Kinetics of the Heterolysis of Benzyl and Cyanobenzyl Complexes of Pentaaquachromium(III) in Acetate and Phosphate Buffers

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The kinetics of the heterolysis of the *o*-CN, *m*-CN, and *p*-CN benzyl complexes of pentaaquachromium(III) have been studied in phosphate buffers, and both heterolysis and homolysis have been studied in acetate buffers. Previous work on the parent benzyl system in acetate has been extended to heterolysis in phosphate and methyl phosphate buffers. All of the results are at 25 °C at a total ionic strength of 1.00 M, adjusted with $NaClO_4$. The pH total buffer dependence of the rate constants for heterolysis indicate that the conjugate bases ($H_{n-x}A^{x-}$) of the buffer species form mono complexes, $[(H_{n-x}A)(H_2O)_4Cr-(CH_2C_6H_4X)]^{2-x}$, whose formation constants correlate with the pK_a of the parent acid ($H_{n-x+1}A^{1-x}$). The effectiveness of the buffer components in promoting heterolysis generally depends on the basicity of $H_{n-x}A^{x-}$, but species with an ionizable proton are much more reactive than the fully deprotonated species OAc^- and $MeOPO_3^{2-}$. Acetate ion causes the rate of homolysis to increase by modest factors of 1.5–2.5 for the benzyl and *m*-CN and *p*-CN systems but causes a reduction in rate for the *o*-CN complex.

Introduction

Pentaaquachromium(III) forms a wide range of organometallic complexes,[1] $(H_2O)_5Cr-R^{2+}$, which decompose in aqueous solution by either heterolysis (eq 1) or homolysis (eq 2). The heterolysis can be studied by adding Cr_{aq}^{2+} to suppress homolysis, while homolysis plus heterolysis can be observed if scavengers for Cr_{aq}^{2+} or $\{R^\bullet\}$ are added.

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

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

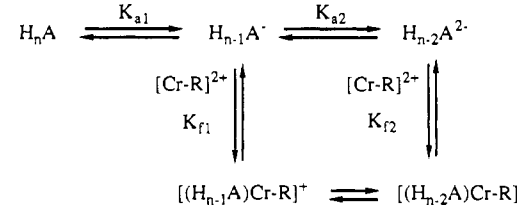
In a previous study,[2] we found that acetate increases the heterolysis rate for the $R = -CH_2C_6H_5$ system but by much less than for the $R = -(C(CH_3)_nH_{2-n}OH)$ systems examined earlier by Ogino et al.[3] and Cohen and co-workers.[4] These observations led to the suggestion that the α-OH function may not be an innocent bystander in the process and to the recognition that there are possible kinetic ambiguities in the mechanistic interpretation of the results. We also observed that homolysis of the Cr–benzyl bond shows a modest enhancement in the presence of acetate.

The present study examines the heterolysis kinetics of benzyl and cyano-substituted benzyl complexes in the presence of acetate/acetic acid, dihydrogen phosphate/hydrogen phosphate, and methyl hydrogen phosphate/methyl phosphate. It is hoped that an examination of systems with such diverse acidities will elucidate the mechanistic factors important for the assisted heterolysis of these systems and may clarify the kinetic ambiguities inherent in the rate laws. The homolysis study has been extended to the cyano-substituted benzyl derivatives in acetate buffers.

Results

Earlier studies[2-4] have shown the general reactions which can be expected to describe the kinetic observations. Therefore, we will proceed directly to develop a general rate law and symbolism and then adapt them to the specific systems. The complexation equilibria of a general polybasic acid H_nA with $(H_2O)_5Cr-R^{2+}$ can be represented by Scheme I. It is known that these complexes undergo rather rapid replacement of the *trans* aqua ligand[5-8] so that only formation of the mono complex is considered. There is the possibility of ion pairing as well as inner-sphere complex formation in these systems, although this is not formally included in Scheme I. The net formation constant (K_f) defined in Scheme I is actually the sum of the ion pair formation constant (K_i) and the inner-sphere complex formation constant (K_c). Scheme I has been simplified by neglecting the third ionization which gives $H_{n-3}A^{3-}$, because the highest experimental pH of ~5 is much smaller than pK_{a3} of 12.3 of H_3PO_4, so that PO_4^{3-} is never a significant species under our conditions.

Scheme I



On the basis of previous experience with these systems, the reaction pathways for heterolytic cleavage of the Cr–R bond can be represented in a general way by Scheme II. Only the organo ligand and the one trans to it are included in the scheme, and charges are omitted for generality. The k_0 and k_H pathways are observed in the absence of any complexing agents. The other pathways are grouped together according to the number of ionizable protons in the reactants and therefore will show the same $[H^+]$ dependence in the final rate law expression. This may also be true for different pathways involving different $H_{n-x}A^{x-}$ species, and it is apparent that there are a number of possibilities for the so-called proton ambiguity to arise in such a system. In addition, there are kinetic ambiguities for reactions involving free or complexed $H_{n-x}A^{x-}$, since $(H_{n-x}A)Cr-R + H_2O$ is

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Scheme II

$$(H_2O)Cr\text{-}R + H_2O \xrightarrow{k_0}$$
$$(H_2O)Cr\text{-}R + H_3O^+ \xrightarrow{k_H}$$
$$(H_{n-x}A)Cr\text{-}R + H_2O \xrightarrow{k_{ax}}$$
$$(H_2O)Cr\text{-}R + H_{n-x}A \xrightarrow{k_{ax}'}$$
$$(H_{n-x}A)Cr\text{-}R + H_3O^+ \xrightarrow{k_{bx}}$$
$$(H_2O)Cr\text{-}R + H_{n-x+1}A \xrightarrow{k_{bx}'}$$
$$(H_{n-x}A)Cr\text{-}R + H_{n-x+1}A \xrightarrow{k_{cx}}$$
$$(H_{n-x}A)Cr\text{-}R + H_{n-x}A \xrightarrow{k_{dx}}$$

equivalent to $(H_2O)Cr\text{-}R + H_{n-x}A^{x-}$. Scheme II is not an exhaustive list of the possibilities. Complexes $(H_nA)Cr\text{-}R$ are omitted on the assumption that the acid must lose at least one proton to form a complex. Reactions of $(H_{n-x+1}A)Cr\text{-}R + H_{n-x}A^{x-}$ are not included because the coordinated ligand is more acidic so that this combination would involve minor species and will have the same H^+ dependence as the k_{cx} path. In the formalism of Scheme II, k_{a1}' and k_{b2}' are the same and the latter is not included in the analysis.

