Kinetics of the Heterolysis and Homolysis of Pentaaqua(benzyl)chromium(III) in Acetate Buffers

Zhongsheng Zhang and R. B. Jordan*
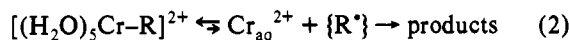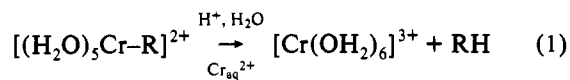
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

The kinetics of the heterolysis and homolysis of pentaaqua(benzyl)chromium(III) have been studied in acetate/acetic acid buffers (pH 3.0–5.0) at 25 °C and ionic strength 1.0 M (NaClO$_4$). Both reactions show saturation kinetics for the acetate dependence of the pseudo-first-order rate constant, which is consistent with formation of an acetato complex with a formation constant $K_f = 65 \pm 6$ M^{-1}. The pH and acetate dependences of the heterolysis are described by the rate law $k_{obsd} = (K_f[\text{OAc}^-] + 1)^{-1}(a[\text{OAc}^-] + c[\text{H}^+][\text{OAc}^-]^2)$ with $a = (4.5 \pm 2.4) \times 10^{-3}$ M^{-1} s^{-1} and $c = (6.2 \pm 0.2) \times 10^4$ M^{-3} s^{-1}. The dominant c pathway is ascribed to acetic acid acting as an electrophile toward [(OAc)(H$_2$O)$_4$Cr–CH$_2$C$_6$H$_5$]$^+$; thus $c = k_c K_f/K_a$, where K_a is the ionization constant of acetic acid and $k_c = (1.9 \pm 0.06) \times 10^{-2}$ M^{-1} s^{-1}. The a pathway may be due to [(OAc)(H$_2$O)$_4$Cr–CH$_2$C$_6$H$_5$]$^+$ + H$_2$O or to [(H$_2$O)$_5$-Cr–CH$_2$C$_6$H$_5$]$^{2+}$ + OAc$^-$. In the former case, the specific rate constant $k_a = a/K_f = (6.9 \pm 3.6) \times 10^{-5}$ M^{-1} s^{-1}, while, for the latter, $k_d = a$. The latter pathway has not been considered previously, but it is favored in the present interpretation on the basis of rate constant comparisons to other systems. For the homolysis, the acetate-dependent pathway is assigned to homolysis of [(OAc)(H$_2$O)$_4$Cr–CH$_2$C$_6$H$_5$]$^+$ with $k_1 = (3.6 \pm 0.08) \times 10^{-3}$ s^{-1}. The acetato complex undergoes homolysis only 1.8 times faster than its parent [(H$_2$O)$_5$Cr–CH$_2$C$_6$H$_5$]$^{2+}$.

Introduction

Organometallic complexes of pentaaquachromium(III) are known[1] to undergo Cr–C bond breaking in aqueous solution by either heterolysis (eq 1) or homolysis (eq 2). Since Cr$_{aq}^{2+}$

$$[(\text{H}_2\text{O})_5\text{Cr–R}]^{2+} \xrightarrow[\text{Cr}_{aq}^{2+}]{\text{H}^+, \text{H}_2\text{O}} [\text{Cr(OH}_2)_6]^{3+} + \text{RH} \qquad (1)$$

$$[(\text{H}_2\text{O})_5\text{Cr–R}]^{2+} \rightleftharpoons \text{Cr}_{aq}^{2+} + \{\text{R}^\bullet\} \rightarrow \text{products} \qquad (2)$$
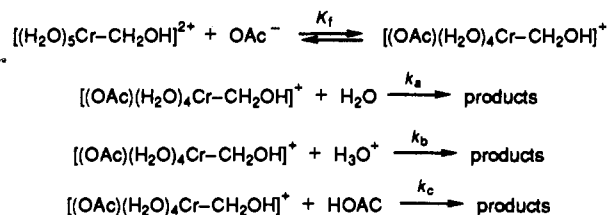
suppresses the homolysis reaction, the heterolysis can be studied by adding Cr$_{aq}^{2+}$ to the system. The heterolysis reaction typically shows pathways which are independent and first order in [H$^+$]. The homolysis can be promoted by the addition of scavengers for either Cr(II) or (R$^\bullet$), and then the observed decomposition is a mixture of heterolysis and homolysis. The kinetics of the latter can be determined by difference from the two sets of conditions.

