J. Am. Chem. Soc. **1982**, *104*, 1249–1255

Homolysis and Acidolysis Reactions of (α-Hydroxyalkyl)- and (α-Alkoxyalkyl)chromium(III) Complexes: Kinetics, Steric Effects, and Bond Energies[1]

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Abstract: The rates of homolysis of 12 organochromium complexes were determined by the addition of oxidizing scavengers to prevent recombination of Cr^{2+} and the carbon-centered radicals. The rate constants for complexes derived from aliphatic alcohols span the range 3.7×10^{-5} s^{-1} for $CrCH_2OH^{2+}$ to $\sim 3 \times 10^2$ s^{-1} for $CrC(CH_3)(t\text{-}C_4H_9)OH^{2+}$ at 25 °C. There is a good correlation between the free energies of activation for homolysis of the organochromium complexes and corresponding substituted symmetrical ethanes. On the basis of the activation parameters and the literature data, estimates of the Cr–C bond dissociation enthalpies were made. Rate constants for the acidolysis reaction, previously known for some of these complexes, were evaluated for the others. Means were developed, by control of reaction conditions, to permit independent measurements of homolysis and acidolysis. The organochromium complex derived from isopropyl ether, $CrC(CH_3)_2OCH(CH_3)_2{}^{2+}$, undergoes a rapid ($0.05 < k < 2$ s^{-1}) conversion to $CrC(CH_3)_2OH^{2+}$ in dilute perchloric acid.

Among the most fundamental reactions that a metal–alkyl complex can undergo are the unimolecular (or solvent-assisted) processes leading to the cleavage of a metal–carbon bond. A complicating but intriguing aspect of this chemistry is found in a series of organochromium complexes in which the Cr–C bond may cleave by both heterolytic and homolytic reactions that can be made to occur concurrently under suitable conditions. In the general case that situation can be represented by the competitive dissociation of a M–R bond to $M^+ + {:}R^-$ (actually MOH + RH) vs. $M\cdot + \cdot R$.

It is useful first to consider one specific complex representative of those we have examined, $(H_2O)_5CrC(CH_3)_2OH^{2+}$. Under conditions in which the homolytic dissociation process predominates, the immediate products are Cr^{2+}(aq) and $\cdot C(CH_3)_2OH$. These species then undergo subsequent reactions with suitable substrates in steps which occur more rapidly than the rate-limiting homolysis reaction. On the other hand, the ultimate products of heterolytic dissociation in acidic, aqueous solution are Cr^{3+}(aq) and 2-propanol. The latter reaction is termed acidolysis in general, or protonolysis in the specific case in which H_3O^+ is the reactant. A determination of the mechanisms of the two processes is important in our developing an understanding of the chemical reactivity of metal alkyls toward dissociation and toward other reagents.

In our opinion a system that is to provide the discrimination we consider necessary must meet certain conditions. A sufficient number of closely related complexes must be available so that the steric and electronic requirements of each reaction type can be explored systematically. The previously characterized[2] α-hydroxyalkyl complexes $CrCH_2OH^{2+}$, $CrCH(CH_3)OH^{2+}$, and $CrC(CH_3)_2OH^{2+}$ are the first members of such a series; by the use of analogous reactions we have extended it to include several other members of the family $CrC(R^1R^2)OH^{2+}$. Closely related to this group of complexes are the α-alkoxyalkyl analogues consisting of the previously known[2] $CrCH(CH_3)OC_2H_5{}^{2+}$ along with other members of the family $CrC(R^1R^2)OR^{2+}$. A second requirement, and perhaps the more important, is the development of experimental methods to permit the rate constants for the two alternative modes of reaction, homolysis and acidolysis, to be independently determined with good accuracy for the same complexes. The development of the techniques required to attain that end is given in this paper.

The variation of the rate constants for either of the reactions along such a homologous series can be examined in terms of parameters which are known to reflect the steric and electronic effects. This was done[3] earlier for the homolysis reactions of a series of para-substituted benzylchromium ions, $(H_2O)_5CrCH_2C_6H_4Z^{2+}$, in which the electronic influences of the para ring substituent Z was accurately reflected by a linear free energy correlation using the Hammett equation ($\rho = 1.01$). In the alkyl complexes, however, steric effects will certainly play a substantial role, which we sought to quantify through these studies.

Results

Organochromium Ions. The complexes studied in the course of this work were either previously reported[2,4,5] species or closely related analogues prepared by the same general method. That route is referred to as the modified Fenton's reagent method and consists of the reaction of aqueous solutions of Cr^{2+} and H_2O_2 containing a low concentration, 0.01–1 M, of an alcohol or ether. Some of the organochromium complexes are sufficiently stable that they can be isolated by cation-exchange chromatography and characterized on the basis of the products of various reactions they undergo.[2,6] Others, particularly the highly substituted analogues, have such short lifetimes that the evidence for their formation is based primarily upon their UV–vis absorption spectrum which is similar for all the complexes studied.[2,5,6] The main spectral features consist of absorption bands at 395 ± 10 nm (ϵ 200–700 M^{-1} cm^{-1}) and 300 ± 15 (ϵ 1500–2800). Their composition is inferred from the free-radical reactions employed in their preparation and confirmed in some instances by a determination of reaction products with[6] and without other reagents present. Radicals formed by hydrogen abstraction from other than the α carbon are either β-hydroxyalkyls which oxidize Cr^{2+} to Cr^{3+} with accompanying olefin formation or else radicals which form a low concentration of an unreactive organochromium complex. Fortunately, the observations for those complexes which are sufficiently stable for chromatographic separation and purification give identical rate constants whether so purified or not, which we take as evidence in support of the methods used for the nonisolable, short-lived members of the family.

Reaction Control. It has proved possible, by the selection of reaction conditions and the addition of other reagents, to control which process, acidolysis or homolysis, dominates the experimental

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0002-7863/82/1504-1249$01.25/0

Table I. Variation of the Nature and Concentrations of the Oxidizing Scavengers to Promote "Homolysis Conditions" for Two (α-Hydroxyalkyl)chromium(III) Ions[a]

	$CrC(CH_3)(C_2H_5)OH^{2+}$		$CrC(CH_3)_2OH^{2+}$	
ox	range of 10^3[ox]/M	k_H[b]/s^{-1}	range of 10^3[ox]/M	k_H[c]/s^{-1}
$Co(NH_3)_5F^{2+}$			4-10	0.128 ± 0.003
$Co(NH_3)_5Cl^{2+}$	2.0-11	0.90 ± 0.02	4-10	0.127 ± 0.004
$Co(NH_3)_5Br^{2+}$	1.0-12	0.94 ± 0.03		
H_2O_2	10-60	0.90 ± 0.07	130-750	~0.13[e]
VO^{3+}			5-99	0.128 ± 0.004
Cu^{2+}	20-100	0.96 ± 0.05[d]	4-100	0.138 ± 0.011[d]
Fe^{3+}	24-69	0.92 ± 0.10[d]	17-74	0.120 ± 0.016[d]
		av 0.92 ± 0.03		av 0.127 ± 0.003

[a] At 25 °C, 1.00 M ionic strength, 1.0 M 2-butanol or 2-propanol. [b] $k_H = k_{obsd} - k_A$, with $k_A = 0.055$ s^{-1} at $[H^+] = 0.100$ M, as in these experiments. [c] $k_H = k_{obsd} - k_A$, with k_A as in Table IV over the range of $[H^+]$ studied for homolysis, 0.10-0.96 M. [d] By least-squares extrapolation to zero concentration of oxidizing agent. [e] At high $[H_2O_2]$, small amounts of a direct reaction are seen, the highest value being $k_H = 0.15$ s^{-1} at 0.75 M H_2O_2; the value given is extrapolated to $[H_2O_2] = 0$.

observations in nearly every system. Because they are central to all the individual results that follow, these methods will be described first.