If the reactions in Scheme I are treated as rapidly maintained equilibria, then the pseudo-first-order rate constant ($[A]_{tot} \gg [Cr\text{-}R]_{tot}$) can be expressed as in eq 3, where $F_m = 1 + K_{f1}[H_{n-1}A] + K_{f2}[H_{n-2}A]$.

$$k_{obsd} = (F_m)^{-1}(k_0 + k_H[H^+] + k_{a1}K_{f1}[H_{n-1}A] + k_{a1}'[H_{n-1}A] + k_{b1}K_{f1}[H^+][H_{n-1}A] + k_{b1}'[H_nA] + k_{a2}K_{f2}[H_{n-2}A] + k_{a2}'[H_{n-2}A] + k_{b2}K_{f2}[H^+][H_{n-2}A] + k_{c1}K_{f1}[H_{n-1}A][H_nA] + k_{c2}K_{f2}[H_{n-2}A][H_{n-1}A] + k_{d1}K_{f1}[H_{n-1}A]^2 + k_{d2}K_{f2}[H_{n-2}A]^2) \quad (3)$$

In order to identify the distinguishable terms in eq 3, it is necessary to express the concentrations of the various conjugate base species in terms of the total concentration $[A]_{tot}$ ($=[H_nA] + [H_{n-1}A] + [H_{n-2}A]$) and the acid dissociation constants of the acid and then group terms according to their $[A]_{tot}$ and $[H^+]$ dependencies. If one assumes for generality a tribasic acid, then it is convenient to define $F_A = [A]_{tot}([H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})^{-1}$. Substitution into eq 3 and rearrangement yields eq 4, where $k_1 = k_{a2}K_{f2} + k_{a2}'$, $k_2 = k_{a1}K_{f1} + k_{a1}' + k_{b2}K_{f2}K_{a2}$, $k_3 = k_{b1}K_{f1}K_{a1} + k_{b1}'$, $k_4 = k_{d2}K_{f2}$, $k_5 = k_{c2}K_{f2}$, $k_6 = k_{d1}K_{f1}$, and $k_7 = k_{c1}K_{f1}$.

$$k_{obsd} = (F_m)^{-1}(k_0 + k_H[H^+] + F_A\{k_1K_{a1}K_{a2}[H^+] + k_2K_{a1}[H^+]^2 + k_3[H^+]^3 + F_A(k_4(K_{a1}K_{a2})^2[H^+]^2 + k_5K_{a1}^2K_{a2}[H^+]^3 + k_6K_{a1}^2[H^+]^4 + k_7K_{a1}[H^+]^5)\}) \quad (4)$$

Heterolysis in Aqueous Acetate–Acetic Acid. Acetic acid is the simplest system because it is a monobasic acid so that all terms containing k_{i2} and K_{f2} are zero, and $F_A = [OAc]_{tot}[H^+]^{-2}(K_{a1} + [H^+])^{-1}$. Then eq 4 simplifies to eq 5. Qualitatively, this rate

$$k_{obsd} = \{1 + K_{f1}K_{a1}(K_{a1} + [H^+])^{-1}[OAc]_{tot}\}^{-1}\{k_0 + k_H[H^+] + \{k_2K_{a1} + k_3[H^+] + (k_6K_{a1}^2 + k_7K_{a1}[H^+])[OAc]_{tot}(K_{a1} + [H^+])^{-1}\}[OAc]_{tot}(K_{a1} + [H^+])^{-1}\} \quad (5)$$

law predicts that a saturation effect may be observed when $K_{f1}K_{a1}(K_{a1} + [H^+])^{-1}[OAc]_{tot}$ becomes larger than 1, but this will be mitigated by the $[OAc]_{tot}$ squared dependence of the k_6 and k_7 terms. The k_2 and k_3 terms are distinguishable because of the $[H^+]$ dependence of the latter, but the proton ambiguity prevents distinction between k_{a1} and k_{a1}' or k_{b1} and k_{b1}'.

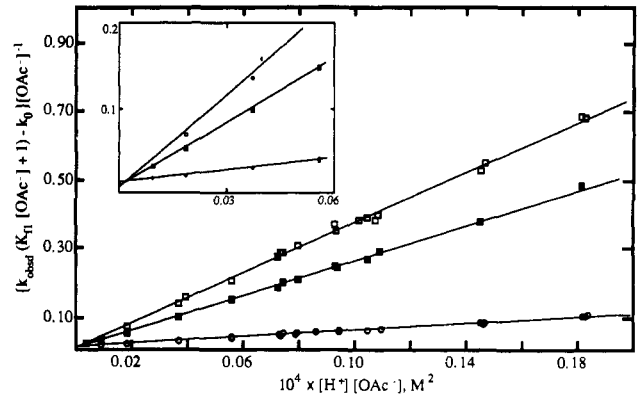

Figure 1. Variation of $\{k_{obsd}(K_{f1}[OAc^-] + 1) - k_0\}[OAc^-]^{-1}$ with $[H^+][OAc^-]$ as predicted by eq 6 for the heterolysis of the complexes of $(H_2O)_5Cr^{III}$– with *o*-cyanobenzyl (○), *m*-cyanobenzyl (□), *p*-cyanobenzyl (■), at 25 °C in 1.00 M NaOAc/$NaClO_4$.