It was reported by Kochi and Buchanan[2] that acetate/acetic acid buffers effectively catalyze these decomposition reactions for the benzyl complex [(H$_2$O)$_5$Cr–CH$_2$C$_6$H$_5$]$^{2+}$ in ethanol–water mixtures. This study was done anaerobically, but without added scavengers for radicals (except possibly ethanol) or Cr(II). Recent work[3] has shown that homolysis has a larger rate constant than heterolysis for this system, so that Kochi and Buchanan were probably observing homolysis initially but heterolysis in the later stages of the reaction as Cr(II) increased and suppressed homolysis. This accounts for the mixture of products (toluene from heterolysis, bibenzyl from homolysis) that was observed.

Ogino et al.[4] studied the acetate/acetic acid dependence of the decomposition of [(H$_2$O)$_5$Cr–CH$_2$OH]$^{2+}$ in aqueous buffers and discussed the results in terms of the reaction pathways shown in Scheme I. This study was done in the presence of excess H$_2$O$_2$, which is a scavenger for Cr$_{aq}^{2+}$, but it is known[1] that heterolysis is still the dominant pathway for this system. The analysis gave $K_f = 11$ M^{-1}, $k_a = 1.12$ s^{-1}, $k_b < 2 \times 10^2$ M^{-1} s^{-1}, and $k_c = 0.6$

Scheme I

$$[(\text{H}_2\text{O})_5\text{Cr–CH}_2\text{OH}]^{2+} + \text{OAc}^- \underset{\quad}{\overset{K_f}{\rightleftharpoons}} [(\text{OAc})(\text{H}_2\text{O})_4\text{Cr–CH}_2\text{OH}]^+$$

$$[(\text{OAc})(\text{H}_2\text{O})_4\text{Cr–CH}_2\text{OH}]^+ + \text{H}_2\text{O} \xrightarrow{k_a} \text{products}$$

$$[(\text{OAc})(\text{H}_2\text{O})_4\text{Cr–CH}_2\text{OH}]^+ + \text{H}_3\text{O}^+ \xrightarrow{k_b} \text{products}$$

$$[(\text{OAc})(\text{H}_2\text{O})_4\text{Cr–CH}_2\text{OH}]^+ + \text{HOAc} \xrightarrow{k_c} \text{products}$$

M^{-1} s^{-1}. The k_b path could not be characterized, presumably because of the small [H$_3$O$^+$] in the pH range 3.5–4.5 of the study.

In a series of papers, Cohen and co-workers[5] have further explored the heterolysis of [Cr–C(CH$_3$)$_n$(H)$_{2-n}$OH]$^{2+}$ systems and the effect of nonreacting ligands such as acetate, nta, and [15]aneN$_4$ on the reaction kinetics and volumes of activation. In the most recent study[5c] of [(H$_2$O)$_5$Cr–CH$_2$OH]$^{2+}$, Cohen et al. found $K_f = 26$ M^{-1} and $k_a = 0.94$ s^{-1}, with $\Delta V^\circ(K_f) \approx 6$ and $\Delta V^*(k_a) \approx 8$ cm^3 mol^{-1}. The latter value was taken as indicative of dissociative activation for the heterolysis reaction; however, subsequent discussion here indicates that this reaction may be proceeding by a mechanistically different but kinetically equivalent pathway.

The present study is an investigation of the effect of acetate/acetic acid buffers on both the heterolysis and homolysis of the benzyl complex [(H$_2$O)$_5$Cr–CH$_2$C$_6$H$_5$]$^{2+}$. This system differs from [(H$_2$O)$_5$Cr–CH$_2$OH]$^{2+}$ in that homolysis is the dominant process[3] in the absence of Cr(II), so that the effect of acetate on both decomposition modes can be studied. For applications of these systems to generate aqueous organic radicals, it would be very useful if the homolysis could be controlled by the addition of complexing ions. The earlier work of Kochi and Buchanan[1] suffers from the uncertain mixture of heterolysis and homolysis that was being observed.

