Kinetics of Heterolysis of Pentaaquachromium(III) Complexes of Benzyl and 4-Methyl-, Cyano-, and Fluoro-Substituted Benzyl Ligands

Zhongsheng Zhang and R. B. Jordan*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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The kinetics of the heterolysis have been studied for $(H_2O)_5Cr-CH_2C_6H_5^{2+}$ and the 2-, 3-, and 4-cyano derivatives; the 4-fluoro and 2,4- and 3,5-difluoro derivatives, and the 4-CH_3 complex. The reactions were studied in the general temperature range 60–75 °C in 0.01–0.95 M $HClO_4$ at an ionic strength of 1.00 M ($NaClO_4/HClO_4$). Chromium(II) was added to suppress homolysis. The reaction rate has terms first order and independent of $[H^+]$ and pathways involving catalysis by sulfate ion have been characterized for all but the more reactive 2- and 4-cyano systems. The latter is the most reactive (studied at 25–43 °C) and is also unusual in showing a saturation effect with $[H^+]$ which is attributed to protonation of the ligand to give $(H_2O)_5Cr-CH_2C_6H_4(4\text{-}CNH)^{3+}$ with $pK_a = 1.50$ (25 °C, 1.00 M $NaClO_4/HClO_4$). The results are discussed in terms of substituent effects on the general reactivity and the activation parameters, ΔH^* and ΔS^*.

Introduction

Pentaaquachromium(III) forms a wide range of organometallic derivatives[1] of the general formula $(H_2O)_5Cr-R^{2+}$ that decompose in aqueous solution by heterolysis (eq 1) and homolysis (eq 2).

$$(H_2O)_5Cr-R^{2+} \xrightarrow{H^+,H_2O} Cr(OH_2)_6^{3+} + RH \qquad (1)$$

$$(H_2O)_5Cr-R^{2+} \rightleftarrows Cr^{2+}(aq) + \{R^\bullet\} \rightarrow \text{products} \qquad (2)$$

The addition of aqueous chromium(II), as done in this study, suppresses the initial homolysis equilibrium and allows the heterolysis reaction to be studied. Homolysis is promoted by the addition of scavengers for chromium(II) and/or $R^\bullet$, and this reaction will be the subject of a separate publication for the systems studied here.

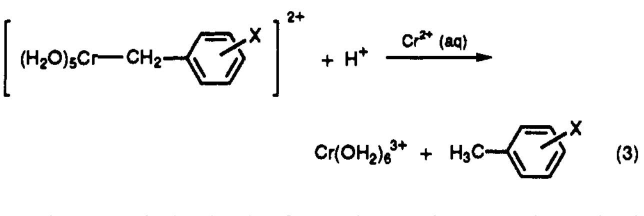
The decomposition of the benzyl complex, $(H_2O)_5Cr-CH_2C_6H_5^{2+}$, was studied initially by Kochi and Buchanan[2] and later by Nohr and Espenson[3] who found much lower heterolytic reactivity than reported previously. More recent work[4] has established the heterolytic and homolytic reactivity of the benzyl complex.

The present study involves an examination of the effect of substituents on the benzene ring on the heterolytic reactivity of the benzyl derivatives. Nohr and Espenson[3] studied the homolysis of the 4-CH_3, 4-Br, 4-CF_3, and 4-CN derivatives and found that homolysis is slower with more electron-withdrawing substituents, with a good correlation of the rate constant and the Hammett σ parameter. However, there is no information on the substituent effects on heterolysis. It is also found here that the 4-CN system is more complex than reported by Nohr and Espenson because it undergoes a protolytic equilibrium.

Results

The benzyl derivatives of $(H_2O)_5Cr-R^{2+}$ were prepared by reaction of the appropriate benzyl bromide with chromium(II) perchlorate in a 40:20 by volume methanol–water solution, and were isolated by ion exchange chromatography at 0 °C in 1.0 M $NaClO_4$ containing 0.01 M $HClO_4$. The electronic spectra of the $(H_2O)_5Cr-R^{2+}$ complexes are given in Table I. The results are in agreement with earlier observations of Kochi and Davis[5] on similar systems. It should be noted that these complexes have a longer wavelength, weak absorption[4] at ~530 nm which has not been characterized here. Below 400 nm, the longest wavelength maximum shifts to lower wavelength with increasing electron-withdrawing power of the substituents on the benzene ring.

The organic products of the heterolysis were identified by ^1H NMR in $CDCl_3$, after extraction into chloroform and evaporation of the organic extract. The reactant solutions contained (1.8-3.2) × 10^{-3} M $(H_2O)_5Cr-R^{2+}$ (0.12–0.20 mmol) and 0.04 M Cr(II) in 0.10 M $HClO_4$. The product was 100% of the corresponding toluene derivative, except for ≤4% aldehyde with benzyl and ≤10% bibenzyl with the 3-cyano complex. The latter minor products probably arise from reaction with O_2 and spontaneous homolysis, respectively, and may be contaminants in the starting solution. Therefore the reaction being observed is described by eq 3.