Table I. Kinetic Parameters for the Heterolysis of Pentaaqua(benzyl)chromium(III) Complexes in Acetate/Acetic Acid Buffers

benzyl substituent	10^6k_0, s^{-1}	10^5k_H, $M^{-1}\,s^{-1}$	K_{f1}, M^{-1}	10^3k_2, $M^{-1}\,s^{-1}$	k_7, $M^{-2}\,s^{-1}$
H	3.3	1.7	65 ± 6	4.5	1.16
o-CN	14.8		128 ± 7	12.2 ± 0.1	0.0883 ± 0.004
m-CN	0.89	0.24	107 ± 5	4.14 ± 0.65	0.68 ● 0.025
p-CN	64		127 ± 7	7.02 ± 0.01	0.47 ± 0.02

The kinetics of the heterolysis of the ortho-, meta-, and para-substituted (cyanobenzyl)chromium(III) complexes have been studied between pH 3 and 5 with total acetate concentrations of 0.05 to 1.0 M in 1.0 M $NaClO_4$/NaOAc, at 25.0 °C. The rate constants are given in the supplementary material. The kinetic behavior is similar to that observed previously[2] with the benzyl system. In all cases, it was possible to determine K_{f1} from the kinetic data, but only the k_2 and k_7 kinetic terms could be identified. Under these circumstances, eq 5 simplifies to eq 6,

$$k_{obsd} = \{1 + K_{f1}[OAc]\}^{-1}\{k_0 + \{k_2 + k_7(K_{a1})^{-1}[H^+][OAc^-]\}[OAc^-]\} \quad (6)$$

where $[OAc^-]$ is the acetate ion concentration ($=K_{a1}(K_{a1} + [H])^{-1}[OAc]_{tot}$). Rearrangement of eq 6 shows that the plots in Figure 1 should be linear with slope k_7/K_{a1} and intercept k_2. It is apparent from Figure 1 that the k_7 pathway is dominant, but the k_2 contribution is determinable, as shown by the inset on Figure 1.

The kinetic results are summarized in Table I, but a consideration of the values will be deferred until all of the results are presented.

Heterolysis in Aqueous Hydrogen Phosphate/Dihydrogen Phosphate. The presence of phosphate species in the pH 2–5 range substantially accelerates the rate of heterolysis of the benzyl systems. Since there are no previous studies of the total phosphate and hydrogen ion dependence of such reactions, these results will be presented more fully.

Since $K_{a3} \ll [H^+]$, the expression for F_A simplifies to $F_A = [PO_4]_{tot}[H^+]^{-1}([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})^{-1} = F_P[H^+]^{-1}$, and $F_m = 1 + (K_{f1}K_{a1}[H^+] + K_{f2}K_{a1}K_{a2})F_P$, where $[PO_4]_{tot} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}]$. Then k_{obsd} is given by eq 7.

$$k_{obsd} = (F_m)^{-1}\{k_0 + k_H[H^+] + \{k_1K_{a1}K_{a2} + k_2K_{a1}[H^+] + k_3[H^+]^2 + (k_4(K_{a1}K_{a2})^2 + k_5K_{a1}^2K_{a2}[H^+] + k_6K_{a1}^2[H^+]^2 + k_7K_{a1}[H^+]^3)F_P\}F_P\} \quad (7)$$

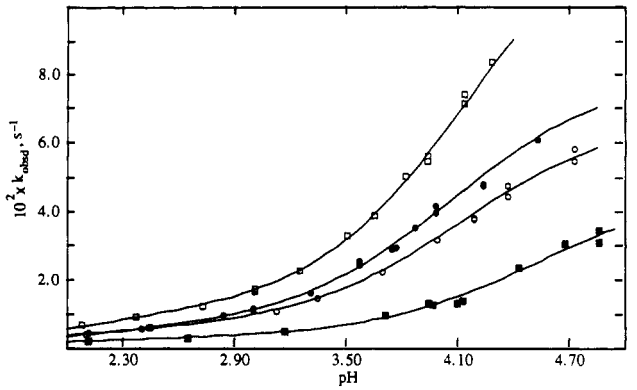

Figure 2. Variation of the rate constant for heterolysis in phosphate buffers with pH for the complexes of $(H_2O)_5Cr^{III}$– with benzyl (□), 0.30 M $[PO_4]_{tot}$; *m*-cyanobenzyl (●), 0.30 M $[PO_4]_{tot}$; *p*-cyanobenzyl (○), 0.50 M $[PO_4]_{tot}$; and *o*-cyanobenzyl (■), 0.50 M $[PO_4]_{tot}$, at 25 °C in 1.00 M $NaH_2PO_4/NaClO_4$.

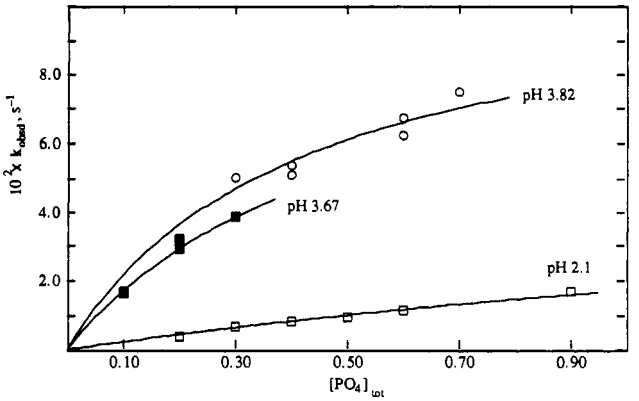

Figure 3. Variation of the rate constant for heterolysis of $(H_2O)_5Cr$–$CH_2C_6H_5^{2+}$ in phosphate buffers with total phosphate concentration at several pH values and at 25 °C in 1.00 M $NaH_2PO_4/NaClO_4$.