In most of the systems, the unsubstituted complexes $CrCH_2OH^{2+}$ and $CrCH_2OCH_3^{2+}$ being exceptions, homolysis occurs more rapidly than acidolysis. But the former reaction, being reversible, can be inhibited by addition of Cr^{2+}(aq), a product of homolytic scission. The mass law retardation effect produced by added Cr^{2+} is sufficient to repress nearly completely the contribution of homolysis to the observed rate constant. The residual reaction, measured directly under what we thus term "acidolysis conditions", is essentially acidolysis alone.

The other experimental goal, the determination of the rate constant for homolysis, can be realized also by the use of added reagents. Addition of a substance which reacts with either or both of the homolysis fragments prevents their recombination; the homolysis reaction thus is drawn to completion by chemical scavenging of its products. Cobalt(III) complexes such as $Co(NH_3)_5X^{2+}$ (X = F, Cl, and Br) are particularly useful in this context, since they do not react directly with the organochromium ions; hydrogen peroxide, which reacts only slightly if at all by direct attack, is also successful. Other metal ions such as Cu^{2+} and Fe^{3+}, which also react rapidly with Cr^{2+} and the organic radicals, can be employed although corrections are required for the direct reaction (if any, in the given case) by extrapolation to zero concentration. In the case of $CrC(CH_3)_2OH^{2+}$, VO^{2+} was also used. Addition of such scavenging reagents promotes what can be called "homolysis conditions", although the observed rate constant is the sum of those for the concurrent homolysis and acidolysis reactions, $k_{obsd} = k_H + k_A$. Provided the former is much larger, as it is in many of the cases studied, k_H can easily be calculated by making but a minor correction for k_A. Product analyses as well as the kinetic rate laws were used in several reactions to confirm the assignments made. In the case of $CrCH_2OH^{2+}$, where even under "homolysis conditions", homolysis is a minor pathway compared to acidolysis, the product analysis permits a direct determination of k_H, the rate constant for the homolysis reaction.

These matters are clarified if we consider the rate constants actually determined (at 25 °C, 1.00 M ionic strength) by using these methods for one complex. Return to the example used earlier and consider the following reactions:

Acidolysis:[2]

$$CrC(CH_3)_2OH^{2+} + H_2O \rightarrow CrOH^{2+} + CH(CH_3)_2OH \qquad (1)$$

$$CrC(CH_3)_2OH^{2+} + H_3O^+ \rightarrow Cr^{3+}(aq) + CH(CH_3)_2OH \qquad (2)$$

$$k_A = k_1 + k_2[H^+] = (3.3 \times 10^{-3} + (4.7 \times 10^{-3})[H^+])\ s^{-1}$$

Homolysis:

$$CrC(CH_3)_2OH^{2+} \rightleftarrows Cr^{2+} + \cdot C(CH_3)_2OH \qquad (3)$$

$$k_H = k_3 = 0.127\ s^{-1}$$

$$k_{-3} = 5.1 \times 10^7\ M^{-1}\ s^{-1}\ {}^{5}$$

Assume the addition of a reagent such as $Co(NH_3)_5Cl^{2+}$, which reacts rapidly with Cr^{2+}[7] and with the free radical:[8]

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} \xrightarrow{5H^+} CrCl^{2+} + Co^{2+} + 5NH_4^+ \qquad (4)$$

$$k_4 = 2.6 \times 10^6\ M^{-1}\ s^{-1}\ {}^{7}$$

$$Co(NH_3)_5Cl^{2+} + \cdot C(CH_3)_2OH \xrightarrow{4H^+} (CH_3)_2CO + Co^{2+} + Cl^- + 5NH_4^+ \qquad (5)$$

$$k_5 = 4 \times 10^7\ M^{-1}\ s^{-1}\ {}^{8}$$

The expression for the pseudo-first-order rate constant under homolysis conditions is $k_{obsd} = k_A + k_H$ since the net consumption of the homolysis fragments via eq 4 and 5 is much faster than their recombination via the reverse of eq 3 in the concentration ranges studied. In the example given, one notes that $k_{obsd} \simeq k_H$, since $k_H \gg k_A$. In this and other similar complexes, addition of the oxidizing agent produces a large increase in the observed rate constant, from $k_{obsd} \simeq k_A$ in its absence to $k_{obsd} \simeq k_H$.

On the other hand, if $Co(NH_3)_5Cl^{2+}$ or other scavengers for the reducing intermediates are not added, then the organic free radical may disproportionate (eq 6)[9] rather than recombine with Cr^{2+}

$$2\cdot C(CH_3)_2OH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH \qquad (6)$$

$$2k_6 \sim 10^9\ M^{-1}\ s^{-1}\ {}^{9}$$

In that case, with the steady-state approximation for the concentration of the radical, the observed first-order rate constant is

$$k_{obsd} = k_A + 2k_6\left(\frac{k_3}{k_{-3}[Cr^{2+}]}\right)^2[CrC(CH_3)_2OH^{2+}] \qquad (7)$$

Substitution of the typical concentrations, $[CrC(CH_3)_2OH^{2+}]_0 \sim 10^{-3}$ M and $[Cr^{2+}]_0 = 3 \times 10^{-3}$ M, reveals that the second term of eq 7 contributes about 0.1% of the value of k_A. The approximation $k_{obsd} = k_A$ under acidolysis conditions is thus very good.[10]

Homolysis Reactions. Values of k_{obsd} determined for the decomposition of $CrC(CH_3)(C_2H_5)OH^{2+}$ at $[H^+] = 0.10$ M and 1.0 M ionic strength in the presence of varying concentrations of several oxidizing scavengers are shown in Figure 1; each value of k_{obsd} is the average of about seven duplicate determinations. The data for H_2O_2, $Co(NH_3)_5Cl^{2+}$, and $Co(NH_3)_5Br^{2+}$ lie along

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(10) The most rapidly homolyzing complex, $CrC(CH_3)(t\text{-}C_4H_9)OH^{2+}$, may not be amenable to this treatment; for that reason the rate constant determined with added Cr^{2+} (~10 s^{-1} at 0.1 M H^+) may not consist solely of acidolysis and is not reported as such here.