Results and Analysis

The decomposition of [(H$_2$O)$_5$Cr–CH$_2$C$_6$H$_5$]$^{2+}$ was monitored spectrophotometrically in aqueous solutions containing varying

(1) Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 1.
(2) Kochi, J. K.; Buchanan, D. *J. Am. Chem. Soc.* **1965**, *87*, 853.
(3) Kita, P.; Jordan, R. B. *Inorg. Chem.* **1989**, *28*, 3489.
(4) Ogino, H.; Shimura, M.; Tanaka, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1063.

(5) (a) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1984**, *23*, 84. (b) Rotman, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1985**, *24*, 4158. (c) Cohen, H.; Gaede, W.; Gerhard, A.; Meyerstein, D.; van Eldik, R. *Inorg. Chem.* **1992**, *31*, 3805.

Table I. Kinetic Results for the Anaerobic and Aerobic Decomposition of $[(H_2O)_5Cr-CH_2C_6H_5]^{2+}$ in Acetate/Acetic Acid Solutions (μ = 1.0 M (NaClO$_4$), 25 °C)

[OAc]$_{tot}$, M	pH	[OAc], M	$10^3 k_{obsd}$, s^{-1} anaerobic[a]	aerobic[b]	homolysis[c]
0.04	4.73	0.020	0.259	3.17	2.91
0.10	4.73	0.050	0.676	3.82	3.14
0.20	4.73	0.100	1.40	4.74	3.34
0.40	4.73	0.200	3.22	6.59	3.37
0.60	4.73	0.300	5.08	8.70	3.62
0.80	4.73	0.400	7.89	11.35	3.46
1.00	4.73	0.500	9.56	13.41	3.85
0.60	4.04	0.102	7.68	11.10	3.42
0.60	4.36	0.180	7.08		
0.60	5.02	0.397	3.73	7.32	3.59
0.40	3.01	0.0073	2.35		
0.60	3.01	0.011	4.24	6.52	2.28
0.80	3.01	0.0146	6.71		
1.00	3.01	0.0183	8.97		

[a] Heterolysis rate constants under an argon atmosphere with 2 × 10^{-3} M Cr$_{aq}^{2+}$ present. [b] Exposed to air so that O$_2$ scavenges the immediate homolysis products. [c] Obtained from the difference of the anaerobic and aerobic runs.

amounts of total acetate and at pH 3.0–5.0 and 1.0 M ionic strength (NaClO$_4$) at 25.0 °C. The heterolysis reaction was studied under an argon atmosphere with solutions containing 2 × 10^{-3} M Cr$_{aq}^{2+}$ to suppress homolysis. The combination of homolysis and heterolysis was studied using O$_2$ from air as a scavenger for Cr$_{aq}^{2+}$ and radicals produced. The homolysis rate constants were determined by difference from the two types of studies for runs under the same acetate and pH conditions. The results are summarized in Table I.

The heterolysis data were analyzed initially in terms of the reactions in Scheme I, which predict that the pseudo-first-order rate constant will be given by eq 3 where [OAc] represents the

$$k_{obsd} = \frac{1}{K_f[OAc] + 1} \times$$
$$\left(k_a K_f[OAc] + k_b K_f[H^+][OAc] + \frac{k_c K_f[H^+][OAc]^2}{K_a} \right) \quad (3)$$

acetate ion concentration, K_a is the mixed acid dissociation constant of acetic acid (2.0 × 10^{-5} M),[6] and [H$^+$] = 10^{-pH}. From the observations of Ogino et al.,[4] one might expect the k_b term to be negligible, so that eq 3 can be simplified and rearranged to give eq 4. A plot of the left-hand side of eq 4 (with K_f = 65.3

$$k_{obsd} \frac{K_f[OAc] + 1}{[OAc]} = \left(k_a K_f + \frac{k_c K_f[H^+][OAc]}{K_a} \right) \quad (4)$$

M^{-1}, as determined from least-squares analysis of k_{obsd} in eq 3) versus [H$^+$][OAc] is shown in Figure 1, for our data, and for that of Ogino et al.[4] (K_f = 11 M^{-1}). Clearly this model gives a good fit of data. It is also apparent that the systems are different in that the plot for the $[(H_2O)_5Cr-CH_2C_6H_5]^{2+}$ system has only a marginally perceptible intercept, implying that the k_a path makes at most a small contribution. A least-squares analysis, including the k_a term, gives k_a = (6.9 ± 3.6) × 10^{-5} s^{-1}, K_f = 65.3 ± 6 M^{-1}, and $k_c K_f/K_a$ from which one calculates k_c = (1.9 ± 0.06) × 10^{-2} M^{-1} s^{-1}.