Table II. Kinetic Parameters for the Heterolysis of Pentaaqua(benzyl)chromium(III) Complexes in Phosphate and Methyl Phosphate Buffers

benzyl substituent	K_{f1}, M^{-1}	$10^{-3}K_{f2}$, M^{-1}	k_1, M^{-1} s^{-1}	10^2k_2, M^{-1} s^{-1}
H	0.75 ± 0.19	4.21 ± 0.44	565 ± 24	4.4 ± 0.2
H[a]	(0.2)[b]	0.55	2.7	0.1
o-CN	1.02 ± 0.14	1.42 ± 0.13	66.3 ± 3.3	0.92 ± 0.028
m-CN	0.37 ± 0.13	5.08 ± 0.30	417 ± 16	2.4 ± 0.009
p-CN	1.37 ± 0.13	4.03 ± 0.27	275 ± 13	2.05 ± 0.05

[a] Results in monomethyl phosphate buffers. [b] This value is not defined by the data and has been assumed for reasons described in the text.

Typical results for the dependence of k_{obsd} on pH at constant $[PO_4]_{tot}$ are shown in Figure 2. It is apparent from this plot that the reactivity order is benzyl > *m*-CN > *p*-CN > *o*-CN and that the rate increases with increasing pH for all these systems. Since the upper pH limit of this study is far below the pK_a of 7.2 of $H_2PO_4^-$, the pH dependence indicates that HPO_4^{2-} is very effective at promoting heterolysis. The incipient leveling (saturation) at high pH also implies strong complexation by HPO_4^{2-}. This is shown more clearly in Figure 3 for the benzyl system for rate constants at nearly constant pH and varying $[PO_4]_{tot}$.

Least-squares analysis of the variation of k_{obsd} with $[PO_4]_{tot}$ and $[H^+]$ reveals that K_{f1} and K_{f2} are defined for all the systems and that terms second order in $[PO_4]_{tot}$ (i.e. k_4, k_5, k_6, k_7 in eq 7) are indeterminant as is the term k_3 second order in $[H^+]$. Therefore the kinetic terms that can be evaluated are $k_1 = (k_{a2}K_{f2} + k_{a2}')$ and $k_2 = (k_{a1}K_{f1} + k_{a1}' + k_{b2}K_{f2}K_{a2})$. The best-fit parameters are summarized in Table II and the observed and calculated rate constants are given in the supplementary material. The curves in Figures 2 and 3 are drawn with these parameters.

Table III. Rate Constants for Various Pathway Assignments of the Experimental Rate Constants for Heterolysis of $(H_2O)_5Cr(CH_2C_6H_5X)^{2+} + H_nA$

		k_2		k_1		k_7
H_nA	X	$10^3k_{a1}'$	10^4k_{a1}	k_{a2}'	k_{a2}	10^3k_{c1}
HOAc	H	4.5	0.67			19
H_2MePO_4	H	1	0.5	2.7	0.0049	
H_3PO_4	H	44	590	565	0.134	
H_3PO_4	*o*-CN	9.0	93	65.7	0.046	
H_3PO_4	*m*-CN	24	650	417	0.082	
H_3PO_4	*p*-CN	19.3	170	265	0.068	
HOAc	*o*-CN	12.2	0.95			0.69
HOAc	*m*-CN	4.14	0.39			6.4
HOAc	*p*-CN	7.16	0.57			3.7

As noted in the Introduction, the K_f values are the sum of ion pair and inner-sphere complex formation constants, K_i and K_c, respectively. The magnitudes of the K_i can be estimated from previous work. Ferrer and Sykes[9] found $K_i = 2$ M^{-1} (1.00 M $LiClO_4$, 40 °C, $\Delta H° \approx 0$) for $Cr(NH_3)_5OH_2^{3+} + H_2PO_4^-$, and Boreham et al.[10] obtained $K_i \approx 60$ M^{-1} (1.0 M $NaClO_4$, 25 °C) for $Co(en)_2(OH_2)(NH_2CH_2CO_2C_3H_7)^{3+} + HPO_4^{2-}$ or $CH_3PO_4^{2-}$. These should be upper limits for our system because of the lower charge of the $(H_2O)_5Cr$–R^{2+} complexes. Since our K_{f2} values are $>1.4 \times 10^3$ M^{-1} and K_i for HPO_4^{2-} is <60 M^{-1}, then the K_{f2} values are essentially identical to the inner-sphere complex formation constants. For K_{f1}, the situation is not so clear because the values are of the magnitude of 1 M^{-1}, while the K_i for $H_2PO_4^-$ is <2 M^{-1}, and one must expect some ion pairing contribution to the K_{f1} values.

The acid dissociation constant (K_{a2}') for coordinated $H_2PO_4^-$ in $(H_2PO_4)Cr$–R^+ can be calculated from $K_{a2}' = K_{a2}K_{f2}/K_{f1}$ if one assumes that K_{f1} has a minor ion pairing component. This calculation gives $10^4K_{a2}'$ values of 3.5, 0.9, 8.6, and 1.8 for the benzyl, *o*-CN, *m*-CN, and *p*-CN complexes, respectively. The magnitude of these values seems reasonable, given that the analogous values are 2.2×10^{-4} M[11] for $(NH_3)_5CoOPO_3H_2^{2+}$ and 2.3×10^{-3} M[12] for $(H_2O)_5CrOPO_2H_2^{2+}$ and that the (R^-) ligand reduces the overall charge and should reduce K_{a2}'. The implication is that the K_{f1} values have a substantial inner-sphere complexation component.