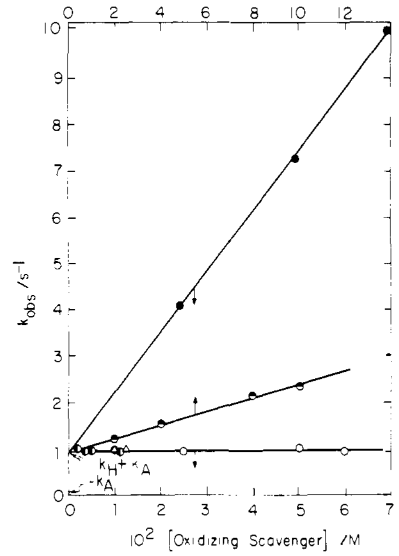

Figure 1. Values of the pseudo-first-order rate constants at 25 °C and 0.10 M H^+ (μ = 1.00 M) for decomposition of $CrC(CH_3)(C_2H_5)OH^{2+}$ in the presence of reagents which react indirectly, H_2O_2(○), $Co(NH_3)_5Cl^{2+}$(◐), and $Co(NH_3)_5Br^{2+}$(Δ), and in the presence of reagents which also react directly, Cu^{2+}(⊖) and Fe^{3+}(●). The common intercept is $k_H + k_A$; the latter value, determined independently, is shown by an arrow near the origin.

Table II. Rate Constants for the Homolytic Decomposition of $[(H_2O)_5CrC(R^1R^2)OR]^{2+\,a}$

complex	alcohol or ether precursor	formula R	formula R^1	formula R^2	$k_H{}^b/s^{-1}$
1	methanol	H	H	H	$(3.7 \pm 0.2) \times 10^{-5}$
2	ethanol	H	H	CH_3	$(8.5 \pm 0.3) \times 10^{-4}$
3	1-propanol	H	H	C_2H_5	$(1.01 \pm 0.04) \times 10^{-3}$
4	2-propanol	H	CH_3	CH_3	$(1.27 \pm 0.03) \times 10^{-1}$
5	2-butanol	H	CH_3	C_2H_5	$(9.2 \pm 0.3) \times 10^{-1}$
6	3-pentanol	H	C_2H_5	C_2H_5	8.39 ± 0.09
7	3-methyl-2-butanol	H	CH_3	i-C_3H_7	$(2.16 \pm 0.01) \times 10^1$
8	3.3-dimethyl-2-butanol	H	CH_3	t-C_4H_9	$\sim 3 \times 10^{2\,b}$
9	dimethyl ether	CH_3	H	H	$<10^{-6}$
10	diethyl ether	C_2H_5	H	CH_3	$(2.04 \pm 0.02) \times 10^{-3}$
11	diisopropyl ether	i-C_3H_7	CH_3	CH_3	5.77 ± 0.15
12	2.2.2-trifluoroethanol	H	H	CF_3	$<3 \times 10^{-5}$

[a] At 25.0 °C. 1.00 M ionic strength in solutions containing 0.01–1.0 M alcohol or ether. [b] Corrected as appropriate for contributions from the parallel acidolysis reactions. [c] Extrapolated from determinations at lower temperature.

the same horizontal line, showing that k_{obsd} is concentration independent. This value, 0.98 ± 0.03 s^{-1}, represents $k_H + k_A$, as discussed previously, although the latter amounts to only 0.055 s^{-1} under these conditions. The values of k_{obsd} in the presence of Cu^{2+} or Fe^{3+} vary linearly with concentration for this complex, as has been found for others.[6a] Least-squares extrapolation to zero concentration gives values of the intercept which correspond within experimental error to the same value of $k_H + k_A$. The details of the individual determinations for this complex and for $CrC(CH_3)_2OH^{2+}$ are given in Table I.

Similar experiments were done for each of the 11 organochromium complexes. In those cases where determinations were done at different [H^+], proper allowance was made for the [H^+]-dependent value of k_A in the calculation of k_H. The latter values, where determined as a function of hydrogen ion concentration, were independent of [H^+] throughout the range studied, 0.10 to 1 M. The values of k_H so determined are summarized in Table II.

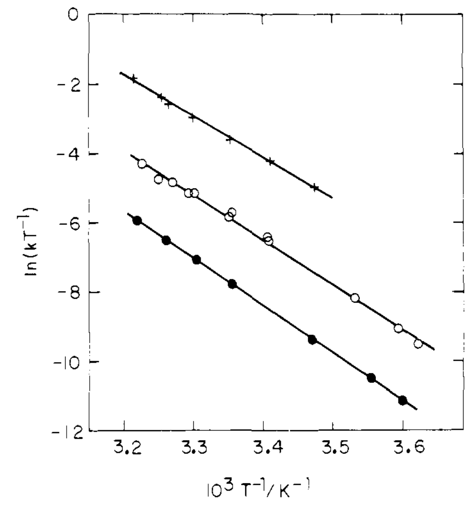

Figure 2. Plots of ln (k/T) vs. $1/T$ to determine the activation parameters according to activated complex theory. Data are shown for $CrC(CH_3)(C_2H_5)OH^{2+}$ (open circles), $CrC(CH_3)_2OH^{2+}$ (filled circles), and $CrC(C_2H_5)_2OH^{2+}$ (crosses).

Table III. Activation Parameters for the Homolysis of $[(H_2O)_5CrC(R^1R^2)OH^{2+}]$ at 1.00 M Ionic Strength and 0.10–0.98 M H^+

complex[a]	range[b] of T/°C	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal mol^{-1} K^{-1}
1	25.0–40.2 (2)	30	22
3	25.0–35.0 (2)	32.5	37
4	4.4–37.3 (9)	27.2 ± 0.1	28.6 ± 0.3
5	3.0–36.8 (15)	25.9 ± 0.5	27.9 ± 1.8
6	14.5–38.0 (7)	23.2 ± 0.5	23.6 ± 1.6
7	14.4–38.3 (5)	21.6 ± 0.4	20.1 ± 1.2
8	14.9–20.2 (3)	22	27
10	15.0–35.0 (3)	30.1 ± 0.1	30.2 ± 0.3
11	13.9–39.0 (11)	23.9 ± 0.7	25.2 ± 2.2

[a] From Table II. [b] Number of temperatures studied within the stated range is given in parentheses for each complex.

