yellow-orange powder which was washed with CH_2Cl_2 (10 ml), and Et_2O (10 ml), yield 105 mg (100%).

Hydridoethanethiolatobis(triphenylphosphine)platinum (**11**). $Pt(PPh_3)_4$ (520 mg) was dissolved in benzene (20 ml) and the solution filtered. Evaporation to a volume of 5 ml followed by addition of EtSH gave a pale solution. Hexane (25 ml) was slowly added and the mixture stirred for 30 min. The precipitate was filtered and washed with ether: 295 mg (90%); mp 125–128°.

Bis(methanethiolato)bis(triphenylphosphine)platinum (**12**). To a filtered solution of $Pt(PPh_3)_4$ (650 mg) in benzene was added Me_2S_4 or Me_2S_3 (0.5 ml). The solution was stirred for 2 hr. The solvent was removed and the residue recrystallized twice from CH_2Cl_2 and ethanol to give the complex: 210 mg (49%); mp 210° with decomposition.

(1,2-Ethanedithiolato)palladium (**15**). This material is most easily prepared by the reaction of $Pd(COD)Cl_2$ in CH_2Cl_2 solution with esH_2 (equal weight) followed by addition of Et_3N (equal weight). After stirring 1 hr the brown orange polymeric material is removed by filtration and washed sequentially with CH_2Cl_2, EtOH, H_2O, EtOH, and Et_2O. The yield is essentially quantitative.

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Acidolysis and Oxidative Cleavage Reactions of Benzylchromium Cations

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Abstract: The organometallic complex $[(H_2O)_5CrCH_2C_6H_5]^{2+}$ is oxidized in aqueous perchloric acid by Fe^{3+}, Cu^{2+}, $[Co(NH_3)_5Cl^{2+}]$, $[Co(NH_3)_5Br^{2+}]$, O_2, and H_2O_2 at an identical rate, independent of the nature and concentration of the oxidizing agent. The first-order rate constant is $10^3 k_1$ (sec^{-1}) = 2.63 ± 0.21 (25.0°, μ = 1.00 M). The organic products and Cr(III) products were determined. In certain instances, the reaction initiates polymerization of acrylonitrile but in other instances it does not. The rates of para-substituted derivatives correlate with the Hammett σ_p parameter, giving ρ = −1.01. The reactions are discussed in terms of a unimolecular homolysis of the Cr–C bond by the S_H1 mechanism, followed by rapid oxidation of one or both of the fragments so formed.

In studies of the reduction of organic molecules by metal ions, solutions of benzyl halides and Cr(II) were shown to generate (eventually) Cr(III) and an organic product which, under anaerobic conditions, is largely toluene.[2,3] In the course of those studies, separation and identification the benzylpentaaquochromium(III) cation, $[(H_2O)_5CrCH_2C_6H_5]^{2+}$ (**1**), were realized. Further, it was confirmed that **1** was formed quantitatively, and that its decomposition via the acidolysis reaction (eq 1) is responsible for the final products.

An intriguing puzzle attended the study[4] of the rate of reaction 1 in $HClO_4$ solutions in the absence of dioxygen: the kinetics showed not a first-order dependence upon [**1**], but (under a limited set of concentration conditions) approximated a half-order dependence.[5-9] A mechanism which accounts for the kinetic observations under these circumstances has not as yet been formulated, although a
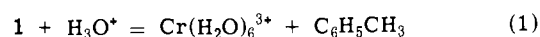
$$1 + H_3O^+ = Cr(H_2O)_6^{3+} + C_6H_5CH_3 \qquad (1)$$