Heterolysis in Aqueous Methyl Phosphate/Methyl Hydrogen Phosphate. This system was studied with $(H_2O)_5Cr$–$CH_2C_6H_5^{2+}$ in order to evaluate the influence of ionizable hydrogens on the phosphate. The system can be described by eq 7 with the replacement of H_3PO_4 by $MeOPO_3H_2$, $H_2PO_4^-$ by $MeOPO_3H^-$ and HPO_4^{2-} by $MeOPO_3^{2-}$. In general, methyl phosphate is about 10 times less reactive than phosphate. The pH dependence at constant $[MeOPO_3]_{tot}$ is shown in Figure 4, where it should be noted that the k_{obsd} scale is 10 times smaller than in Figure 2.

Least-squares analysis has been used to fit the k_{obsd} values to eq 7. The results indicate that K_{f1} is too small to be evaluated, with an upper limit of ~ 2 M^{-1} which causes the standard error of the fit to be 12% larger than the best value. If $K_{f1} < 1$, then the other parameters are reasonably independent of the value assigned to K_{f1}, and one obtains $K_{f2} = (5.5 \pm 0.5) \times 10^2$, $k_1 = 2.7 \pm 0.17$, $k_2 = (1.0 \pm 0.09) \times 10^{-3}$, and k_6 $(2.4 \pm 0.38) \times 10^{-3}$, where uncertainties are the standard error of the parameter and also reflect the range of values for K_{f1} between 0.1 and 1. In subsequent analysis, we have assumed a value of $K_{f1} = 0.2$ M^{-1} because it gives a value of K_{a2}' (7.2×10^{-4} M) for coordinated $MeOPO_3H^-$ in the same range as noted earlier for $H_2PO_4^-$. The k_6 term was not detected with phosphate, possibly because it is swamped by the much larger k_1 and k_2 with phosphate.

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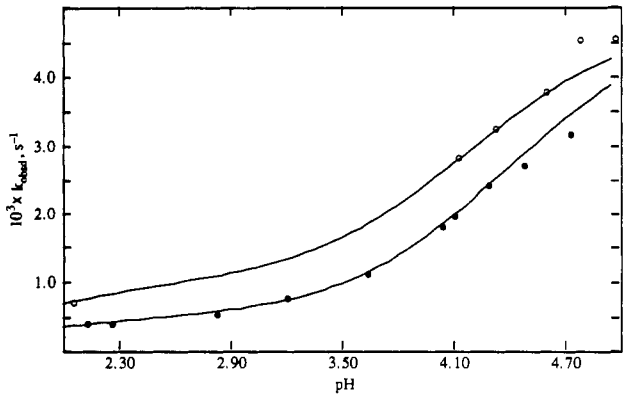
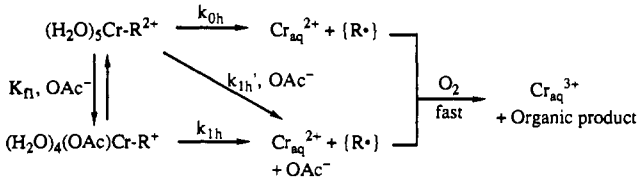


Figure 4. Variation with pH of the rate constant for heterolysis of $(H_2O)_5Cr-CH_2C_6H_5^{2+}$ in methyl phosphate buffers with total phosphate concentrations of 0.30 M (●) and 0.50 M (○) at 25 °C in 1.00 M $NaMeHPO_4/NaClO_4$.

Table IV. Kinetic Parameters for the Homolysis of Pentaaqua(benzyl)chromium(III) Complexes in Acetate/Acetic Acid Buffers

benzyl substituent	10^4k_{0h}, s^{-1}	$(k_{1h}' + k_{1h}K_{f1})$, M^{-1} s^{-1}	
		10^4k_{1h}	k_{1h}'
H	20	36 ± 0.8	0.23 ● 0.008
o-CN	3.8	3.0 ± 0.05	0.038 ± 0.0007
m-CN	2.1	5.5 ± 0.14	0.059 ± 0.0015
p-CN	3.4	5.2 ± 0.12	0.066 ± 0.0016

Scheme III



Homolysis in Aqueous Acetate–Acetic Acid. This reaction was studied using O_2 as a scavenger for Cr(II) with the *o*-CN, *m*-CN, and *p*-CN complexes. Results have been previously reported[2] for the benzyl system. Because heterolysis cannot be suppressed, these studies actually measure the sum of the homolysis and heterolysis rate constants ($k_T = k_{homo} + k_{het}$). Although homolysis typically has a larger rate constant than heterolysis for these systems,[13,14] we find that acetate is much more effective at promoting heterolysis. As a result, the processes become kinetically competitive and the determination of k_{homo} is less accurate because it is obtained from the often small difference $k_T - k_{het}$.

The homolysis contribution to the experimental rate constant has been analyzed in terms of Scheme III. Then the observed rate constant is predicted to be given by eq 8, where k_{het} and K_{f1}

$$k_T = k_{het} + (k_{0h} + (k_{1h}' + k_{1h}K_{f1})[OAc^-])(1 + K_{f1}[OAc^-])^{-1} \quad (8)$$

have been determined from the best-fit parameters from the heterolysis study, and k_{0h} was determined from studies in the absence of acetate[14] and in 0.01–0.9 M $HClO_4$, and $(k_{1h}' + k_{1h}K_{f1})$ was determined by least-squares fitting of k_T to eq 8. The experimental conditions and observed and calculated values of k_T are given in the supplementary material. The values of k_{0h}, $(k_{1h}' + k_{1h}K_{f1})$, and k_{1h} are given in Table IV.