A modified procedure is required in the case of $CrCH_2OH^{2+}$ for which k_H is much smaller than k_A. In this case the rate constant under acidolysis conditions is 7.14×10^{-4} s^{-1} (25.0 °C, [H^+] = 0.10 M, μ = 1.0 M, with 1.0 M CH_3OH), compared to 7.49×10^{-4} s^{-1} in an otherwise identical experiment with 5.0×10^{-3} M $Co(NH_3)_5Cl^{2+}$. The difference can be taken as k_H = 3.5 ± 0.5 × 10^{-5} s^{-1}. Because of comparative inaccuracy owing to the differences involved, this number was confirmed by determining the yield of formaldehyde—a product of homolysis but not acidolysis—in a reaction to which $Co(NH_3)_5Br^{2+}$ was added. The yield[11] of 4.9% HCHO together with $k_{obsd} = 7.49 \times 10^{-4}$ s^{-1} gives $k_H = 3.7 \times 10^{-5}$ s^{-1} and confirms the less precise value determined from the kinetic difference.

The rate constants for homolysis proved to depend strongly on temperature. Figure 2 depicts for three of the complexes a plot of ln (k/T) vs. $1/T$, according to the equation of activated complex theory. The values of the activation parameters, calculated by a least-squares analysis, are given in Table III.

In view of the extensive product analysis done for the reactions[6] of these complexes with Cu^{2+}, Fe^{3+}, and Hg^{2+}, only a spot survey of typical reactions was required here. The yield of Co^{2+} produced from homolysis of $CrC(CH_3)_2OH^{2+}$ in the presence of $Co(NH_3)_5Cl^{2+}$ or $Co(NH_3)_5F^{2+}$ was exactly 2.00 times the initial concentration of the organochromium ion. This is consistent with the sequence of reactions shown earlier: eq 3–5. The reaction of 100 mL of 2.10×10^{-3} M $CrC(CH_3)_2OH^{2+}$ with excess $Co(NH_3)_5F^{2+}$ produces 0.212 mmol of CrF^{2+}, the correct species and amount expected from eq 4. Homolysis of CrC-

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[11] In this case $CrCH_2OH^{2+}$ was first isolated and purified by ion-exchang chromatography since formaldehyde is a minor byproduct of the synthesis. Removal is not complete, however, and the yield of HCHO cited in the text is the difference between that observed in the reaction containing scavenger (8.8% HCHO) and the blank experiment in its absence (3.9%).

Table IV. Rate Constants and Activation Parameters for the Acidolysis of $[(H_2O)_5CrC(R^1R^2)OR]^{2+}$

complex[a]	k_1 (25 °C), s^{-1}	$\Delta H_1^\ddagger$, kcal mol^{-1}	$\Delta S_1^\ddagger$, cal mol^{-1} K^{-1}	k_2 (25 °C), M^{-1} s^{-1}	$\Delta H_2^\ddagger$, kcal mol^{-1}	$\Delta S_2^\ddagger$, cal mol^{-1} K^{-1}
1	6.6×10^{-4} [b]			4.65×10^{-4} [b]		
2	1.90×10^{-3} [b]			1.22×10^{-3}		
3	3.17×10^{-3} [b]			2.14×10^{-3}		
4	3.3×10^{-3} [b]	17.1 ± 0.7	−11 ± 2	4.7×10^{-3} [b]	19.4 ± 0.8	−5 ± 2
5	8×10^{-3}			0.469	15.6 ± 1.2	−8 ± 4
6	3×10^{-2}			0.858	12.1 ± 0.1	−18.3 ± 0.5
7	3.5×10^{-2}	19.7 ± 2.2	0.5 ± 7.5	0.30	15.4 ± 1.7	−10 ± 6
9	$<10^{-6}$			$<10^{-6}$		
10	$\leqslant 5 \times 10^{-7}$ [b]			3.8×10^{-5} [b]		
11[c]						
12	$<10^{-6}$			$<10^{-6}$		

[a] See Table II. [b] Reference 2 and this work. [c] This complex is converted to complex 4 under acidolysis conditions.

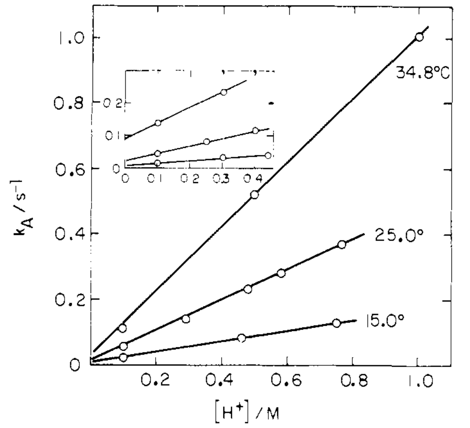

Figure 3. Plots illustrating the linear $[H^+]$ variation at three temperatures of the pseudo-first-order rate constant for acidolysis, according to eq 11, for $CrC(CH_3)(C_2H_5)OH^{2+}$. Inset: Similar plots for $CrC(CH_3)(i\text{-}C_3H_7)OH^{2+}$.

$(CH_3)(C_2H_5)OH^{2+}$ yields only 2-butanone. Homolysis of $CrCH(CH_3)OC_2H_5^{2+}$ in the presence of Cu^{2+} (which does not react directly in this case) produces CH_3CHO in 83% yield, which can be regarded as quantitative, considering its volatility. Acetaldehyde is produced from the following sequence of reactions:

$$CrCH(CH_3)OC_2H_5^{2+} \xrightarrow{k_H} Cr^{2+} + \cdot CH(CH_3)OC_2H_5 \quad (8)$$

$$\cdot CH(CH_3)OC_2H_5 + Cu^{2+} \rightarrow [CuR^{2+}] \xrightarrow{H_2O} Cu^+ + HOCH(CH_3)OC_2H_5 + H^+ \quad (9)$$

$$HOCH(CH_3)OC_2H_5 \rightarrow CH_3CHO + C_2H_5OH \quad (10)$$

where the oxidation of the radical by Cu^{2+} in eq 9 is believed to occur by way of an organocopper intermediate.[12]

Acidolysis Reactions. Several of these complexes were studied previously[2] under what amounted to acidolysis conditions. Results with $CrCH_2OH^{2+}$, $CrCH(CH_3)OH^{2+}$, $CrCH(C_2H_5)OH^{2+}$, and $CrC(CH_3)_2OH^{2+}$ agreed with previous results. These values and those for the new complexes as well all show a linear dependence upon $[H^+]$, as in eq 11. Plots of k_A vs. $[H^+]$ are shown in Figure

$$k_A = k_1 + k_2[H^+] \quad (11)$$

3. A least-squares analysis of the data, at a constant ionic strength of 1.0 M, was carried out. Table IV summarizes the rate constants k_1 and k_2 and, where available, their activation parameters.

