, at 50°, the pseudo-first-order rate constant for the disappearance of complex was 1.8×10^{-4} sec^{-1}. The ~100-fold increase in the rate of disappearance of complex was quite the opposite of the effect expected. In the presence of Al^{3+}, unlike the previous experiments, a plot of ln absorbance of the complex against time gives a straight line to 90% of the reaction. Also, unlike the experiments in which free fluoride is in solution, the only chromium product found under the conditions of excess Al^{3+} was $Cr(H_2O)_6^{3+}$. The carbon-containing products formed in the presence of Al^{3+} have not yet been determined. However, work is continuing in this area.

Discussion

The primary organic product of the aquation of $CrCF_3^{2+}$ is carbon monoxide which suggests difluorocarbene, $:CF_2$, as an intermediate since it is well known that dihalocarbenes produce CO in aqueous acidic solution.[15] One way to produce $:CF_2$ from $CrCF_3^{2+}$ would be the transfer of a fluoride ion from carbon to the adjacent Cr(III)



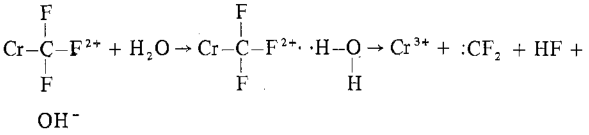
$$\mathrm{Cr{-}\underset{F}{\overset{F}{C}}{-}F^{2+} \rightarrow Cr{-}\underset{F}{\overset{F}{C}}{-}F^{2+} \rightarrow CrF^{2+} + {:}CF_2} \qquad (1)$$

A similar mechanism has been postulated by Castro[16] in his study of the reduction of polyhaloalkyls by Cr(II) and would be analogous to the mechanism of decomposition of ICH_2ZnI.[17] However, CrF^{2+} would be the principal chromium product, and although this ion is found in the reaction mixture, it is not formed in the initial stages of the reaction. Thus (1) must be discounted as a major path.

If the first step in the aquation mechanism was the heterolytic dissociation of the chromium-carbon bond the initial carbon-containing product would be CF_3^-. The CF_3^- anion could then decompose to form the carbene and fluoride ion. However, under the acidic conditions of our experiments CF_3^- would be expected to protonate more rapidly to form HCF_3[18] than it would lose a F^- to form the carbene. The absence of HCF_3, which is stable in acidic solution, indicates that this is not a significant path for aquation.

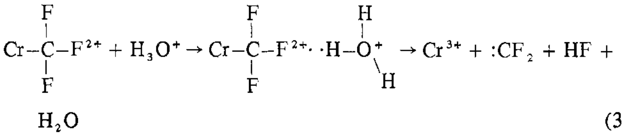
Since dihalocarbenes are generally formed from the anion,[18] it is possible that the CF_3 entity in the $Cr{-}CF_3^{2+}$ complex has properties approaching those of the trifluoromethyl anion. This suggests the formation of $:CF_2$ possibly through a concerted mechanism involving bond breaking between both chromium-carbon and carbon-fluorine. The idea of the concerted formation of $:CF_2$ is analogous to mechanisms postulated for formation of fluorocarbenes in organic reactions.[19]

A plausible mechanism which would produce $:CF_2$ would be a solvent-assisted abstraction of fluoride ion. The water molecule involved would very likely take advantage of the well-known H-bonding properties of fluorine.



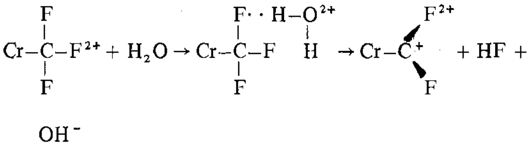
$$\mathrm{Cr{-}\underset{F}{\overset{F}{C}}{-}F^{2+} + H_2O \rightarrow Cr{-}\underset{F}{\overset{F}{C}}{-}F^{2+}\cdot\cdot H{-}\underset{H}{O} \rightarrow Cr^{3+} + {:}CF_2 + HF + OH^-} \qquad (2)$$

The OH^- produced would rapidly be neutralized by H^+ in solution. Equation 2 is meant to imply that the dissociation of the activated complex takes place in a concerted fashion. A similar mechanism can be written to explain the acid-dependent path.