Under aerobic conditions in the absence of acetate, the homolysis reaction (k = 2 × 10^{-3} s^{-1})[7] is much faster than the heterolysis (k = 0.33 × 10^{-5} + 1.7 × 10^{-5}[H$^+$]).[3] However, acetate accelerates the rate of heterolysis to the extent that heterolysis makes a significant contribution under homolysis (aerobic) conditions. Therefore the heterolysis rate constants are subtracted from the experimental aerobic rate constant to
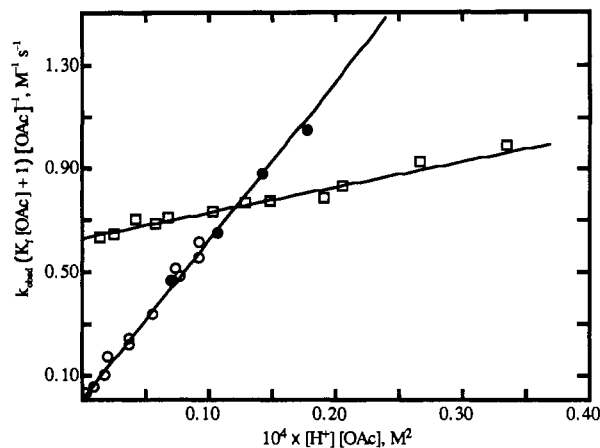
Figure 1. Variation of $k_{obsd}(K_f[OAc] + 1)[OAc]^{-1}$ with [H$^+$][OAc] as predicted by eq 4 for the heterolysis of $[(H_2O)_5Cr-CH_2C_6H_5]^{2+}$ (O, pH 4.0–5.0; ●, pH 3.01) and for $[(H_2O)_5Cr-CH_2OH]^{2+}$ (□, pH 3.5–4.5; ordinate values divided by 20; data from ref 4).

Scheme II
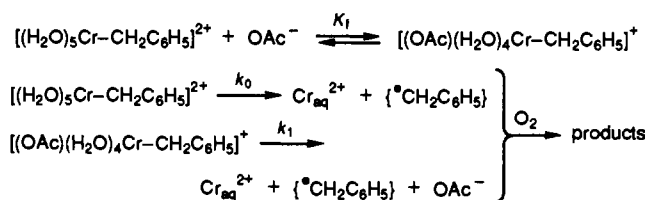
obtain the homolysis rate constants given in the last column of Table I. Examination of these values shows that they increase with increasing acetate ion concentration but level off to a constant value above about 0.10 M acetate. The maximum rate constant in the presence of acetate is only about 1.8 times larger than that in the absence of acetate so that the pathway not involving acetate must be retained in the model in Scheme II to describe the homolysis results.

Scheme II predicts that the pseudo-first-order rate constant for homolysis should be given by eq 5. Since k_0 has been

$$k_{obsd} = \frac{k_0 + k_1 K_f[OAc]}{K_f[OAc] + 1} \quad (5)$$

determined independently[7] and K_f has been evaluated from the heterolysis kinetics described above, k_1 is the only unknown in eq 5. A least-squares analysis gives k_1 = (3.6 ± 0.08) × 10^{-3} s^{-1}, and the experimental results are compared to the calculated dependence on [OAc] in Figure 2.

Discussion

The results of this and related work are summarized in Table II. Since the effect of acetate complexing on homolysis had not been investigated previously, a significant new observation is that this effect is a rather minor enhancement of 1.8 on the homolysis rate constant of the benzyl complex.

Our results for the heterolysis are qualitatively similar to the observations of Kochi and Buchanan[2] in that the rate increases with increasing acetic acid concentration. The different conditions (35 vol % ethanol–water, variable LiOAc–LiCl, 28.3 °C) make quantitative comparisons difficult, but one run (ref 2, Table II, 0.55 M HOAc, pH 3.00, k = 1.78 × 10^{-2} s^{-1}) has a rate constant ~4 times larger than the third last run in Table I at similar pH and HOAc conditions.

A comparison of the heterolysis pathways H$_3$O$^+$ + [(H$_2$O)$_5$Cr–R]$^{2+}$ (k_H) and HOAc + [(OAc)(H$_2$O)$_4$Cr–R]$^+$ (k_c) for R = CH$_2$OH[4] and CH$_2$C$_6$H$_5$ reveals that the HOAc reaction is close

(6) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1989; Vol. 6, p 300.