Table I. Products of the Reactions of **1** with Various Oxidizing Agents

[O]	Solvent	Organic product $(R = C_6H_5CH_2)$	Cr(III) product	Ref
None	EtOH–H$_2$O	RH (~90%)	Cr(H$_2$O)$_6$$^{3+}$ (100%?)	a, b, c
		R$_2$ (~1–6%)		
O$_2$	EtOH–H$_2$O	C$_6$H$_5$CHO	Cr$_2$O^{4+} (>90%)	a, c, d
CuSO$_4$	EtOH–H$_2$O	ROH (7%)		c
		ROEt (60%)		
Fe(ClO$_4$)$_3$	EtOH–H$_2$O	ROH		c
		ROEt		
Fe(ClO$_4$)$_3$	HClO$_4$ (aq)	ROH (95%)	Cr(H$_2$O)$_6$$^{3+}$ (>90%)	d, e
[Co(NH$_3$)$_5$Cl](ClO$_4$)$_2$	HClO$_4$ (aq)	R$_2$ (–)	(H$_2$O)CrCl^{2+} (>90%)	d

^{a} Reference 2. ^{b} Reference 3. ^{c} Reference 4. ^{d} This work. ^{e} Reference 13.

suggestion[4] has been made that the following is one of the important steps.

$$1 \rightleftharpoons Cr^{2+}_{aq} + C_6H_5CH_2 \cdot \qquad (2)$$
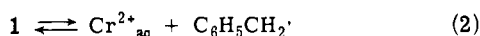
Considerable importance attaches to the mechanism of cleavage of σ bonds between carbon atoms and transition elements, for which extensive and systematic data are not available. The excellent electrophile H$_3$O$^+_{aq}$, present at high concentration in aqueous perchloric acid, apparently does not directly react with **1**. In contrast, rapid, bimolecular reactions of **1** with other electrophiles have been noted, and a straightforward SE2 mechanism seems applicable.[10,11]

In the particular case of **1**, interest is heightened by the observation[4] of a reaction between **1** and dioxygen, suggesting the Cr–C bond is capable of oxidative as well as electrophilic cleavage. Moreover, the reducing character of **1** was suggested by its reaction with mild oxidants such as Fe(III) and Cu(II) salts. In each of these instances it was reasonably presumed that direct oxidative reactions were occurring. With this in mind, we undertook a systematic kinetic study of such oxidative cleavage reactions. It soon became apparent, however, that direct reaction of **1** is not observed for most oxidants.[12] Rather, the first step of the acidolysis process is involved in the reactions of **1** with a variety of mild oxidizing agents. Further, the Cr–C bond cleavage in this process is *not* the SE2 reaction of the electrophile H$^+_{aq}$, but appears instead to be the SH1 dissociation as in reaction 2. This paper reports the results of these experiments.

Results

Stoichiometry and Products. The organic products of the acidolysis of **1**, and of its oxidation by a variety of reagents, were studied in detail by Kochi and Buchanan,[4] utilizing for the most part experiments in EtOH–H$_2$O. Our efforts in this regard (see Table I) have been confined to checks of the applicability of those results to the strictly aqueous solvent, and to the reaction of **1** with [Co(NH$_3$)$_5$Cl]$^{2+}$ which was not examined previously.

The reaction of **1** with Fe^{3+} in aqueous HClO$_4$ forms C$_6$H$_5$CH$_2$OH exclusively,[13] consistent with the formation of C$_6$H$_5$CH$_2$OEt + C$_6$H$_5$CH$_2$OH in the mixed EtOH–H$_2$O solvent. The stoichiometry of the reaction of Fe^{3+} (in excess) and **1** was determined spectrophotometrically as outlined in the Experimental Section; at various [H$^+$] the ratio of moles of Fe^{3+} reacted:moles of **1** initially present is 2.02:1 (1.1 × 10^{-3} M H$^+$), 1.8:1 (2.3 × 10^{-3} M H$^+$), 1.94:1 (1.5 × 10^{-2} M H$^+$), and 1.96:1 (8.5 × 10^{-1} M H$^+$). These data confirm the reaction to be