The heterolysis kinetics for each complex were determined from the decrease in absorbance of the peak or shoulder at 310–362-nm region. The rate was studied as a function of $[H^+]$ and temperature. All of the systems, except the 2- and 4-cyano complexes, show a common pattern for the variation of rate constant with $[H^+]$, and typical results for the 2,4-difluoro and benzyl systems are shown in Figure 1. From past experience,[1] one expects the heterolysis rate constant to be composed of two terms, one independent of and one first order in $[H^+]$. The representative results in Figure 1 correspond to this expectation, at least for $[H^+] > 0.2$ M. However, in the lower acidity region, the rate constant appears to have an $[H^+]^{-1}$ dependence. To make a long story short, this appearance is deceptive, and the rate is actually varying with sulfate ion concentration. For reasons of convenience and economy, many runs were done using

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Table I. Electronic Spectra of $(H_2O)_5Cr{-}R^{2+}$ Complexes[a]

R	λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})			
$4\text{-}CH_3C_6H_4CH_2$	362 (2.16)	304 (7.25)		
$C_6H_5CH_2$	356 (2.25)	296 (6.97)	274 (7.67)	242 (9.45)
$4\text{-}FC_6H_4CH_2$	354 (2.10)	292 (6.60)	272 (8.07)	238 (6.17)
$2,4\text{-}F_2C_6H_3CH_2$	350 (2.155)	294 (6.85)	270 (7.91)	236 (6.80)
$3,5\text{-}F_2C_6H_3CH_2$	348 (2.25)	294 (7.62)	274 (7.53)	240 (5.91)
$2\text{-}NCC_6H_4CH_2$[b]	316 (6.57)	282 (8.51)		230 (9.88)
$3\text{-}NCC_6H_4CH_2$[c]	318 (4.56)	282 (9.36)		232 (11.27)
$4\text{-}NCC_6H_4CH_2$[d]	316 (7.42)	292 (5.33)	259 (4.61)	224 (6.05)

[a] Spectra recorded in aqueous 0.10 M $HClO_4$/0.90 M $NaClO_4$. [b] From fitting the experimental spectrum with peaks at 316 nm (ϵ 6.57 × 10^3) and 282 nm (ϵ 8.51) to two Gaussian curves to obtain the positions and ϵ's tabulated. [c] From fitting the experimental spectrum with a peak a 284 nm (ϵ 9.76 × 10^3) and shoulder at ~315 nm (ϵ 5.0 × 10^3) to two Gaussian curves to obtain the positions and ϵ's tabulated. [d] From fitting the experimental spectrum with peaks at 310 nm (ϵ 9.18 × 10^3), 264 nm (ϵ 5.31), and 224 nm (ϵ 6.05 × 10^3) to four Gaussian curves to obtain the positions and ϵ's tabulated.

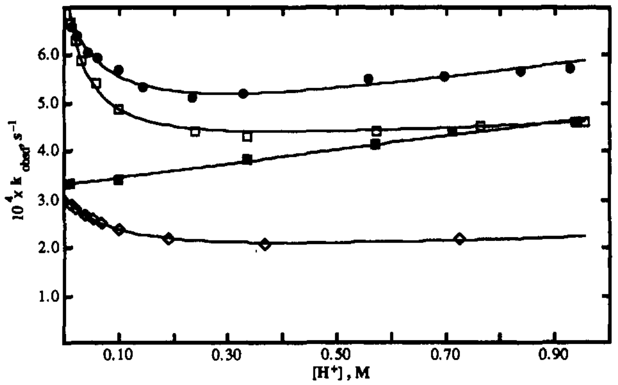


Figure 1. Dependence of the heterolysis rate on hydrogen ion concentration for $(H_2O)_5\text{-}Cr(III)$ complexes of 2,4-difluorobenzyl (□, 74.0 °C, 0.0247 M chromium(II) sulfate; ◇, 64.0 °C, 0.044 M chromium(II) sulfate) and benzyl (●, 67.3 °C, 0.0426 M chromium(II) sulfate; ■, 67.3 °C, 0.0426 M chromium(II) perchlorate).