(7) Zhang, Z. Unpublished results in 1.0 M NaClO$_4$, using O$_2$, Fe(III), and (NH$_3$)$_5$CoBr^{2+} as scavengers under homolysis conditions.

Table II. Summary of Rate Constants at 25 °C for Heterolysis and Homolysis of $[(H_2O)_5Cr-R]^{2+}$ Systems

reaction		R		
		$CH_2C_6H_5$[a]	CH_2OH^B	$C(CH_3)_2OH^b$
Heterolysis				
$[(H_2O)_5Cr-R]^{2+} + H_2O$	k_w, s^{-1}	3.3×10^{-6} [c]	6.6×10^{-4}	3.3×10^{-3}
$[(H_2O)_5Cr-R]^{2+} + H_3O^+$	k_H, M^{-1} s^{-1}	1.7×10^{-5} [c]	4.65×10^{-4}	4.9×10^{-3}
$[(OAc)(H_2O)_4Cr-R]^+ + H_2O^d$	k_a, s^{-1}	6.9×10^{-5}	1.1^e $(0.95)^f$	
$[(H_2O)_5Cr-R]^{2+} + OAc^-$ ^{d}	k_d, M^{-1} s^{-1}	4.5×10^{-3}	12.1^e $(24.7)^f$	2.1×10^2
$[(OAc)(H_2O)_4Cr-R]^+ + HOAc$	k_c, M^{-1} s^{-1}	1.9×10^{-2}	0.6^e	
Homolysis				
$[(H_2O)_5Cr-R]^{2+}$		2.0×10^{-3} [c]	3.7×10^{-5}	0.13
$[(OAc)(H_2O)_4Cr-R]^+$		3.6×10^{-3}		

^{a} This work in 1.0 M NaClO₄. ^{b} Values for ref 1 unless otherwise indicated. ^{c} Zhang, Z. Unpublished work in 1.0 M NaClO₄. ^{d} There is a kinetic ambiguity between k_a and k_d as discussed in the text. ^{e} Taken from ref 4 in 1 M LiClO₄. ^{f} Taken from ref 5c in 0.5 M NaClO₄.
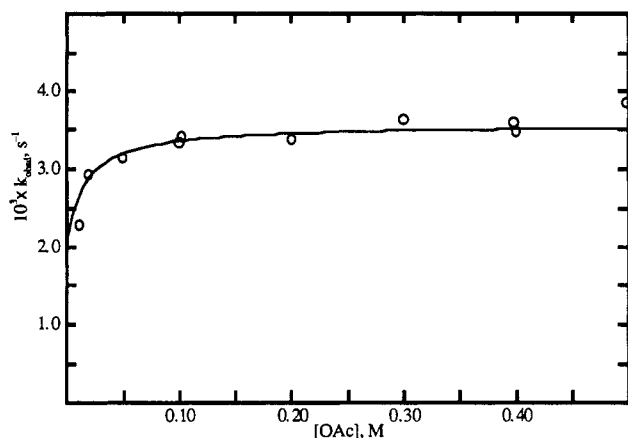

Figure 2. Variation of the rate constant for homolysis of $[(H_2O)_5Cr-CH_2C_6H_5]^{2+}$ with acetate ion concentration. The curve is calculated on the basis of a least-squares fit to eq 5.

to 1.2×10^3 times more effective in both systems. However, the H₂O pathways (k_a and k_w) in these systems reveal no such consistency. For R = CH₂OH, the pathway involving acetate ion has a 1.7×10^3 times larger rate constant, whereas this factor is only 21 for R = CH₂C₆H₅. This leads one to question whether the –OH function is such an innocent bystander for the reaction involving acetate ion or whether the kinetics have been properly interpreted.