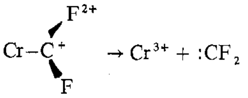
$$\mathrm{Cr{-}\underset{F}{\overset{F}{C}}{-}F^{2+} + H_3O^+ \rightarrow Cr{-}\underset{F}{\overset{F}{C}}{-}F^{2+}\cdot\cdot H{-}\underset{H}{\overset{H}{O^+}} \rightarrow Cr^{3+} + {:}CF_2 + HF + H_2O} \qquad (3)$$

Whether the breaking of the C-F bond is accompanied by the simultaneous dissociation of the Cr-C bond or the latter occurs immediately after the C-F bond breaks cannot be determined from these experiments. If the carbon-fluorine bond breaks first, the reaction mechanism could involve a carbonium ion intermediate.



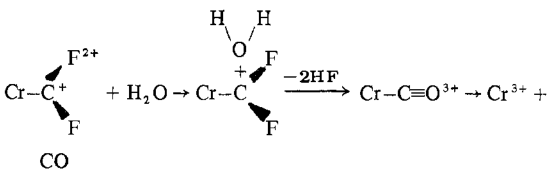
(4)

The empty p orbital of the carbonium ion has the correct symmetry to overlap with the filled t_{2g} orbitals of Cr(III) and might provide a means of stabilization. The carbonium ion intermediate could then dissociate to form $:CF_2$ and Cr^{3+}



(5)

or could be hydrolyzed by water to give CO without the intermediate formation of the carbene[20]



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(20) Attempts were made to trap the possible carbene intermediates by adding either 2,5-dihydrofuran or 3-buten-1-ol to solutions of $Cr(OH_2)_5CF_3^{2+}$, allowing time for aquation, and analyzing by glc for addition products of $:CF_2$ to the double bond. No addition products were found, but this cannot be taken as conclusive evidence against the formation of $:CF_2$ because the hydrolysis reaction to form CO may be extremely rapid.

The values of $\Delta H^\ddagger$ for the acid-independent and acid-dependent paths, 24.9 and 22.9 kcal, are consistent with breaking relatively strong bonds, while the negative $\Delta S^\ddagger$ values, −9 and −14 eu for acid-independent and dependent, respectively, are appropriate for an activated complex in which solvent molecules participate.[21]

While the data do not differentiate the order of the bond breaking between carbon–chromium and carbon–fluorine, the experimental evidence does suggest a mechanism involving concerted action in breaking these two bonds. The data also suggest the involvement of a solvent molecule, H_2O, or other ions such as H^+ or Al^{3+} in the activated complex. These molecules or ions most probably form a bond with the fluorine in CF_3 and thereby affect the lability of the carbon–fluorine bond.

The aquation of $CrCF_3^{2+}$ increased in rate as the reaction proceeded, indicating that a product of the initial reaction was acting as a catalyst. This autocatalyst was identified as fluoride ion since the rate also increased when NaF was added. A pink +1 chromium species, $FCrCF_3^+$, was isolated from solutions of NaF and $CrCF_3^{2+}$, and this same species was also separated from solutions with low $[H^+]$ which originally contained only $CrCF_3^{2+}$. The $FCrCF_3^+$ ion is a possible means by which fluoride affects the aquation reaction. The following sequence is consistent with the data if the Cr–C bond in $FCrCF_3^+$ is more labile than that in $CrCF_3^{2+}$

$$CrCF_3^{2+} + HF \rightleftarrows FCrCF_3^+ + H^+ \qquad (7)$$

$$FCrCF_3^+ + H_2O \xrightarrow{H^+} FCr^{2+} + CO + 3HF \qquad (8)$$

where (7) is an equilibrium reaction which is rapidly established relative to the rate of aquation. The Cr–C bond could then be labilized by the fluoride ion in $FCrCF_3^+$. A similar mechanism has been postulated by Kochi[22] in his study of the aquation of benzylpentaaquochromium(III) ion. There are a number of reports that ligands such as iodide[23] and hydroxide[24] ion affect substitution rates in chromium complexes, although no similar studies have been done with fluoride ion.