Conversion of $CrC(CH_3)_2OCH(CH_3)_2^{2+}$ to $CrC(CH_3)_2OH^{2+}$. The organochromium complex prepared from diisopropyl ether was a distinct entity when prepared under homolysis conditions (entry 11, Table II). That is, its homolysis rate constant (5.8 s^{-1} at 25 °C) was characteristic of the complex $CrC(CH_3)_2OCH(CH_3)_2^{2+}$, and the organic products were acetone and 2-propanol, consistent with oxidation of the organic radical:

$$\cdot C(CH_3)_2OCH(CH_3)_2 \xrightarrow[H_2O]{Co(NH_3)_5Cl^{2+}} HOC(CH_3)_2OCH(CH_3)_2 + H^+ \rightarrow (CH_3)_2CO + (CH_3)_2CHOH \quad (12)$$

On the other hand, when an oxidizing scavenger was not present, in an attempt to measure the acidolysis rate constant for this complex, the rate constant observed at each temperature and the product obtained (2-propanol) corresponded exactly to those for acidolysis of $CrC(CH_3)_2OH^{2+}$. To assure that the agreement in rate constant was not accidental, we performed the following experiment. The complex was prepared with a slight excess of Cr^{2+}, and then within a few seconds an excess of $Co(NH_3)_5Cl^{2+}$ or H_2O_2 was added. The homolysis rate constant observed was 0.132 ± 0.007 s^{-1}, the value found independently for $CrC(CH_3)_2OH^{2+}$, as compared to 5.8 s^{-1} observed when $CrC(CH_3)_2OCH(CH_3)_2^{2+}$ was prepared using an excess of H_2O_2. Moreover, the yield of $CrC(CH_3)_2OH^{2+}$, as estimated by the absorbance change during homolysis, indicated that it was not a minor product but was formed in (approximately) the amount expected if it were produced quantitatively from the original complex. These observations suggest the reaction

$$CrC(CH_3)_2OCH(CH_3)_2^{2+} + H_2O \rightarrow CrC(CH_3)_2OH^{2+} + (CH_3)_2CHOH \quad (13)$$

Consistency with the observations cited above places certain limits on the rate of eq 13. Its rate constant must be much smaller than 5.8 s^{-1}, the homolysis rate constant of the parent complex, yet larger than $\sim 10^{-2}$ s^{-1}, such that the few seconds in which the parent complex is present with the excess of Cr^{2+} is sufficient to ensure its complex reaction by eq 13. The likely limits, based on these considerations, are $0.05 < k_{13} < 2$ s^{-1} at 25 °C.

Photochemical Generation of (α-Hydroxyalkyl)chromium Complexes. Methods for the preparation of certain organochromium ions based on the UV photolysis of ketones such as 2-propanone and 2-butanone were explored, both to supplement the modified Fenton's reagent and to examine the validity of this approach to their synthesis. Oxygen-free solutions of chromium(II) perchlorate, $\sim 2 \times 10^{-3}$ M, were photolyzed by using one or more short 300-J bursts of light emitted by xenon flash lamps. Some experiments used 2-propanone alone; others, with slightly better yields, used 2-propanone and 2-propanol together. Small but easily detectable amounts of $CrC(CH_3)_2OH^{2+}$, some 2–9% conversion of Cr^{2+}, were formed; the complex was identified by its absorption spectrum and by the rate constants for acidolysis and homolysis, which were identical with earlier values. This result is consistent with the known photochemistry of acetone[13] and with the effect of hydrogen donors (such as 2-propanol) in improving yields:

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(13) (a) Becket, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2038. (b) Zeldes, H.; Livinston, R. *J. Chem. Phys.* **1966**, *45*, 1946. (c) Anpo, M.; Kubokawa, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1913. (d) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966; Chapter 5.

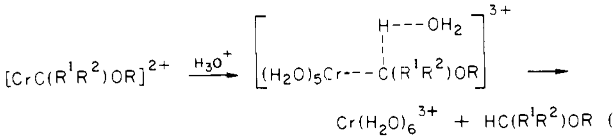
$$(CH_3)_2CO + (CH_3)_2CHOH \xrightarrow{h\nu} 2{\cdot}C(CH_3)_2OH \quad (14)$$

Similar results were obtained for photolysis of Cr^{2+} solutions containing 2-butanone and 2-butanol, but in addition to $CrC(CH_3)(C_2H_5)OH^{2+}$, there was produced a comparable quantity of a second, longer lived organochromium cation. It was not identified, but might be the known ethylchromium ion on the basis of kinetic comparisons, since ethyl radicals are known to be formed by the α cleavage of the triplet excited state of 2-butanone.[13d]

Interpretation and Discussion

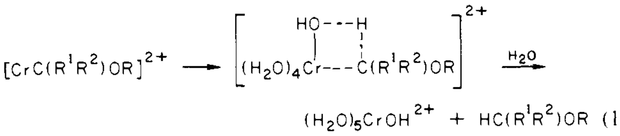
Acidolysis Reactions. Previous studies of this reaction of the simpler derivatives have now been supplemented by studies of some analogues more substituted at the α carbon. In each case the reaction rate follows the two-term rate law of eq 11. This is consistent with a mechanism consisting of two parallel pathways for which the transition states differ in composition by one proton. It should be noted that similar complexes[14] lacking the α-OH group, such as $CrCH_2CH_3^{2+}$ and $CrCH_2C_2H_5^{2+}$, also follow eq 11, although others, including $CrCH_3^{2+}$ and $CrCH(CH_3)OC_2H_5^{2+}$, have $k_1 \sim 0$. The presence of a nonzero value of k_1 does not, therefore, require a special involvement of the OH group in this pathway. That is not to say that hydrogen bonding of the OH group is unimportant, however, since the α-OH alkyls do undergo acidolysis more rapidly than their alkyl counterparts.[14] The acceleration by the OH group is, on the other hand, not the result of its electron-withdrawing characteristics either, since complexes such as $CrCH(CF_3)OH^{2+}$ (Table IV, **12**) are very stable toward acidolysis.

One can formally regard acidolysis as an electrophilic process involving heterolytic cleavage of the chromium–carbon bond. This does *not* suggest, however, that the transformation should be viewed as a dissociative process, such as $CrR^{2+} \rightarrow Cr^{3+} + {:}R^-$, in which a free carbanion is formed. The strong basicity of R^- precludes its formation and release in solution during the reaction. Indeed, the rate law reflects mechanistic pathways which are designed, among other features, to avoid just that. The way in which the acid-assisted pathway does so is easily appreciated, in that formation of the C–H bond can be nearly complete in the transition state. This conclusion is supported by the large deuterium isotope effect[2,15] on k_2 for reaction of D_3O^+ with $(D_2O)_5CrCH_3^{2+}$, for which $k_H/k_D = 6.3 \pm 0.2$.[15] The mechanism along the k_2 pathway is therefore proposed to be as shown in eq 15, in which it is suggested that coordination number six is preserved for chromium in the intermediates.