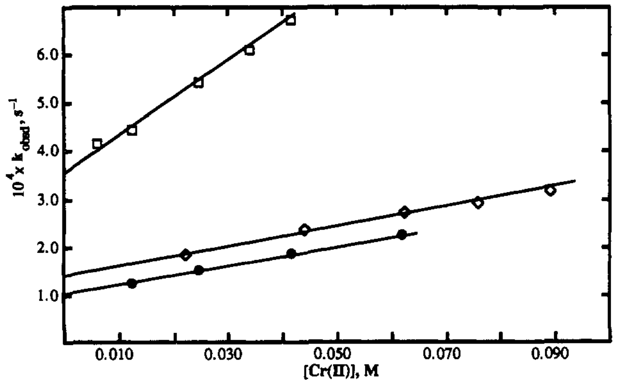
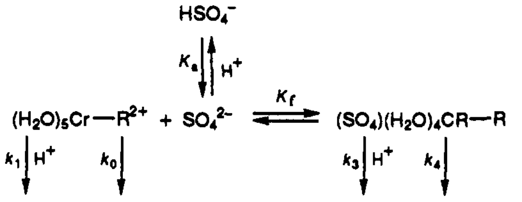


Figure 2. Dependence of the heterolysis rate on chromium(II) sulfate concentration for $(H_2O)_5Cr(III)$ complexes of 2,4-difluorobenzyl (□, 74.0 °C, 0.040 M H^+; ◇, 64.0 °C, 0.100 M H^+) and 3-cyanobenzyl (●, 64.0 °C, 0.100 M H^+).

Scheme I



chromium(II) prepared by zinc amalgam reduction of chromium(III) sulfate solutions. If sulfate is replaced by perchlorate as the source of Cr(II), the $[H^+]^{-1}$ dependence disappears, as shown for the benzyl complex in Figure 1. In Figure 2, at fixed $[H^+]$, the rate constant appears to depend on the chromium(II) concentration, but this is due to sulfate catalysis, as shown by experiments with the benzyl complex, in which chromium(II) perchlorate was used and in which zinc and sodium sulfate were added. The increase in rate at low $[H^+]$ is largely due to acid dissociation of HSO_4^- to yield SO_4^{2-}. There is no sulfate ion dependence of the rate for the more reactive 2-cyano and 4-cyano complexes. Except for the latter systems, the heterolysis is described by the reactions in Scheme I. Rapid preequilibrium formation of a sulfato complex is based on previous work, which has shown that one H_2O ligand is rapidly replaced in $(H_2O)_5Cr{-}R^{2+}$ systems, even at 25 °C, by a variety of anions including thiocyanate,[6] carboxylates,[7] and phosphates.[8] In Scheme I, the k_3 step is formulated as acid catalyzed heterolysis of the sulfato complex, but it could equally be reaction of free or complexed HSO_4^-. These alternatives will be analysed in the Discussion section below. From Scheme I, with the assumption that K_a and K_f describe rapidly maintained equilibria, the predicted pseudo-first order rate constants is given by eq 4, where the total sulfate

$$k_{obsd} = \frac{(k_1[H^+] + k_0) + (k_3K_fK_a[H^+] + k_4K_fK_a)\left(\dfrac{[SO_4^{2-}]_t}{K_a + [H^+]}\right)}{1 + \left(\dfrac{K_fK_a[SO_4^{2-}]_t}{K_a + [H^+]}\right)} \tag{4}$$

concentration $[SO_4^{2-}]_t \gg [Cr(III)]$. To analyze the data with eq 4, the K_a values have been interpolated from the results of Dickson et al.[9] in aqueous NaCl solutions. For most experiments, it should be noted that $[SO_4^{2-}]_t$ is 1.5 times the chromium(II) concentration, because the chromium is derived from chromium(III) sulfate. In all cases, the free H^+ concentration has been calculated after taking into account the H^+ bound to HSO_4^-.

Least-squares analysis of the k_{obsd} values to eq 4 indicates that $K_fK_a[SO_4^{2-}]_t(K_a + [H^+])^{-1} < 1$, so that K_f cannot be evaluated from the data. The quality of the least-squares fits indicates an upper limit of $K_f < 10$. Therefore, only the composite values k_3K_f and k_4K_f can be evaluated, and the data were fit assuming $K_f = 1$. The temperature dependence of the rate constants or composites in eq 4 were represented by the transition state equation with activation parameters ΔH^* and ΔS^*, and the k_{obsd} values at three temperatures were fitted by least-squares to determine the activation parameters. The values are given in Table II, and the complete data set and calculated and experimental k_{obsd} values are given in the supplementary material (Tables S1–S6). Reactivity trends are assessed in the Discussion section, but it should be noted that the activation parameters for k_1 and k_3K_a are less well defined than those for k_0 and k_4K_a because the former make rather minor contributions. This can be seen for k_1 in Figure 1 where the increase in k_{obsd} for $[H^+] \geq 0.2$ M is distinct for the benzyl complex, but marginal for the 2,4-F_2 complex.