It is known[1] that changing from R = CH₂OCH₃ to RCH₂OH increases the heterolysis rate constant from $<10^{-6}$ to 6.6×10^{-4} s^{-1}, and such effects have been attributed[5a,8] to stabilization of the transition state through hydrogen bonding of the –OH to cis ligands on chromium. Complexation by acetate would enhance this effect by making the cis H₂O ligands more basic, but it is not clear that the further rate enhancement would be so large. A comparison of $[(edta)Cr-R]^{2-}$ [9] or cis-$[(nta)(H_2O)Cr-R]^-$ [5c] and $[(H_2O)_5Cr-R]^{2+}$ complexes[8] (R = CH₂OH, CH(CH₃)OH, C(CH₃)₂OH) reveals that heterolysis is affected by modest factors of <5. Therefore, it seems suprising that a single coordinated acetate would increase the heterolysis rate constant by a factor of 1.7×10^3 in the $[(H_2O)_5Cr-CH_2OH]^{2+}$ system.

It has not been previously recognized that the k_a path in Scheme I is kinetically equivalent to reaction 6, in which acetate ion is reacting with the uncomplexed chromium complex. Then eq 3

$$[(H_2O)_5Cr-R]^{2+} + OAc^- \xrightarrow{k_d} \text{products} \qquad (6)$$
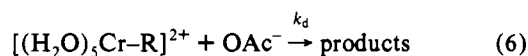
must be modified by the addition of the term $k_d[OAc]/(K_f[OAc] + 1)$, and there is a kinetic ambiguity between k_d and k_aK_f. If this term is assigned exclusively to k_d, then one obtains values of 4.5×10^{-3}, 12, 140, and 210 M^{-1} s^{-1} for R = CH₂C₆H₅, CH₂OH,

CH(CH₃)OH, and C(CH₃)₂OH, respectively, and the ratios of k_d to k_w are 1.4×10^3, 1.8×10^4, 7.4×10^4, and 6.4×10^4 M^{-1}, respectively. This analysis implies that the acetate catalysis is somewhat enhanced by an α-OH on the alkyl group, but by a factor of 10–40 rather than 1.7×10^3 as required by the k_a pathway assignment. The k_d reaction might proceed by a conjugate base mechanism, with acetate ion acting as a base toward a coordinated water ligand. This pathway might be enhanced by hydrogen bonding of the conjugate base and the α-OH, Cr–OH- - -HO-C. For the cis-$[(nta)(H_2O)Cr-R]^-$ systems,[5a] the k_d to k_w ratio drops to $\sim 10^2$, which is consistent with the expected lower acidity of the cis H₂O in the nta complexes.

The above assumption that $k_d \gg k_aK_f$ is not necessarily universally true, but it is suggested to be reasonably valid for acetate and bases of similar basicity. The mechanistic suggestion involving eq 6 predicts that other bases should catalyze the heterolysis of these complexes and that the magnitude of this catalysis should correlate with the pK_a of the conjugate acid of the base until the basicity drops to a level where k_aK_f becomes significant or dominant.

Experimental Section

Materials. Aqueous solutions of $[(H_2O)_5Cr-CH_2C_6H_5]^{2+}$ were prepared by mixing 40 mL of deoxygenated methanol containing 2 mmol of benzyl bromide with 20 mL of 0.3 M chromium(II) perchlorate in water, prepared by amalgamated zinc reduction of aqueous chromium(III) perchlorate. After $\sim$10 min at ambient temperature, the solution had changed from pale blue to dark greenish yellow, and it was loaded onto a column (8 × 2 cm) of Dowex 50W-X2 (200) ion-exchange resin in either the H$^+$ or Na$^+$ form under an argon atmosphere at 0 °C. Excess Cr(II) was eluted with 0.6 M NaClO₄ in 0.01 M HClO₄, and the desired product was eluted with 1.0 M NaClO₄ in 0.01 M HClO₄. The product was stored at –10 to –15 °C.

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 sufficient sodium perchlorate to give a final ionic strength of 1.0 M.

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 procedures to a first-order model.

For the heterolysis reaction, 10 mL of acetate buffer and sodium perchlorate, to control ionic strength, were placed in the cell, which was sealed with serum caps, and the mixture was deoxygenated for 20 min by bubbling purified argon. Then syringes were used to add aqueous chromium(II) perchlorate and $[(H_2O)_5Cr-CH_2C_6H_5]^{2+}$ to give final concentrations of 2×10^{-3} and 1×10^{-4} M, respectively. For the homolysis, the chromium(II) was omitted and the reaction solution was exposed to air throughout the run.

(8) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.

(9) Ogino, H.; Shimura, M.; Tanaka, N. *Inorg. Chem.* **1982**, *21*, 126.