$$[CrC(R^1R^2)OR]^{2+} \xrightarrow{H_3O^+} \left[(H_2O)_5Cr{\cdots}\overset{\overset{\displaystyle H{\cdots}OH_2}{\vdots}}{C}(R^1R^2)OR\right]^{3+} \longrightarrow Cr(H_2O)_6^{3+} + HC(R^1R^2)OR \quad (15)$$

The acid-independent pathway can be regarded as analogous, with H_2O rather than H_3O^+ being the attacking electrophile. It is reasonable to suggest, although no experimental proof is available, that a coordinated water molecule rather than the bulk solvent is implicated. The former is much more acidic ($pK_a \sim 4$ vs. 14); it is just such an acidic or electrophilic property which is needed for this reaction. Thus the process we suggest for the k_1 pathway is given by eq 16.



$$[CrC(R^1R^2)OR]^{2+} \longrightarrow \left[\overset{\overset{\displaystyle HO{\cdots}H}{|\quad\ \vdots}}{(H_2O)_4Cr{\cdots}C(R^1R^2)OR}\right]^{2+} \xrightarrow{H_2O} (H_2O)_5CrOH^{2+} + HC(R^1R^2)OR \quad (16)$$

The acid-independent (or internal) pathway for acidolysis varies but little among the compounds studied in comparison with the value of the H_3O^+-assisted pathway. The latter, represented by the rate constant k_2, is subject to pronounced changes by substituents on the alkyl group, particularly those on the α-carbon. Thus $CrCH(CF_3)OH^{2+}$ reacts negligibly slowly compared to $CrCH(CH_3)OH^{2+}$, and a similar effect is seen for the haloalkyls:[16,18] $CrCF_3^{2+}$[16a] ≪ $CrCH_2Cl^{2+}$[16b] < $CrCHCl_2^{2+}$[16c,17,18] ≪ $CrCH_3^{2+}$.[2] In addition to effects such as these, which probably reflect the electron-withdrawing character of the halogenated substituents, the steric bulk of the alkyl groups is also important. The change in rate from 1-hydroxy-1-propyl (**3**) to 2-hydroxy-2-propyl (**4**) is marginal: $k_2 = 2.1 \times 10^{-3}$ as compared to $4.7 \times 10^{-3}\ M^{-1}\ s^{-1}$. On the other hand, the 2-hydroxy-2-butyl (**5**) and 3-hydroxy-3-pentyl (**6**) complexes react much faster, $k_2 = 0.47$ and $0.86\ M^{-1}\ s^{-1}$, respectively, illustrating the effect of a β-CH_3 substituent. The activation parameters identify the rate increases as rising entirely from the lower values of $\Delta H^\ddagger$; indeed, the changes in $\Delta S^\ddagger$ act in the opposite direction. The analogous β-CH_3 substitution, $CrCH(CH_3)OH^{2+}$ to $CrCH(C_2H_5)OH^{2+}$, produces but a modest increase in k_2, 1.22×10^{-3} to $2.14 \times 10^{-3}\ M^{-1}\ s^{-1}$. This may mean that the largest steric accelerations are to be found for more highly substituted members, in which steric interactions[19] between γ-hydrogen atoms on β-CH_3 groups with cis coordinated water molecules create preferred geometries which are prone to attack of the *external* H_3O^+ electrophile at the α-carbon. In comparison, a similar effect would not be expected for the k_1 pathway, which is interpreted in eq 16 as being an *internal* electrophilic process involving a coordinated water molecule.

$CrC(CH_3)_2OCH(CH_3)_2^{2+}$. Evidence given above was used to establish that the organochromium cation derived from diisopropyl ether, if allowed to stand but a few seconds in acidic solution, was converted to $CrC(CH_3)_2OH^{2+}$ (eq 13). Acid-catalyzed cleavages of ethers are well-known,[20,21] although very vigorous conditions are normally required. The reactivity of dialkyl ethers R_2O increases with the stability of the carbonium ion R^+, and reaction is thus more facile for R = i-C_3H_7 than for R = C_2H_5. In keeping with this, one notes the stability of $CrCH(CH_3)OC_2H_5^{2+}$ toward the analogous reaction.

Homolytic Dissociation—Rates and Equilibria. We would argue that the initial and rate-limiting reaction occurring in the presence of the oxidizing scavengers is the homolytic dissociation of the chromium–carbon bond, occurring by the S_H1 mechanism. The principal lines of evidence that argue for this are the following: (1) The reaction does not proceed unless the oxidizing scavenger is added, yet the value of the rate constant is independent of its nature and its concentration. (2) This reaction is suppressed by addition of Cr^{2+}, suggesting mass-law retardation of eq 3. To attribute the inhibiting effect of Cr^{2+} to the reverse of reaction 3 is consistent with the direct observation[5] of the very rapid formation of organochromium complexes in the reactions between Cr^{2+} and carbon-centered radicals. (3) The inorganic and organic products—such as $(H_2O)_5CrX^{2+}$ from reactions using $Co(NH_3)_5X^{2+}$ complexes, and aldehydes and ketones—are consistent with the known products obtained from independent studies of Cr^{2+}(aq) and α-hydroxyalkyl radicals with these oxidizing agents.

The activation parameters for homolysis (Table III) are also consistent with the S_H1 mechanism. The activation enthalpies are 22–30 kcal mol^{-1}, consistent with dissociation of a single chemical bond, largely uncompensated by other bond-making processes. The activation entropies are large, positive numbers between 20 and 37 cal $mol^{-1}\ K^{-1}$, also suggesting a major degree of bond breaking has occurred in reaching the transition state. The values are so large, in fact, that it suggests an additional

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(14) Acidolysis rate constants at 25 °C are $CrCH_2CH_3^{2+}$, $k_A/s^{-1} = 2.2 \times 10^{-4} + 1.15 \times 10^{-4}[H^+]$; $CrCH_2C_2H_5^{2+}$, $3.0 \times 10^{-4} + (6.5 \times 10^{-5})[H^+]$. Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463.

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(17) Dodd, D.; Johnson, M. D. *J. Chem. Soc. A* **1968**, *34*.

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Table V. Equilibrium Constants[a] for Homolysis

complex[b]	$10^{-7}k_{rev}$,[c] M^{-1} s^{-1}	$-\log (K_H/M)$	$\Delta G°_{H,298}$, kcal mol^{-1}
1	16	12.64	17.2
2	7.9	10.96	15.0
3	(8)	10.9	14.9
4	5.1	8.6	11.7
5	(5)	7.7	10.6
6	(≤5)	6.8	9.5
7	(≤5)	6.4	8.7
8	(<5)	5.2	7.1
9	(7)	>13.8	>18.9
10	3.4	10.22	13.9
11	(≤3)	6.7	9.2

[a] K_H calculated as k_H/k_{rev}, with k_H at 25 °C from Table II. [b] See Table II. [c] Experimental values at 22 ± 2 °C are from ref 5; estimated values are in parentheses.