$$1 + 2Fe^{3+} + 2H_2O = Cr(H_2O)_6^{3+} +$$
$$2Fe^{2+} + C_6H_5CH_2OH + H^+ \qquad (3)$$
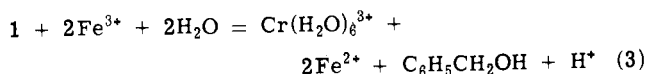
A major line of evidence concerning the mechanism of the reactions of **1** with the various oxidizing agents is the nature of the Cr^{III} products (results are in Table I). This point will be amplified in the Discussion, but for the moment we note that in each case in which the Cr(III) product was identified, it is the same product known to result from the reaction of Cr$^{2+}_{aq}$ with the oxidant in question. Likewise, the production of bibenzyl in the reaction of **1** with [Co(NH$_3$)$_5$Cl](ClO$_4$)$_2$ appears to be a significant point, particularly in contrast to the formation of benzyl alcohol in the reaction with Fe(ClO$_4$)$_3$.

Kinetics Determinations. Reaction rate studies were carried out on the oxidation of **1** by the mild oxidizing agents Fe(ClO$_4$)$_3$, Cu(ClO$_4$)$_2$, O$_2$, H$_2$O$_2$, [Co(NH$_3$)$_5$Cl^{2+}], and [Co(NH$_3$)$_5$Br^{2+}]. In each case the rate of disappearance of **1** conformed quite closely to the rate expression

$$-d[1]/dt = k_1[1] \qquad (4)$$

as evidenced by the linearity of the first-order plots and particularly by the lack of variation of k_1 in runs with varying initial concentrations of chromium complex. The values obtained for k_1 are independent of the concentration of oxidant, independent of [H$^+$], and independent of which of the six oxidizing agents was used. These observations are applicable over a wide range of conditions, as summarized in Table II; the mean value of 34 determinations is 10$^3k_1$ (sec^{-1}) = 2.63 ± 0.21 (25.0°, μ = 1.00 M).

For purposes of comparison, a limited set of measurements was made on the acidolysis of **1** in the absence of oxygen or other oxidant. Kochi and Buchanan[4] had reported a relatively rapid acidolysis reaction following half-order kinetics in 80% EtOH–H$_2$O; the reaction was markedly accelerated by HClO$_4$ in the range 0.1–2.0 F. We find that in aqueous HClO$_4$, however, the reaction occurs more slowly, *apparently following a first-order rate expression.*[14] The dependence of rate constant upon [H$^+$], values at 25.0° and μ = 1.0 M, is as follows: k (sec^{-1}), 7.0 × 10^{-5} ([H$^+$], 3.73 × 10^{-3} M), 1.64 × 10^{-4} (7.3 × 10^{-2}), 2.13 × 10^{-4} (8.2 × 10^{-2}), 5.05 × 10^{-4} (7.3 × 10^{-1}), and 5.38 × 10^{-4} (9.3 × 10^{-1}).

The complexes Co(en)$_3$$^{3+}$ (4.6 × 10^{-3} M), Cr(H$_2$O)$_6$$^{3+}$ (1.26 × 10^{-2} M), or Fe(H$_2$O)$_6$$^{2+}$ (3.5 × 10^{-3} M) do not react with **1** in 0.97 M HClO$_4$, the acidolysis proceeding in each instance at the same rate as in the absence of such ions.

Addition of Cr(ClO$_4$)$_2$ (10^{-2} to 10^{-3} M) greatly slowed the decomposition of **1**, although this effect was not studied quantitatively.

Activation Parameters. The value of k_1 (sec^{-1}) at 35.0° is 1.46 × 10^{-2} and at 18.0°, 6.56 × 10^{-4}. The respective values of $\Delta H_1^{\ddagger}$ (kJ mol^{-1}) and $\Delta S_1^{\ddagger}$ (J mol^{-1} K^{-1}) are consequently 133 ± 3 and 153 ± 11.