The 2-CN and 4-CN complexes differ from the others in that there is no apparent effect of sulfate ion and the $[H^+]$ dependence of k_{obsd} is different. The $[H^+]$ dependence for the 4-CN system is shown in Figure 3 and the saturation effect on k_{obsd} indicates a protonation equilibrium for the complex. Since this was not

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(9) Dickson, A. G.; Wesolowski, D. J.; Palmer, D. A.; Mesmer, R. E. *J. Phys. Chem.* **1990**, *94*, 7978. The K_a for HSO_4^- at various temperatures in 1.00 M NaCl is calculated from the empirical formula $\log K_a = -9.7267 + 4117.9T^{-1} - 456890T^{-2}$, obtained from a least-squares fit of the data between 25 and 100 °C of Dickson et al.

Table II. Activation Parameters[a] for the Heterolysis of Substituted Benzyl Complexes of Pentaaquachromium(III)

	k_1		k_0		k_3K_f		k_4K_f	
substituent	ΔH^*	ΔS^*	ΔH^*	ΔS^*	ΔH^*	ΔS^*	ΔH^*	ΔS^*
4-CH_3	12.6 ± 3	−39.5 ± 9	19.1 ± 0.4	−18.0 ± 1	24.3 ± 2	7.4 ± 7	23.6 ± 0.8	−0.6 ± 3
−H	8.6 ± 3	−51.6 ± 8	21.7 ± 0.4	−11.0 ± 1	20.8 ± 2	−3.0 ± 6	22.0 ± 0.8	−4.3 ± 2
4-F	17.1 ± 3	−26.7 ± 8	20.8 ± 0.4	−13.6 ± 1	23.3 ± 3	4.2 ± 9	27.5 ± 1	12.5 ± 3
2,4-F_2	7.5 ± 11	−57.3 ± 31	22.9 ± 0.9	−8.5 ± 3	18.0 ± 6	−13.0 ± 18	25.1 ± 1	9.6 ± 4
3,5-F_2	10.7 ± 3	−46.0 ± 9	21.4 ± 1	−13.9 ± 3	35.9 ± 3	40.3 ± 8	27.5 ± 1	10.7 ± 3
3-CN	13.9 ± 5	−37.6 ± 15	23.0 ± 1	−8.9 ± 3	24.4 ± 3	6.6 ± 8	24.6 ± 1	7.6 ± 4

[a] Values of ΔH^* (kcal mol^{-1}) and ΔS^* (cal mol^{-1} K^{-1}) obtained from least-squares fits of data at three temperatures to eq 4: error limits are 1 standard deviation.

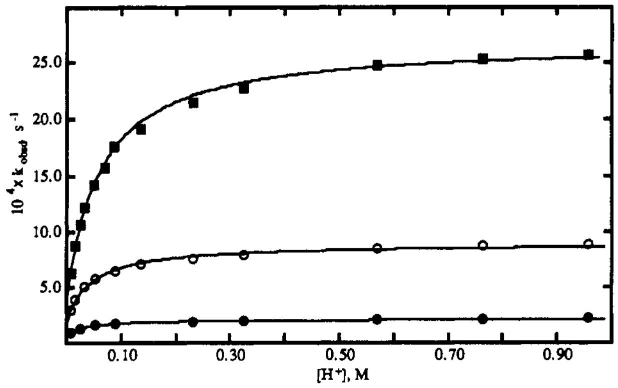

Figure 3. Dependence of the rate constant for heterolysis of the 4-cyanobenzyl complex of pentaaquachromium(III) on hydrogen ion concentration at 25.0 (●), 35.0 (○) and 43.0 °C (■).

Scheme II

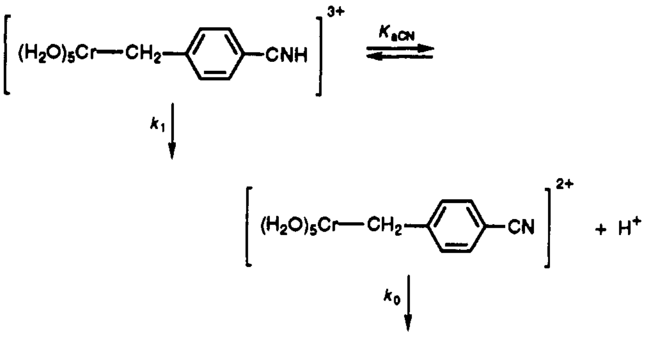

Table III. Kinetic Parameters for the Heterolysis of the 4-Cyanobenzyl and 2-Cyanobenzyl Complexes of Pentaaquachromium(III)