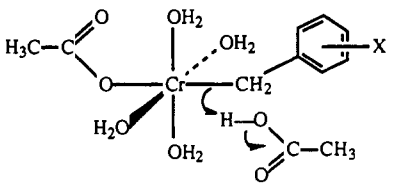
Discussion

In an earlier study[8b] of complexation of $(H_2O)_5Cr-CH_2CN^{2+}$ by various carboxylates, a correlation was noted between the formation constant and the pK_a of the carboxylic acid. A similar correlation is found here for K_{f1} and K_{f2} for the benzyl complex with the phosphates and acetate as given by eq 9, where pK_a is for the conjugate acid of the complexing anion.

$$\log(K_f) = 0.75(pK_a) - 1.76 \quad (9)$$

The kinetic results yield values for k_1 and k_2, and the problem is to determine if these can be assigned to a dominant pathway among the kinetically equivalent terms. This will be attempted by assuming that there are rational reactivity relationships between the rate constants for particular pathways which will depend on the properties of the $H_{n-x}A$ species involved.

It is simplest to start with the k_7 values for the acetate system because there is no reasonable kinetic ambiguity for this pathway. This reaction involves electrophilic attack of acetic acid on the acetato complex and is expected to have a transition state with the general structure of **I**, where X is H, *o*-CN, *m*-CN, or *p*-CN.



I

The specific rate constants k_{c1} $(=k_7/K_{f1})$ are given in Table III and show a relative reactivity of 1:0.36:0.21:0.038 for X = H, *m*-CN, *p*-CN, and *o*-CN, respectively. This pattern can be rationalized on the basis of the inductive withdrawing power of the –CN substituent, which will make electrophilic attack at CH_2 less favorable. The effect is accentuated by resonance for the *p*-CN and *o*-CN systems, and the reactivity of the latter may be further reduced by steric inhibition for approach of HOAc to the CH_2.

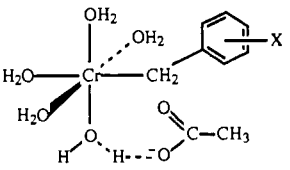
The values of k_{c1} provide some upper limits on the other rate constants k_{b1} and k_{b1}' which also involve electrophilic attack by H_3O^+ and HOAc, respectively. Since k_3 (eq 5) is not detected for this system, the implication is that $k_{b1} < k_{c1}[OAc]_{tot}(K_{a1} + [H^+])^{-1}$ and $k_{b1}' < k_{c1}K_{f1}K_{a1}[OAc]_{tot}(K_{a1} + [H^+])^{-1}$. To establish upper limits, one can use the lowest experimental $[OAc]_{tot}$ (0.10 M) and pH (~2.0) to calculate that $k_{b1} < 10k_{c1}$ and $80k_{b1}' < k_{c1}$. The latter inequality indicates that replacement of coordinated acetate in **I** by H_2O reduces the electrophilic reactivity of HOAc by at least 80 times. A parallel argument may be applied to the reactivity of H_3O^+ in the k_H and k_{b1} terms to imply $k_{b1} > 80k_H$ $(=80 \times 1.7 \times 10^{-5}$ for $CH_2C_6H_5)$, which is easily consistent with the upper limit of $10k_{c1}$ $(=0.18$ for $CH_2C_6H_5)$. In other words, the failure to observe a k_3 term in the rate law does not present any anomalies in the reactivity patterns.

The k_7 term could not be evaluated in the $H_2PO_4^-/HPO_4^{2-}$ system, even though H_3PO_4 is ~300 times stronger an acid than HOAc. Least-squares analysis including the k_7 term in eq 7 provides an upper limit of $<5 \times 10^{-3}$ for k_{c1}. This is of the same magnitude as k_{c1} with HOAc but does not reflect the greater electrophilicity which might be expected for the more acidic H_3PO_4. There is a compensating factor in that the K_{f1} for $H_2PO_4^-$ is ~10^2 smaller than for OAc^-, so that $H_2PO_4^-$ coordination may not enhance the electrophilic susceptibility of the CH_2 as much as OAc^-.

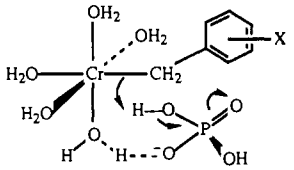
If a common mechanistic pathway is assumed for all of the phosphate systems, then one possibility is to assign k_2 to k_{a1}' and k_1 to k_{a2}' so that reaction always involves $(H_2O)_5Cr-R^{2+}$ with some phosphate species. For the benzyl complex, this gives k_{a1}' values of 4.4×10^{-2}, 0.10×10^{-2}, and 0.44×10^{-2} M^{-1} s^{-1} for $H_2PO_4^-$, $MeOPO_3H^-$, and OAc^-, respectively, and k_{a2}' values of 5.7×10^2 and 3 M^{-1} s^{-1} for HPO_4^{2-} and $MeOPO_3^{2-}$, respectively.

(13) Kita, P.; Jordan, R. B. *Inorg. Chem.* **1989**, *28*, 3489.
(14) Zhang, Z. Results to be published.

These make no sense in terms of an electrophilic mechanism (analogous to k_{c1}) because the more acidic species, $H_2PO_4^-$ and $MeOPO_3H^-$, are the least reactive, and $MeOPO_3^{2-}$ and OAc^- do not have an electrophilic proton. Furthermore, the rate constants are all larger than the upper limit estimate for the much more acidic H_3PO_4. With this assignment, the reactivity pattern indicates some type of nucleophilic attack because the more basic species are more reactive. A conjugate base type of mechanism proceeding through a structure such as **II** could be invoked, but then one would expect the more basic acetate ion to be more reactive than $H_2PO_4^-$, which is contrary to the observations. This problem, and the 200-fold reactivity difference between HPO_4^{2-} and $MeOPO_3^{2-}$, lead one to suspect that an ionizable proton is important for transition-state reactivity, and the reactive species could be a structure like **III**.