The formation of $FCrCF_3^+$ is not sufficient to explain the kinetic data with added fluoride ion. The aquation rates in the presence of added F^- more than double for a twofold increase in fluoride, and zero-charged chromium species were detected in solutions containing higher amounts of added fluoride. This indicates that species such as F_2CrCF_3 might be formed and participate in the increase in aquation rate. However, species like F_2CrCF_3 are not likely to be important in the aquation of $CrCF_3^{2+}$ in the absence of added fluoride since the concentration of fluoride remained low (maximum of three times the original concentration of $CrCF_3^{2+}$).

The $FCrCF_3^+$ ion is rapidly formed when fluoride is added to solutions containing $CrCF_3^{2+}$. Rapid color changes are also noted when azide and thiocyanate ions are added to $CrCF_3^{2+}$. The CF_3 moiety must therefore exhibit a very pronounced labilizing effect on the other ligands in the inner coordination sphere of chromium(III). The labilization does not appear to be a trans effect since zero-charged species, F_2CrCF_3, are also rapidly formed. Observations on other organochromium(III) complexes indicate that the labilizing ability is a general property of the Cr–C bond and is not restricted to $CrCF_3^{2+}$. A study of the substitution rates in organochromium(III) complexes is now being made.

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Registry No. $Cr(OH_2)_5CF_3^{2+}$, 51652-63-2; $Cr(OH_2)_4FCF_3^+$, 51652-64-3; $Cr(OH_2)_6^{3+}$, 14873-01-9; HF, 7664-39-3.

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Reduction of Coordinated Nitrosyls. III. Alternative Routes to Chromium(III) Dimers and Evidence for Coordinated Hydroxylamine[1,2]

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The kinetics and mechanism of reduction of $Cr(NH_3)_5NO^{2+}$ by Cr^{2+} have been investigated. The reduction consumes 2 mol of Cr^{2+}/mol of $Cr(NH_3)_5NO^{2+}$, resulting in 1 mol of NH_3OH^+/mol of $Cr(NH_3)_5NO^{2+}$ consumed. However, the rate of reduction of $Cr(NH_3)_5NO^{2+}$ is only first order in the $[Cr^{2+}]$ and $[Cr(NH_3)_5NO^{2+}]$. The stoichiometry and the rate law are similar to those observed for the Cr^{2+} reduction of $Cr(H_2O)_5NO^{2+}$. Greater than 78% of the products consist of three different polymeric Cr(III) complexes. Some $[Cr(H_2O)_4OH]_2^{4+}$ is observed in the product mixture, but the use of the pentaammine in place of the pentaaquo complex produces two new additional polymeric products, which we suggest may be represented by the formula $(NH_3)_5Cr\text{–}X\text{–}Cr(H_2O)_4Y^{n+}$, $X = OH^-$ or NH_2OH, $Y = H_2O$ or NH_2OH. Hydroxylamine analysis of each of the eluents from the ion exchange of the product mixture indicates that at least 50% of the NH_2OH is initially held up in the highly charged fractions. This leads us to propose a metal complex containing coordinated hydroxylamine. These products demonstrate the existence of at least two separate paths for chromium dimer formation upon reduction of a chromium nitrosyl.

Introduction

Some efforts have been made to study the reduction of ligands containing nitrogen atom centers. Mukaida[3] and

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