parameter	4-cyanobenzyl	parameter	2-cyanobenzyl
k_1, s^{-1} (25 °C)	1.95×10^{-4}	k_1', M^{-1} s^{-1} (65 °C)	3.3×10^{-4}
ΔH_1^*, kcal mol^{-1}	25.5 ± 0.04	$\Delta H_1'^*$, kcal mol^{-1}	26.1 ± 0.5
ΔS_1^*, cal mol^{-1} K^{-1}	10.3 ± 0.3	$\Delta S_1'^*$, cal mol^{-1} K^{-1}	2.5 ± 2.7
k_0, s^{-1} (25 °C)	6.4×10^{-5}	k_0, s^{-1} (65 °C)	1.6×10^{-3}
ΔH_0^* kcal mol^{-1}	16.5 ± 0.5	ΔH_0^*, kcal mol^{-1}	22.7 ± 0.06
ΔS_0^*, cal mol^{-1} K^{-1}	−22.5 ± 1.9	ΔS_0^*, cal mol^{-1} K^{-1}	−4.6 ± 0.3
K_{aCN}, M (25 °C)	3.15×10^{-2}		
ΔH°_{aCN}, kcal mol^{-1}	6.14 ± 1.4		
ΔS°_{aCN}, cal mol^{-1} K^{-1}	13.7 ± 4.4		

observed with the other substituents, the protonation appears to involve the 4-CN substituent and the system may be described by Scheme II which predicts that k_{obsd} is given by eq 5.

$$k_{obsd} = \frac{k_1[H^+] + K_{aCN}k_0}{K_{aCN} + [H^+]} \qquad (5)$$

Least-squares analysis gives the kinetic parameters in Table III for the 4-cyano complex. The full data set is given in the supplementary material (Table S7).

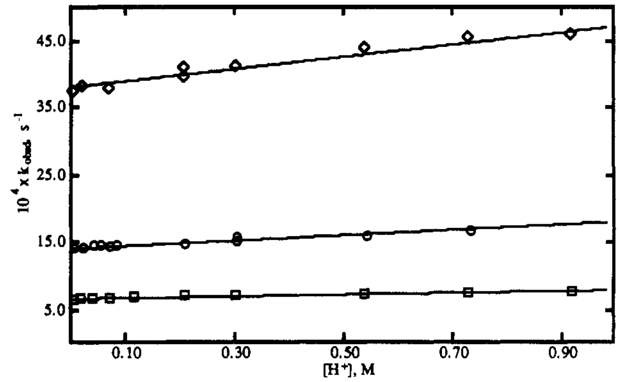

Figure 4. Dependence of the rate constant for heterolysis of the 2-cyanobenzyl complex of pentaaquachromium(III) on hydrogen ion concentration at 57.0 (□), 64.0 (○) and 74.0 °C (◇).

For the 2-cyano complex, the k_{obsd} increases linearly with [H$^+$], with no apparent saturation effect, as shown in Figure 4. This is the hydrogen ion dependence observed for many other such organochromium(III) complexes.[1] The standard interpretation would be that the reaction proceeds by parallel pathways involving attack by hydrogen ion (k_1') and water (k_0), respectively, so that k_{obsd} is given by eq 6. However, the experience with the 4-cyano

$$k_{obsd} = k_1'[H^+] + k_0 \qquad (6)$$

complex raises the possibility that the 2-cyano system also might be described by Scheme II and eq 5, with the modification that $K_{aCN} > [H^+]$, so that no saturation is observed. The K_{aCN} might be increased by the proximity of the Cr(III) in the 2-cyano complex compared to the 4-cyano complex. Then k_1' equals k_1/K_{aCN} in terms of the parameters in Scheme II. A possible selection between these alternatives will be discussed in the light of overall reactivity trends. The kinetic parameters are summarized in Table III, and the full data set is given in the supplementary material (Table S8).

Discussion

From the rate constants given in Table IV, it can be seen that there is a general trend to decreasing reactivity with increasing electron-withdrawing power of the substituent based on the Hammett σ values,[10] except for the 2-CN and 4-CN systems. The latter are much more reactive than expected from their σ values. Aside from these two exceptions, the rate constant changes by less than 10-fold with substituent.

All of the systems studied here show a well defined uncatalyzed heterolysis pathway (k_0) with activation parameters that fall in a narrow range of 21 ± 2 for ΔH_0^* and −13.5 ± 5 for ΔS_0^*, except for the 2-CN and 4-CN complexes. These parameters are similar to those for a number of Cr–CH_2X systems,[1] where it is also observed that electron-withdrawing –X groups reduce k_0. This can be generally understood in terms of reduced susceptibility of the –CH_2 to electrophilic attack, in the absence of steric and hydrogen bonding complications of the organic group.

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[10] Perrin, D. D.; Dempsey, B.; Sergeant, E. P. *pK_a Predictions for Organic Acids and Bases*; Chapman and Hall: London; 1981.