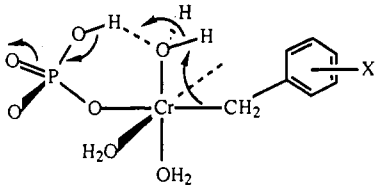


II



III

Another possibility is to assign k_1 and k_2 to k_{a2} and k_{a1}, respectively, and the reaction involves $(Y)(H_2O)_4Cr–R + H_2O$, where Y is acetate ion or a phosphate species. The effect of Y would be to increase the electron density at Cr(III) and favor breaking of the Cr–C bond. The values of k_{a2} and k_{a1} are given in Table III. For the mono- and dihydrogen phosphate species, the reactivity parallels the K_f values as might be expected, because stronger complexing should mean more electron donation from Y to Cr(III). But acetate ion and $MeOPO_3^{2-}$ are then much less reactive than expected from their basicity and K_f values. This again points to the importance of an ionizable proton on Y. It is difficult to rationalize how an ionizable proton on the trans ligand should greatly affect the reactivity. It conceivably could act through a structure such as **IV**, but the relative basicities of oxygen



IV

in coordinated water and phosphate would lead one to expect hydrogen bonding in the opposite sense (i.e. OH_2- - -O–P) and **IV** seems a rather unlikely candidate for a highly reactive structure.

Finally, we consider the possibility that k_2 is assigned to k_{b2}. This assignment involves reaction of H_3O^+ with $(HPO_4)Cr–R$ or $(MeOPO_3)Cr–R$, with k_{b2} values of 168 and 3.8 M^{-1} s^{-1}, respectively, for the benzyl complex. Again one is faced with the difficulty of rationalizing the large kinetic difference due to the replacement of H– by Me– on the trans ligand.

Much of this discussion has emphasized the involvement of cis-H_2O ligands, but it should be acknowledged that there is conflicting evidence on this involvement from other systems. Earlier, Ogino et al.[15] and Rotman et al.[4b] found that the EDTA complexes of Cr–R undergo heterolysis at rates similar to that of the parent pentaaqua complex and suggested that cis-H_2O ligands are not important. Recently, Espenson and co-workers[16,17] found that the *trans*-([15]aneN$_4$)$(H_2O)Cr–R^{2+}$ complexes are very resistant to heterolytic cleavage by H_2O or H_3O^+ and suggested that cis-H_2O ligands are important for heterolytic reactivity. More relevant to the present work are the reports of Cohen and co-workers[4b,c] that the heterolysis of *trans*-([15]-aneN$_4$)$(H_2O)Cr–R^{2+}$ (R = $C(CH_3)_2OH$ or CH_2OH) is catalyzed by acetate ion, but there are several problems with these reports. Our analysis indicates that the published data[4b] (R = $C(CH_3)_2$-OH) do not adequately[18] fit the expected rate law. The protolytic equilibrium at pH 4–6 found by Espenson et al.[16] for analogous systems was not reported by Cohen et al. for either system in acetate buffers. The spectrum published by Cohen et al.[4b] of the complex with R = $C(CH_3)_2OH$ is quite different from that reported by Espenson et al.[17] for R = CH_2OH and $CHCH_2OH$. Espenson et al.[17] were unable to isolate the complex with R = $C(CH_3)_2OH$ and attributed this to rapid homolysis.[19] They found that the R = $CHCH_3OH$ complex undergoes decomposition by β-elimination, and the same may be true for R = $C(CH_3)_2OH$. The data[4b] and graphs[4c] presented by Cohen et al. indicate that decomposition in the absence of acetate ion has k_{obsd} of ~0.04 and ~0.2 s^{-1} at pH 5.1 for R = CH_2OH and $C(CH_3)_2OH$, respectively. However, Espenson et al.[17] found negligible decomposition in 6 h in acidic solution for R = CH_2OH. This shows that the decomposition at pH 5.1 cannot be due to heterolysis of *trans*-([15]aneN$_4$)$(H_2O)Cr–CH_2OH^{2+}$ and is probably a reaction of *trans*-([15]aneN$_4$)$(OH)Cr–CH_2OH^+$.

The overall picture that emerges from our results is that the dominant factor influencing the reactivity enhancement for heterolysis is the basicity of the $H_{n-x}A^{x-}$ species. However, a comparison of $H_{n-x}A^{x-}$ with ionizable protons and the fully deprotonated species A^{n-} reveals that the former are substantially more reactive than expected from basicity considerations. This is most consistent with a reactive state like **III** for the $H_{n-x}A^{x-}$ species with k_2 and k_1 assigned to k_{a1}' and k_{a2}'. It should be noted that the *o*-CN complex has the smallest rate constant with this choice and the reactivity pattern parallels that of k_{c1} for HOAc. This might be expected on the basis of the structural similarity of **I** and **III**.

For the deprotonated species A^{n-} (OAc^- and $MeOPO_3^{2-}$), the choice between k_{ax} and k_{ax}' remains ambiguous. For the k_{ax} assignment one expects a correlation of rate constant with trans-ligand basicity, and one finds that the ratio $k_{a2}(MeOP-O_3^{2-})/k_{a1}(OAc^-) = 73$ is almost identical to 79, the ratio of the K_a's of their conjugate acids. If this correlation is extended to the protonated ligands, one obtains k_{ax} values of 4×10^{-8}, 1.6×10^{-7}, and 2×10^{-2} for $MeOPO_3H^-$, $H_2PO_4^-$, and HPO_4^{2-}, respectively. These are all lower than the experimental values as expected if protonated forms have enhanced reactivity and indicate that the k_{ax} path may only make a significant contribution for HPO_4^{2-}, which has $k_{a2} = 13 \times 10^{-2}$. Therefore, the k_{ax} assignment for OAc^- and $MeOPO_3^{2-}$ seems reasonable and does not cause any inconsistencies with the k_{ax}' assignment for the protonated species.