Table II. Rate Constants for the Reaction of 1 with Oxidizing Agents at 25.0°, $\mu = 1.00\,M$

Oxidant	Range of [oxidant], M	Range of [1], M	Range of [H$^+$], M	$10^3 k_1 \pm \sigma$, sec^{-1} $(n)^a$
Fe^{3+}	$(0.61-9.3) \times 10^{-3}$	$(0.5-2.6) \times 10^{-4}$	0.0034–0.97	2.67 ± 0.19 (11)
O$_2$	saturated, ~1 × 10^{-3}	$(0.1-0.8) \times 10^{-4}$	0.0040–0.98	2.65 ± 0.27 (9)
[Co(NH$_3$)$_5$Cl^{2+}]	$(1.6-3.3) \times 10^{-3}$	$(0.11-2.1) \times 10^{-4}$	0.0035–0.98	2.68 ± 0.13 (5)
[Co(NH$_3$)$_5$Br^{2+}]	3.12 × 10^{-3}	1.26 × 10^{-4}	0.95	2.24 (1)
Cu^{2+}	$(1.3-9.4) \times 10^{-3}$	$(0.12-0.44) \times 10^{-4}$	0.0034–0.97	2.58 ± 0.21 (7)
H$_2$O$_2$	2.09 × 10^{-3}	4.03 × 10^{-4}	0.971	2.49 (1)
				Av k_1 = 2.63 ± 0.21 (34)

a Each entry gives the average first-order rate constant and the standard deviation, σ, for the number of independent determinations, n, given in parentheses.
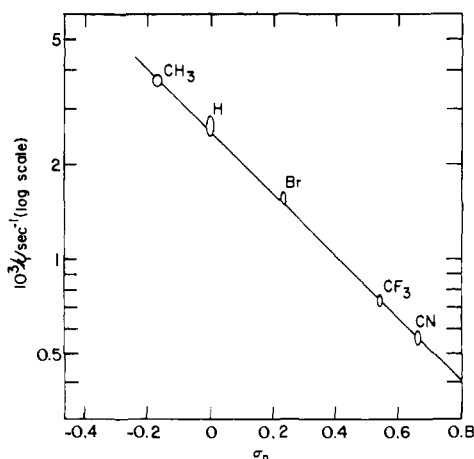

Figure 1. A plot illustrating the LFER correlation of k_1 with the Hammett σ_p substituent constant.

Substituent Effects. Similar kinetics experiments were performed in the case of several para-substituted benzyl-chromium cations with oxidizing agents. As with **1**, each of these complexes reacted following first-order kinetics, the value of k_1 being independent of [H$^+$] (0.0036–0.96 M) as well as independent of the concentration and nature of the oxidizing agent. The rate constants are as follows: p-CH$_3$C$_6$H$_4$CH$_2$Cr^{2+}, $10^3 k_1$ (sec^{-1}) = 3.74 ± 0.04 (5 experiments); p-BrC$_6$H$_4$CH$_2$Cr^{2+}, 1.56 ± 0.07 (3); p-CF$_3$C$_6$H$_4$CH$_2$Cr^{2+}, 0.728 ± 0.008 (3); and p-CNC$_6$H$_4$CH$_2$Cr^{2+}, 0.556 ± 0.034 (3). These data show a good correlation[15] with the Hammett σ_p parameter, as illustrated in Figure 1. The reaction constant ρ is −1.01.

Initiation of Acrylonitrile Polymerization. The reaction of Co(NH$_3$)$_5$Cl^{2+} with **1**, when acrylonitrile is present, results in a copious white flocculent precipitate of poly(acrylonitrile). The reaction of Cu^{2+} with **1**, on the other hand, produces but a faint turbidity. The acidolysis of **1** in the absence of oxidizing agent produces polymer more slowly (and perhaps in lesser amount). Blank experiments established that Cu(ClO$_4$)$_2$, Cr(ClO$_4$)$_2$, and [Co(NH$_3$)$_5$Cl](ClO$_4$)$_2$ fail to initiate polymerization.
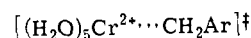
Discussion

Summarized below are various lines of evidence suggesting that the reactions of **1** with the six oxidizing agents proceed by rate-determining unimolecular homolysis, reaction 2. This thus constitutes an example of an SH1 cleavage mechanism. Following reaction 2, one or both of the intermediates so produced, Cr^{2+} and C$_6$H$_5$CH$_2$·, undergo *rapid* reaction with the oxidant present. It is the rapidity of such reaction(s), relative to their recombination (reverse of reaction 2, k_{-1}, which is known to be quite rapid[16]), which reduces the scheme to the simple first-order expression. Based upon this model, any oxidizing agent which reacts rapidly

with *either or both* Cr^{2+} or C$_6$H$_5$CH$_2$· should give this same result; rapid consumption of just *one* of the homolysis fragments would effectively prevent the back reaction.