Table IV. Summary of Rate Constants for the Heterolysis of Substituted Benzyl Complexes of Pentaaquachromium(III)

param	multiplier	t, °C	4-CH_3	–H	4-F	2,4-F_2	3-CN	3,5-F_2	4-CN	2-CN
	σ^a		–0.14	0.0	0.06	0.60	0.62	0.68	0.70	1.06
k_1, $M^{-1}\ s^{-1}$	$\times 10^6$	25.0	7.7	17	2.5	6.2	2.5	7.7	200	1.6
	$\times 10^5$	65.0	11	11	8.5	3.1	4.5	7.4	4000	33
k_0, s^{-1}	$\times 10^6$	25.0	6.9	3.2	3.9	1.4	0.97	1.2	64	15
	$\times 10^4$	65.0	3.6	2.8	2.8	1.5	1.1	0.99	19	16
k_3K_f	$\times 10^4$	25.0	4.1	8.2	4.5	5.8	2.4	0.19		
	$\times 10^2$	65.0	5.9	5.9	5.3	2.4	3.5	2.8		
k_4K_f	$\times 10^5$	25.0	4.7	5.6	2.2	1.2	1.2	0.90		
	$\times 10^3$	65.0	5.8	5.1	6.1	2.9	2.6	2.5		

[a] Hammett substituent constant.

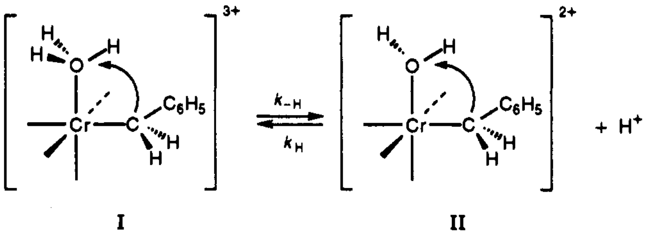
The k_0 values for the 2-CN and 4-CN systems are $>10^2$ times larger than expected from the σ correlation. For the 4-CN complex, the larger k_0 may be attributed to conjugative delocalization of the negative charge of the $-CH_2$ group which should weaken the Cr–C bond. This is consistent with the lower ΔH_0^* and the observation that this ligand undergoes protonation. The conjugative effect also can operate for the 2-CN complex, but proton saturation is not observed, and the ΔH_0^* value is in the normal range. The high reactivity of the 2-CN complex is due to a more favorable ΔS_0^* which seems more indicative of steric acceleration. The failure to detect proton saturation shows that the 2-cyanobenzyl ligand is less basic than the 4-cyano analogue. Protonation might be less favored because of hydrogen bonding of the 2-CN substituent with cis-H_2O ligands. Steric interactions of these same groups may inhibit conjugation by making it more difficult for the $-CH_2$ carbon to approach the sp^2 hybridization required for optimum conjugation.

The acid catalysed pathway (k_1) makes a minor contribution for many of these systems, as can be seen from the small slopes at higher acidities in Figure 1, and the larger uncertainties on ΔH_1^* and ΔS_1^* in Table II. Some of this contribution could be due to medium effects of replacing Na^+ by H^+ to maintain ionic strength, but this cannot be the whole effect because it does vary with the benzyl substituent. In addition, the lower ΔH_1^* than ΔH_0^* and large negative ΔS_1^* values are typical of results on other systems[1] where this is a dominant term.

It is interesting to note that the activation parameters for k_1 show a good isokinetic relationship ($\Delta H_1^* = 25.2 + 0.31\Delta S_1^*$) which also fits the k_1' parameters for the 2-CN complex. However, neither k_1 nor k_1/K_{aCN} for the 4-CN system fit this correlation. If the isokinetic relationship implies a commonality of mechanism, then it appears that the 2-CN ligand reacts by the normal acid-catalyzed process rather than pre-equilibrium ligand protonation.

It is not certain how the H^+ catalysis operates in normal systems of this type. The simplest possibility is electrophilic attack of H_3O^+ on the $-CH_2$ group, but Espenson and coworkers[11] found that the hydrolytic reactivity is profoundly reduced if the cis-water ligands in such complexes are replaced by an N_4-macrocycle. These observations are not consistent with direct electrophilic attack, and suggest involvement of the cis-water ligands in the heterolytic cleavage. The heterolysis might proceed as indicated in Scheme III by structures I and II for k_1 and k_0, respectively. Structure I involves H^+ transfer from a protonated coordinated water ligand. There is some precedent for such species from observations[13] that similar aquachromium(III) complexes undergo proton exchange with solvent water by an H^+-catalyzed path. For $(H_2O)_5CrCH_2CN^{2+}$, $k_H = 6.4 \times 10^4\ M^{-1}\ s^{-1}$ (25 °C), and if one assumes that the proton dissociation is diffusion controlled, with $k_{-H} \approx 1 \times 10^{10}\ s^{-1}$, then the acid dissociation constant ($K_{aM} = k_{-H}/k_H$) of I is $\sim 1.6 \times 10^5$ M. The activation energy for k_H (3.7 kcal mol^{-1}) and a typical diffusion activation energy for k_{-H} gives $\Delta H_{aM}° \approx -2$ kcal mol^{-1}, and one can estimate that $\Delta S_{aM}° \approx 17$ cal mol^{-1} K^{-1}. If I is the reactive species for the acid-catalyzed heterolysis, then the experimental k_1 values are really k_1''/K_{aM} and k_1'' will be in the range of 0.4 – 3 s^{-1} (25 °C) for the systems here, and have a ΔS^* about 17 cal mol^{-1} K^{-1} more positive than the experimental values for k_1. The latter change places the ΔS^* for k_1'' in the same range as those for k_0, and the result that $k_1'' \gg k_0$ is consistent with the expected greater electrophilicity of coordinated H_3O^+ compared to H_2O.