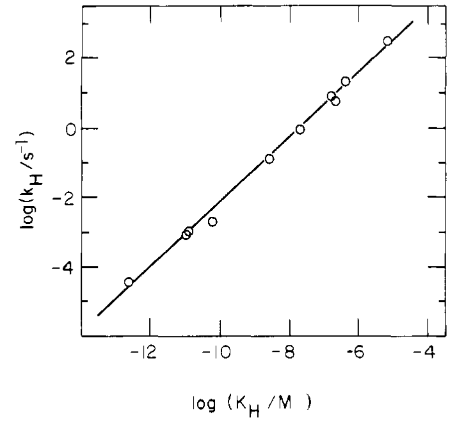

Figure 4. Correlation between the rate constant and the equilibrium constant for homolytic dissociation via a plot of log k_H vs. log K_H.

contribution to $\Delta S^{\ddagger}$ comes from other effects. Disruption of the hydrogen bonding of the solvent as the organic radical is released into it, as compared to the same group in the ground state wherein it resides within the coordination sphere of a cationic pentaaquo metal ion, may provide a major additional contribution to the activation entropy. The homolytic dissociation reactions of benzylchromium ion[3] and of the closely related isomeric 2-, 3-, and 4-pyridinomethyl complexes[22,23] have similar values: $\Delta H^{\ddagger}$ = 29–37 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 11–37 cal mol^{-1} K^{-1}. These comparisons affirm the similar S_H1 mechanism assigned to all of these complexes.

The reversible homolysis equilibrium for the members of this class of complexes is given by eq 17. It is possible to calculate from kinetic data the equilibrium constant K_H for four of the complexes and to estimate it for the others.[24] The resulting equilibrium constants (Table V) lie within the range 10^{-14}–10^{-6} M, corresponding to processes in which equilibrium lies well toward the left, as expected. A plot of log k_H vs. log K_H, given in Figure 4, is linear, with a slope of 0.93. In accord with Hammond's postulate for a highly endothermic reaction,[25] the transition state will closely resemble the products. This is consistent with the picture given by all of the factors listed, including the activation parameters and the correlation between k_H and K_H.

$$[(H_2O)_5CrC(R^1R^2)OR]^{2+} + H_2O \rightleftarrows Cr(H_2O)_6^{2+} + \cdot C(R^1R^2)OR \quad (17)$$

The values of $\Delta G_H°$ are given in Table V. If it is assumed that $\Delta H_{rev}^{\ddagger} \sim 0$, a reasonable approximation for these fast "radical recombination" steps—ignoring the minor contribution made by heat of association with the sixth water ligand in the Jahn–Teller distorted $Cr(H_2O)_6^{2+}$ ion—then the values of $\Delta H_H^{\ddagger}$ may be approximated as the thermodynamic quantity $\Delta H_H°$. One recognizes three contributions to $\Delta H_H°$: (a) the intrinsic bond dissociation enthalpy of the chromium–carbon bond, (b) the enthalpy of association of the entering water molecule with Cr(II), and (c) the differences in solvation energies between reactants and products. If factors b and c can be regarded as nearly negligible, the $\Delta H_H°$ represents largely factor a; since such values are rarely known, this study has afforded a systematic, albeit approximate, evaluation. If complete neglect of factors b and c is rash, then at least the approximation that their contributions would be nearly constant throughout the series is not, and bond dissociation enthalpies on a relative scale are thus obtained. One notes the general trend in the values shown, the high values of the bond strength declining regularly with the degree of substitution. Analysis of these trends in a more quantitative fashion is the subject of the next section.

Table VI. Activation Free Energies for Homolytic Reactions of Organochromium Ions and Substituted Symmetrical Ethanes at 298 K

complex[a]	$[(H_2O)_5CrC(R^1R^2X)]^{2+}$ X[b]	R¹	R²	$\Delta G^{\ddagger}_{298,H}$	$\Delta G^{\ddagger}_{298,C-C}$
1	(CH_3)	H	H	23.60	73.2
2	(CH_3)	CH_3	H	21.64	71.4
3	(CH_3)	C_2H_5	H	21.54	71.9[c]
4	(CH_3)	CH_3	CH_3	18.67	63.5
5	(CH_3)	CH_3	C_2H_5	17.60	58.6
6	(CH_3)	C_2H_5	C_2H_5	16.2	55.5
7	(CH_3)	CH_3	$i\text{-}C_3H_7$	15.65	54.4
8	(CH_3)	CH_3	$t\text{-}C_4H_9$	14.07	38.7
10	$(n\text{-}C_3H_7)$	CH_3	H	21.1	72.4[d]
11	$(i\text{-}C_4H_9)$	CH_3	CH_3	16.5	56.1
A[e]	CH_3	CH_3	H	22.6	71.4
B[f]	Ph	H	H	21.0	59.3[g]

[a] See Table II. [b] Substituent X when enclosed in parentheses designates the corresponding hydrocarbon used in the correlation (Figure 5) with X = OH replaced by CH_3 and X = OR replaced by CH_2R. [c] The value of $\Delta G^{\ddagger}_{298,C-C}$ was taken as that for 2,3-dimethylbutane (71.4) plus the difference between 3,4-diphenylhexane (54.4) and 2,3-diphenylbutane (53.9). [d] The value of $\Delta G^{\ddagger}_{298,C-C}$ was taken as that for 3,4-dimethylhexane (71.9) plus the difference between 3,4-diphenylhexane and 2,3-diphenylbutane. [e] The complex is $CrCH(CH_3)_2^{2+}$, ref 27. [f] The complex is $CrCH_2Ph^{2+}$, ref 3. [g] Sato, Y. *J. Jpn. Pet. Inst.* 1978, *21*, 110. Quoted in: Poutsma, M. L. *Fuel* 1979, *59*, 335.

Steric and Electronic Factors in Homolysis. The very large increase in homolysis rates among this family of compounds is evident. A factor of 10^7 separates the end members of a series in which the most evident variation is the degree of substitution at the α carbon. Steric factors are not solely responsible, however. One need consider only a pair of complexes for which steric factors would be comparable, such as $CrCH(CH_3)OH^{2+}$ (k_H = 8.5 × 10^{-4} s^{-1}) and $CrCH(CF_3)OH^{2+}$ (<3 × 10^{-5} s^{-1}), to appreciate that electronic effects are also important.

Nonetheless, in the series of complexes studied it is useful to examine the extent to which steric factors alone can account for the variation in k_H with changes in structure. Various approaches are possible,[1] but we consider here only one treatment based on methods developed by Rüchardt.[26] Consider the high-temperature thermolysis of symmetrically substituted ternary or quaternary ethanes, in which the major (and often exclusive) reaction is C–C bond homolysis:

$$(R^1R^2R^3)CC(R^1R^2R^3) \rightarrow 2(R^1R^2R^3)C\cdot \quad (18)$$

Experimental measurements of the reaction rate have been reported at suitable temperatures for each compound and the results expressed in terms of $\Delta G^{\ddagger}$ at a given temperature, 300 °C. The

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[22] Coombes, R. G.; Johnson, M. D. *J. Chem. Soc. A* **1966**, 177.