In support of the homolysis mechanism, and to point out other information that may be gleaned from the results, we note the following. (1) The Cr(III) product (see Table I) in each instance studied is the same kinetically inert Cr(III) product known to result from the reaction of Cr^{2+} with the given oxidizing agent. Moreover, in at least five of the six cases it would appear that the oxidation of Cr^{2+} occurs rapidly enough to give the observed kinetic result of a rate-determining k_1 step.[17,18] (2) The production of benzyl alcohol in the reactions with Fe^{3+} and Cu^{2+} can be interpreted in terms of this scheme as arising from the oxidation of the benzyl radical to the carbonium ion, whose reaction with the solvent produces the alcohol. Since the alternative to the oxidation of benzyl radicals is their rapid[19] coupling, it appears such oxidations by Fe^{3+} and Cu^{2+} occur quite rapidly. (3) The oxidizing agent Co(en)$_3^{3+}$ does not react with **1**, and acidolysis instead proceeds at the same rate as in its absence. This is consistent with the slow reaction of Cr^{2+} with Co(en)$_3^{3+}$.[20] Moreover, it suggests that Co(en)$_3^{3+}$ does not oxidize benzyl radicals rapidly enough to compete with the reverse of reaction 2. (4) Considering the failure of Co(en)$_3^{3+}$ to oxidize C$_6$H$_5$CH$_2$·, it seemed likely to us that [Co(NH$_3$)$_5$Cl]$^{2+}$ also might react with the radical slowly. This inference was borne out by the observation that although this complex does react rapidly with **1** (by virtue of its fast reaction with Cr^{2+} [17]), the product in this case proved to be bibenzyl rather than the alcohol, which is consistent with coupling taking precedence over oxidation. (5) Initiation of polymerization of acrylonitrile by the reaction of **1** with [Co(NH$_3$)$_5$Cl^{2+}], and more slowly during the acidolysis of **1**, constitutes supporting evidence for the importance of benzyl radicals as a reaction intermediate. Further, the occurrence of little if any acrylonitrile polymerization initiated by the reaction of Cu^{2+} with **1** is supportive of the claimed rapid oxidation of C$_6$H$_5$CH$_2$· by Cu^{2+}. By itself, however, these results could not constitute convincing arguments for the involvement of radical intermediates in some processes but not in others since acrylonitrile can be polymerized by other agents as well. (6) The reaction rate shows a first-order dependence upon the concentration of the benzylchromium cation and is independent of the nature and concentration of the oxidizing agent, providing compelling evidence for the lack of involvement of the latter in the rate-determining bond scission step.

The transition state for the SH1 dissociation can be represented as follows.
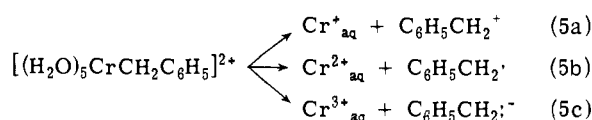
$$[(H_2O)_5Cr^{2+} \cdots CH_2Ar]^{\ddagger}$$

The negative value of ρ reflects the accelerating effect of electron donating substituents and the decelerating effect of electron donating substituents. This suggests that the ben-

zylic carbon is stabilized in the transition state relative to the ground state by increasing electron density; that is, the aralkyl group is less negative in the transition state than in the ground state. The Hammett correlation also supports the assigned S_H1 mechanism in that formation of the radical produces a fragment less negative in the transition state than in the ground state. The value of $\rho = -1.01$ seemed to us somewhat more negative than might be expected for homolysis, but, since the second departing center, Cr^{2+}, carries a dipositive charge, the entire ionic charge of the starting complex will accentuate the charge difference between the aralkyl in the starting complex compared to the transition state. The rather negative value of ρ further suggests that in the transition state the Cr–C bond is largely broken. The latter conclusion is supported[8,21,22] by the large $\Delta H^{\ddagger}$ value (133 kJ mol^{-1}) associated with k_1, and the large, positive $\Delta S_1^{\ddagger}$ (153 J mol^{-1} K^{-1}).