Scheme III



The 4-CN complex is expected to be different because the unique saturation effect with [H^+] implies a quite different type of protonation. The protonation described in Scheme II is analogous to that found[12] for the acetamido complex $(H_2O)_5Cr-CH_2C(O)NH_2^{2+}$, where the protonated carboxamide group has $K_a = 0.071$ M. It appears that these ligands may retain a high degree of anionic character.

For the sulfate-dependent pathways, k_3 and k_4, the latter is more well defined for our experimental conditions. Although typically $k_3K_f[H^+] > k_4K_f$ for $[H^+] > 0.1$ M, the sulfate-dependent pathways are attenuated at the higher [H^+], so that the k_1 pathway tends to dominate the k_3 pathway for these conditions. Scheme I presents the simplest possibility for these reaction, involving $(SO_4)(H_2O)_4Cr-R + H_2O$ for k_4 and $(SO_4)(H_2O)_4Cr-R + H_3O^+$ for k_3. On this basis, one might expect some parallel between k_0 and k_4 and between k_1 and k_3. Indeed, the ΔH^* for k_4K_f is in the same range as that for k_0 as expected if $\Delta H°$ for K_f is small. In our previous study[14] of the effect of acetate, phosphate, and methyl phosphate anions on the heterolysis of these compounds, the various kinetically equivalent alternatives for this reaction were considered in detail. It was concluded that ions without ionizable hydrogens probably react by the k_4 pathway suggested in Scheme I, and produce modest reactivity increases of the same magnitude as observed for sulfate ion (compare k_0 and k_4K_f in Table IV).

The situation with k_3 does not appear so simple. The values of ΔH^* for k_3K_f are generally much larger than ΔH_1^* and are more similar to ΔH_0^*. The values of k_3K_f are typically about 400 times larger than k_1 (see Table IV). This cannot be due to a large K_f because the kinetics establish that $K_f < 10$. The k_3K_f is larger because the higher ΔH^* is offset by a much more favorable ΔS^*. Earlier NMR studies[13] indicate that protonation of a coordinated water in $(H_2O)_5Cr^{III}X$ complexes is not greatly different for X = N_3^-, CH_2CN^-, or OH_2. Therefore, preequilibrium formation of I should not be greatly favored by the presence of a coordinated sulfate ion, and this does not seem to be an explanation for the large k_3K_f values. It could be argued that the coordinated sulfate

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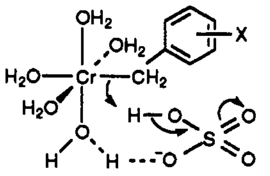
ion increases the negative charge on the $-CH_2$ group and promotes direct electrophilic attack of H_3O^+ on the $-CH_2$, so that the reaction is not proceeding through the intermediate analogous to **I**.

Although direct electrophilic attack cannot be ruled out for the sulfate system, our previous study[14] with phosphate species indicates that this is probably not the reaction pathway. It was found that species with ionizable protons are much better catalysts for heterolysis (e.g., $HPO_4^{2-} \gg H_3COPO_3^{2-}$, $H_3COPO_3H^- \gg H_3COPO_3^{2-}$). These observations suggest that species with ionizable protons, such as HSO_4^- in the present study, catalyse heterolysis by acting as bifunctional catalysts through an intermediate such as **III**. This gives eq 7 as a pathway that is kinetically equivalent to k_3 in Scheme I, but the sulfate ion dependent part of k_{obsd} (eq 4) must be modified by replacing $k_3K_fK_a$ by k_3'. With this change, the ΔH^* for k_3' is ~6.5 kcal mol^{-1} smaller than the values in Table II for k_3K_f and ΔS^* is ~26.2 cal mol^{-1} K^{-1} more negative. Values of k_3' at 25 °C are ~0.11 times those for k_3K_f in Table IV. It is possible to compare the k_3' values of the benzyl complex with several oxyanions proposed[14] to be reacting via **III**. The values of k_3' for HPO_4^{2-}, $H_2PO_4^-$, $(CH_3)HPO_4^-$, and HSO_4^- are 5.7×10^2, 4.4×10^{-2}, 1×10^{-3} and 8.5×10^{-5} M^{-1} s^{-1}, respectively. It appears that the reactivity correlates predominantly with the basicity of the anion, which in turn implies that a critical part of the bifunctional catalysis lies in the ability of the anion to interact with the Cr(III) center. In **III**, this interaction is suggested to be via hydrogen bonding with the cis-H_2O ligand, although it could be a direct interaction with the metal center.