Finally, the effect of acetate ion on the homolysis reaction will be discussed. Again there is a kinetic ambiguity between the paths involving $(OAc)Cr–R^+ + H_2O$ (k_{1h}) and $(H_2O)Cr–R^{2+} + OAc^-$ (k_{1h}'). Since the kinetic effect of acetate ion is small, most of the runs were done at high $[OAc^-]$ so that $K_{f1}[OAc^-] > 1$.

(15) Ogino, H.; Shimura, M.; Tanaka, N. *Inorg. Chem.* **1982**, *21*, 126.
(16) Shi, S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1990**, *29*, 4318.
(17) Huston, P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1991**, *30*, 4826.

(18) Least-squares analysis gives a best-fit in which 7 of the 18 experimental rate constants deviate by more than 20% from the predicted best-fit value.
(19) Some of the differences in observations can be attributed to the fact that Cohen et al. studied products from in situ reactions of Cr(II), [15]aneN$_4$, and acetate + H_2O_2, while Espenson et al. isolated the products by chromatography before studying their reactions. The in situ oxidation explains the failure to observe the protolytic equilibrium, and it may produce a mixture of geometrical isomers and species of variable acetate composition. Complications due to *cis* and *trans* isomers have been suggested by: Richens, D. T.; Adzamli, I. K.; Leupin, P.; Sykes, A. G. *Inorg. Chem.* **1984**, *23*, 3065.

Therefore, most of the data are in the saturation region where the expression $(k_{1h}' + k_{1h}K_{f1})[OAc^-]/(K_{f1}[OAc^-] + 1)$ gives the value of k_{1h}'/K_{f1} or k_{1h}, depending on the assignment. These values are given in Table IV. For the benzyl, *m*-CN, and *p*-CN systems, k_{1h}'/K_{f1} or k_{1h} is 1.5–2.5 times larger than k_{0h}, but for the *o*-CN system the value is actually smaller than k_{0h}. Espenson et al.[16] observed that the trans-OH^- in several ([15]aneN_4)(OH)-Cr–R^+ complexes strongly suppresses homolysis and favors heterolysis relative to the trans-OH_2 system. This would appear to be due to stabilization of the Cr(III) oxidation state relative to Cr(II) by the *trans* ligand. A similar effect might be expected for acetate ion, so that one could expect k_{1h} to be smaller than k_{0h}. The relative balance of k_{1h} and k_{1h}' will determine whether one finds an increased or decreased rate of homolysis with increasing concentrations of acetate ion. This does not permit a separation of k_{1h} and k_{1h}', but it does provide a rationalization for the reactivity difference of the *o*-CN system. It may be that the k_{1h}' pathway is inhibited by the *o*-CN substituent by the same steric and electronic factors suggested for heterolysis by the k_{c1} pathway. Then the k_{1h} contribution may dominate and cause the inhibition to homolysis observed for the *o*-CN complex.

Experimental Section

Materials. Aqueous solutions of $[(H_2O)_5Cr–CH_2C_6H_4X]^{2+}$ (X = H, *o*-CN, *m*-CN, *p*-CN) 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. Tests with the *p*-CN system showed that the mixture before ion exchange gives the same decomposition kinetics as the purified solution.

The acetate/acetic acid buffers were prepared from solutions of sodium acetate trihydrate (BDH) by adding standardized perchloric acid to obtain the desired pH. The initial solutions contained enough sodium perchlorate to give a final ionic strength of 1.0 M. The phosphate buffers were prepared similarly from NaH_2PO_4 (Fisher) by adding sodium hydroxide or $HClO_4$ to obtain the desired pH. The disodium methyl phosphate was prepared by reaction of aqueous Na_3PO_4 with dimethyl sulfate as described by Bailly.[20] The barium salt was isolated by addition of $BaCl_2$ and converted to the sodium salt by treatment with Na_2SO_4. The concentration of Na_2MeOPO_3 in stock solutions was determined by titration with standardized HCl with methyl orange indicator. Sodium perchlorate and $HClO_4$ were added to these solution to obtain the desired ionic strength and pH.

Kinetic Measurements. The absorbance decrease at 356 nm 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 analyzed by nonlinear least squares to a first-order model.

The dependence of the experimental rate constants on pH and H_nA concentration has been analyzed by standard least-squares methods, and the errors quoted are one standard deviation. For this analysis the following pK_a values were used: HOAc, 4.73; H_3PO_4, 2.12, $H_2PO_4^-$, 7.21; $MeOPO_3H_2$, 1.52, $MeOPO_3H^-$, 6.58.

For the heterolysis reaction, 10 mL of buffer and sodium perchlorate, to control ionic strength, was placed in the cell, sealed with serum caps, and deoxygenated for 20 min by bubbling purified argon. Then syringes were used to add aqueous chromium(II) perchlorate and $[(H_2O)_5Cr–CH_2C_6H_4X]^{2+}$ to give final concentrations of 2×10^{-3} M and $(0.6–1) \times 10^{-4}$ M, respectively. For the homolysis, the chromium(II) was omitted and the reaction solution was exposed to air throughout the run.

Acknowledgment. The authors acknowledge the financial support for this work from the Natural Sciences and Engineering Research Council of Canada.

Supplementary Material Available: Tables of total acetate or phosphate species concentration, pH, and experimental and calculated rate constants (Tables S1–S11) (10 pages). Ordering information is given on any current masthead page.

(20) Bailly, O. *Bull. Soc. Chim. Fr.* **1919**, *25*, 240; **1920**, *27*, 744.