A further point should be made about an alternative unimolecular reaction of 1, which would account for the rate behavior noted. In this mechanism the rate-determining step is the loss of a water molecule from the primary coordination sphere of 1, followed by rapid subsequent reactions of the deaquo complex. This mechanism is not an impossible one based on the form of the rate expression and the values of k_1. The rate of dissociation of water molecules from the coordination sphere of Cr(III) complexes is generally extremely slow, but in the case of $(H_2O)_5CrCH_2Cl^{2+}$, the rate of dissociation of the single water trans to the Cr–C bond is much faster, 1.7×10^{-2} sec^{-1}.[6] Nevertheless it seems to us an unlikely step in the present instance of ultimate chromium–carbon cleavage on several counts: the deaquo complex should not be particularly more susceptible to oxidation than the starting complex and the large substituent effect on k_1 could not be accommodated by a kinetic process involving a reaction site so far removed from the substituent on the aromatic ring. Moreover, the products observed, inorganic and organic, arise from Cr^{2+} and the benzyl radical almost unambiguously; if such products were not to be made in the rate-determining step, then it is difficult for us to envisage how two strongly reducing centers could possibly arise from a reaction of the deaquo intermediate with a strongly oxidizing species. For these reasons we discount a mechanism involving rate-determing dissociation of a water molecule.
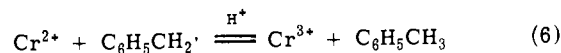
To return to a consideration of mechanism involving rate-determining Cr–C cleavage, we note that a useful framework for discussion of such mechanisms is to consider the possible modes of unimolecular bond scission of the chromium carbon bond, as represented by eq 5a–c. Since all

$$[(H_2O)_5CrCH_2C_6H_5]^{2+} \begin{cases} Cr^+_{aq} + C_6H_5CH_2^+ & (5a) \\ Cr^{2+}_{aq} + C_6H_5CH_2\cdot & (5b) \\ Cr^{3+}_{aq} + C_6H_5CH_2{:}^- & (5c) \end{cases}$$

six oxidants react with identical kinetics, the discussion of alternative mechanisms must encompass the other experimental findings for each one of the oxidants. The absence of a dependence of k_1 upon [H$^+$] would be consistent with the S_E1 reaction of eq 5a,[23] but the mechanism is discounted because formation of Cr^+_{aq} seems unlikely and in particular because evidence exists for radical formation in certain instances (trapping with acrylonitrile and formation of bibenzyl). Equation 5c is inconsistent with the Cr(III) products formed, and also with the variety of organic products, in that toluene would be expected to be the main product.

The formulation of a complete mechanism of acidolysis under conditions where an oxidizing agent is not present is not possible on the basis of the limited data. The dramatic

lowering of rate by Cr^{2+} suggests mass-action reversal of reaction 2, which implies Cr^{2+} and $C_6H_5CH_2\cdot$ exist and react as distinct entities and not (or not only) as an intimate charge-transfer complex. Were their subsequent reaction electron transfer, with accompanying or subsequent protonation