III

$$(H_2O)_5Cr\text{-}R^{2+} + HSO_4^- \xrightarrow{k_3'} R\text{-}H + Cr(OH_2)_6^{3+} + SO_4^{2-} \qquad (7)$$

A reviewer has suggested that a cis-coordinated sulfate could be the source of the catalysis, by analog to cis-effects of ammonia loss from pentaamminechromium(III) complexes.[15] The cis complex could form by isomerization from the labile trans position, a process already studied by Sisley and Jordan[7,8] for oxalate, phosphate, and pyrophosphate reacting with $(H_2O)_5CrCH_2CN^{2+}$. The previous work indicates that the cis complex will coordinate another anion in the labile *trans* position so that the rate of Cr–C bond breaking would be second order in the anion. However, no such term could be detected in our previous study[14] of the phosphate-catalyzed Cr–C bond breaking in benzyl complexes or in the current work with sulfate.

Experimental Section

Materials. Aqueous solutions of the pentaaquabenzylchromium(III) complexes were prepared by mixing 40 mL of deoxygenated methanol containing 2 mmol of the appropriate benzyl bromide (Aldrich) with 20 mL of 0.3 M chromium(II) perchlorate in water, prepared by amalgamated zinc reduction of aqueous chromium(III) perchlorate. After ~10 min at ambient temperature the solution had changed from pale blue to dark greenish yellow, and it was loaded onto a column (8 × 2 cm) of Dowex 50W-X2(200) ion exchange resin in either the H^+ or Na^+ form under an argon atmosphere at 0 °C. Excess Cr(II) was eluted with 0.6 M $NaClO_4$ in 0.01 M $HClO_4$, and the desired product was eluted with 1.0 M $NaClO_4$ in 0.01 M $HClO_4$. The product was stored at -10 to -15 °C.

The chromium(II) used in the kinetic runs to suppress homolysis was commonly prepared from a stock solution of $Cr_2(SO_4)_3$ in perchloric acid by reduction with zinc amalgam. To test the sulfate effect, chromium(II) was prepared by reduction of aqueous $Cr(ClO_4)_3$.

Kinetic Measurements. The absorbance decrease was followed on a Hewlett Packard 8451 diode array spectrophotometer equipped with a thermostated cylindrical cell holder and standard water circulating temperature control system. A 50-mm cylindrical quartz cell was used throughout. The data analysis typically involved 80 points over 5–6 half-lives which were analysed by nonlinear least-squares to a first-order model.

Solutions for kinetic runs were prepared by adding the required amounts of standardized sodium perchlorate and perchloric acid to the spectrophotometer cell. The cell was sealed with serum caps, placed in the thermostated system, and deoxygenated for 20 min by bubbling purified argon. Then syringes were used to add aqueous chromium(II) in varying amounts and the appropriate benzylchromium(III) complex and at ~1 × 10^{-4} M. For the higher temperature runs (>65 °C), it was found advisable to avoid contact between the hot perchloric acid solution and stainless steel syringe needles, and Teflon needles can be used to advantage under such conditions.

Reagent and Product Analysis. Chromium was determined spectrophotometrically as chromate, following oxidation with alkaline hydrogen peroxide.

The organic products were determined from reactant solutions containing 0.12–0.20 mmol ((1.8–3.2) × 10^{-3} M) of the appropriate benzylchromium(III) complex, 0.10 M $HClO_4$, and ~0.04 M Cr(II). The solutions were prepared at ambient temperature and sealed under argon in glass ampules before bringing them to 65 °C in a water bath. Sealing is necessary to minimize evaporation and reaction with dioxygen. The solution changed from yellow to pale blue at completion, and was then exposed to air and extracted with 10 mL of chloroform. The organic extract was evaporated and then redissolved in $CDCl_3$ and the ^1H NMR spectrum was recorded on a Bruker AM 300 system. The products were identified by comparison of their spectra to those of the commercially available substances.

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Supplementary Material Available: Tables of temperature, total H^+, sulfate, and experimental and calculated rate constants (Tables S1–S8) (22 pages). Ordering information is given on any current masthead page.

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