[23] Schmidt, A. R.; Swaddle, T. W. *J. Chem. Soc. A* **1970**, 1927.

[24] The reverse rate constants span a narrow range in which k_{rev} varies systematically with structure; estimates for the other complexes can be made with reasonable accuracy. The correlation shown in Figure 4 is largely a result of the near constancy of k_{rev}.

[25] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

[26] Rüchardt, C.; Beckhaus, H-D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 429.

J. Am. Chem. Soc. 1982, 104, 1255-1263

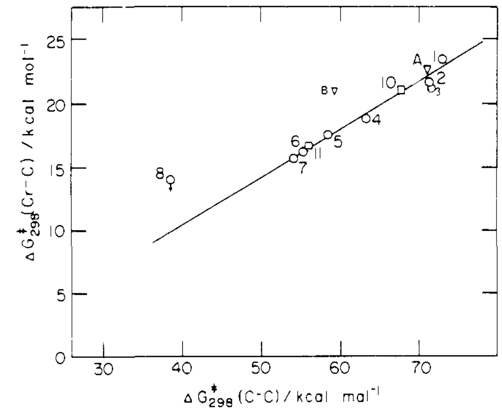

Figure 5. Plot showing a linear relationship between the activation free energies for the homolysis of the organochromium cations, $\Delta G^\ddagger{}_{298}$(Cr–C), and those for homolysis of the correspondingly substituted symmetrical ethanes $\Delta G^\ddagger{}_{298}$(C–C). Data and notation from Table VI.

values of $\Delta G^\ddagger{}_{298}$ for eq 18 vary from 34 to 79 kcal mol^{-1} or a factor $\sim 10^{32}$ in k_{18}. Rüchardt has shown[26] that this large variation in the homolysis rate constant can be accounted for by the steric requirements of the groups R^1, R^2, and R^3 alone.

From the available thermodynamic data we calculated the values of the activation free energies for the C–C bond homolysis in symmetrical ethanes at 298 K, $\Delta G^\ddagger{}_{298,C-C}$. These values are presented in Table VI, along with the values of $\Delta G^\ddagger{}_{298,H}$ for the homolysis of the organochromium complexes. In order to attempt a correlation between the two sets of data, it was necessary to assume that the steric effect of the OH group is identical with the steric effect of the group CH_2H. Similarly, the steric effects of groups OR are as for CH_2R groups, much as Rüchardt included CN groups as CH_3 groups.

The plot of $\Delta G^\ddagger{}_{298,C-C}$ for symmetrical ethanes vs. $\Delta G^\ddagger{}_{298,H}$ for the organochromium complexes is given in Figure 5, which shows that the data for complexes derived from both alcohols and ethers compare rather well with the data for symmetrical ethanes. Also included in the correlation are values for benzyl[3] and 2-propyl[27] complexes. While the latter fits the correlation extremely well, the former deviates somewhat from the line. In view of the fact that benzyl radical is the only nonaliphatic, resonance-stabilized radical in this study, a perfect correlation with the aliphatic radicals was not expected.

The slope of the line in Figure 5 (0.36) confirms the success of the correlation. On the basis of the fact that simultaneous structural variations occur on both of the ethane carbons of eq 18 while changes in the series of the organochromium complexes are only half as large ($Cr(H_2O)_5{}^{2+}$ being common to the entire series), one would predict a slope of 0.50. The experimentally found value of 0.36 is in good agreement with this prediction.

The results of the correlation indicate that for a series such as this in which substituents of widely different polar effects are not included, structural effects alone can account for the variation in reactivity.

Experimental Section

Organochromium complexes, including the previously unreported ones, were prepared from the reaction[2,6] of chromium(II) perchlorate and hydrogen peroxide in dilute aqueous perchloric acid solutions containing 0.01–1 M of the desired alcohol or ether, as solubility and other considerations permitted. Depending on the purpose of a given experiment, Cr^{2+} or H_2O_2 might be in excess, or the two might be in stoichiometric ratio (2:1 Cr^{2+}:H_2O_2).[28] The preparations and reactions were conducted under Cr^{2+}-scrubbed nitrogen.

Reactions were monitored by UV–vis spectrophotometry, most often employing the absorption maximum near 395 nm ($\epsilon \sim$ 200–700). Kinetics determinations of slower reactions were carried out by using a Cary 219 spectrophotometer. Faster reactions were monitored with a Durrum D110 stopped-flow spectrophotometer equipped with the D-132 Multimix accessory. The latter was essential for the shortest lived complexes, as it permitted mixing of the oxidizing scavenger in the third syringe with the organochromium complex which was produced upon mixing Cr^{2+}, H_2O_2, and the organic solute in the first two syringes. All of the data followed pseudo-first-order kinetics, from which rate constants were evaluated by using standard methods. Products were determined by using methods previously reported.[6] A Xenon Model 710C flash photolysis apparatus was used in the photochemical experiments, with the appropriate reagents contained in quartz vessels under a nitrogen atmosphere.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-ENG-82. We are pleased to acknowledge helpful discussions with Professor R. G. Bergman.

Registry No. 1, 32108-95-5; **2**, 32108-94-4; **3**, 80572-83-4; **4**, 32108-93-3; **5**, 80572-84-5; **6**, 80572-85-6; **7**, 80572-86-7; **8**, 80572-87-8; **9**, 78402-17-2; **10**, 32108-97-7; **11**, 80572-88-9; **12**, 80572-89-0; $Co(NH_3)_5F^{2+}$, 15392-06-0; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5Br^{2+}$, 14970-15-1; H_2O_2, 7722-84-1; VO^{2+}, 20644-97-7; Cu^{2+}, 15158-11-9; Fe^{3+}, 20074-52-6.

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Kinetic and Thermodynamic Acidity of Hydrido Transition-Metal Complexes. 1. Periodic Trends in Group 6 Complexes and Substituent Effects in Osmium Complexes

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Abstract: Equilibrium acidities in acetonitrile have been measured for $(\eta^5\text{-}C_5H_5)M(CO)_3H$ (M = Cr, Mo, W) and *cis*-$Os(CO)_4(E)H$ (E = H, CH_3, $Os(CO)_4H$), and periodic trends and substituent effects have been assessed. Rates of proton transfer have been measured or estimated for the reactions of these complexes with their conjugate anions and with nitrogen bases such as morpholine and triethylamine. The rates of proton transfer to metal anions are much slower than those to nitrogen bases of comparable thermodynamic base strength.

While the importance of transition-metal hydrides in organometallic chemistry is manifest, remarkably little is known about their acid–base properties. Although Schunn remarked[2] in 1971 that "there is a definite need for the measurement of the acidity

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