$$Cr^{2+} + C_6H_5CH_2\cdot \xrightarrow{H^+} Cr^{3+} + C_6H_5CH_3 \qquad (6)$$

the reaction products are then reasonably accounted for. Without such an immediate reaction, radical products would predominate, and they do not. The sequence of reactions 2 and 6 would, however, not show rate retardation by Cr^{2+}; consequently, different and as yet unknown subsequent processes apparently enter the mechanism for anaerobic acidolysis. A further difficult point is the following: if reaction 2 proceeds as shown under anaerobic conditions, the rate of recombination of separate Cr^{2+}_{aq} and $\cdot CH_2C_6H_5$ would be in competition with the diffusion-controlled dimerization of benzyl radicals; if the former proceeds at the value found[16] for other such recombinations, k_{-1} (dm^3 mol^{-1} sec^{-1}) = 10^7–10^8, and the latter at k_d (dm^3 mol^{-1} sec^{-1}) $\sim10^9$, then the starting complex would be subject to more rapid anaerobic decomposition, and to different products, than is observed. Whatever other arguments or processes might be involved, it appears to us that recombination of Cr^{2+} and $C_6H_5CH_2$ formed initially by reaction 1 must be so rapid as to preclude radical dimerization; that being the case it seems necessary to conclude that the initial product of reaction 2 is the charge-transfer complex despite the comments made above about Cr^{2+} retardation.

Experimental Section

Materials. The various $[(H_2O)_5CrCH_2C_6H_4Z]^{2+}$ complexes were prepared according to Kochi and Davis.[3] The appropriate benzyl bromide (ca. 0.4 cm^3, 0.2–0.3 mmol) was added to 20 cm^3 of acetone and the solution purged with a vigorous stream of dinitrogen (purified by passage over a heated copper catalyst). A solution of $Cr(ClO_4)_2$ (20 cm^3, 1.0 mmol, prepared by dissolving high-purity electrolytic chromium metal in 0.3 F HClO$_4$[24]) was added. After ca. 5 min reaction time, the solution was poured through a column (10 $\times$ 1 cm) of Dowex 50W-X8 cation exchange resin, 100–200 or 200–400 mesh, in the Li$^+$ form. The column was kept at 0° by water circulating through a condenser-type jacket, and the solution above the resin column was constantly flushed with a solution of purified N$_2$, introduced through a syringe needle and a rubber septum (the positive pressure served also to speed the otherwise painfully slow passage of solution through the column of fine-particle resin). The chromium complexes, after being taken up by the resin column, were eluted with a solution 1 $\times$ 10^{-4} F HClO$_4$, 1.0 F LiClO$_4$. The complex $(H_2O)_5CrBr^{2+}$ eluted quickly, followed by a much slower elution of $[(H_2O)_5CrCH_2C_6H_4Z]^{2+}$. The latter materials are obtained by this procedure at high dilution, typically 2–5 $\times$ 10^{-3} M. The benzylchromium cations were stored under N$_2$ at 0° until used. Their characterization was based in part on the uv–visible spectra which for 1 in H$_2$O were found to occur at values of λ, nm (10^{-3} ϵ, dm^3 mol^{-1} cm^{-1}) as follows: 356 (2.20), 295 (6.97), and 273 (7.67), compared to the published spectrum[3] in 83% (volume) EtOH–H$_2$O: 360 (2.47), 297 (7.92), and 274 (8.38). The para-substituted derivatives in every case exhibited absorption maxima within $\pm$2 nm of the λ_{max} values reported.[3]

Other materials were either reagent grade chemicals or were prepared by standard procedures: $[Cr(H_2O)_6](ClO_4)_3$,[25] $[Fe(H_2O)_6](ClO_4)_3$,[26] $[Co(NH_3)_5Cl](ClO_4)_2$,[27] and $[Co(en)_3]$-$(ClO_4)_3$.[27]

Stoichiometry of Fe^{3+} Reaction with 1. Stoichiometric studies were conducted by measuring the absorbance at 274 nm of solutions prepared by reaction of 1 with excess Fe^{3+}. The method was calibrated by blank determinations of the absorbance due to Fe(III) as a function of [Fe(III)] and [H$^+$] over the concentration ranges of interest.

Identification of Products. Gas chromatography was used to identify the organic products from the acidolysis of **1** in the absence of oxidant and in its reaction with Fe^{3+} (>20-fold excess of Fe^{3+}). The reaction was allowed to run to completion, following which the solution was extracted with two portions of ether-pentane (1:10). The extracts were evaporated to 5 cm^3 on a steam bath using a Snyder column. The reaction products were introduced into a Hewlett-Packard HP 5750 research chromatograph with a 50 × 1 cm column packed with Tenac-GC; the column temperature was 175°, and the peaks were detected by the flame ionization technique.[28] The instrument was calibrated with benzyl alcohol, toluene, and benzaldehyde.

Solutions in which **1** and $[Co(NH_3)_5Cl]^{2+}$ were allowed to react were extracted with pentane, and the extracts were concentrated as before. Further evaporation yielded ca. 10 mg of white crystals, identified as bibenzyl by its melting point, 48° (lit.[29] 52°), and by its ir spectrum,[30] which matched that of a known sample.

The Cr(III) products of the various reactions of **1** are $Cr(H_2O)_6^{3+}$, $(H_2O)_5CrCl^{2+}$, and Cr_2O^{4+}. The reaction solutions were chromatographed on Dowex 50W-X8, and $Cr(H_2O)_6^{3+}$ or $Cr(H_2O)_5Cl^{2+}$ were removed by 1 F HClO$_4$. These products were characterized by their known uv-visible spectra and, in some instances, the yield was determined by analysis of the total chromium content of the combined eluent portions. The green, dimeric 4+ ion was retained on the resin column, consistent in elution characteristics and in appearance with a known sample.

Trapping with Acrylonitrile. Certain reactions of **1** were examined to learn whether they initiated polymerization of acrylonitrile. In cases where positive results were obtained, a copious white flocculent solid separated. This material was identified as poly(acrylonitrile) by its ir spectrum,[30] which matched that of a sample prepared by initiating the polymerization of a refluxing solution of acrylonitrile in EtOH–H$_2$O by addition of benzoyl peroxide. Additionally, the ir spectrum matched that in the literature.[31]

Rate Determinations. The kinetics of reactions of benzylchromium complexes with the various oxidizing agents were determined in solutions of 1.00 M ionic strength maintained with HClO$_4$–LiClO$_4$. The reactions were followed by the change in the uv spectrum of the complex, monitoring the absorbance in each run at a fixed wavelength. These experiments were conducted with the rigorous exclusion of air in quartz cells with rubber serum caps. Temperature control was achieved by immersing the reaction cell in a small water bath positioned in the light beam of the Cary Model 14 spectrophotometer; this bath had quartz windows, and the water it contained was held at the desired temperature by circulation of water through an external jacket. The first-order rate constant in each run was computed from the absorbance readings (D) as the negative of the slope of a plot of ln ($D_t - D_\infty$) vs. time.

References and Notes

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(5) In the presence of potentially coordinating anions such as OAc⁻ and NCS⁻ the rate of reaction 1 does show a first-order dependence upon [1]. The mechanism is different under these circumstances, however, and the suggestion[4] of nucleophilic assistance receives support from the observation[8] that organochromium complexes $(H_2O)_5CrR^{2+}$ undergo trans-anation ca. 10^5 times more rapidly than does $Cr(H_2O)_6^{3+}$.
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(11) Second-order rate constants (dm^3 mol^{-1} sec^{-1}) at 25.0° in HClO$_4$–LiClO$_4$ solutions for reactions of **1** with various electrophiles are as follows: Br$_2$, 8.3 × 10^5 (μ = 1.00 M);[10b] I$_2$, 4.20 × 10^3 (μ = 1.00 M);[10b] Hg^{2+}, 5.0 × 10^4 (μ = 0.10 M);[10c] HgCH$_3^+$, 6.5 × 10^1 (μ = 0.10 M);[10c] and HgC$_6$H$_5^+$, 4.0 × 10^1 (μ = 0.10 M).[10c]
(12) A possible exception is HCrO$_4^-$, where preliminary observation suggest a direct reaction. R. S. Nohr and J. H. Espenson, unpublished observations.
(13) A small quantity, ca. 5%, of benzaldehyde was also detected in the GC experiment but was also found present in the unreacted solution of **1** after acidolysis; it presumably arose from accidental contamination with O$_2$, whose reaction with **1** is known to produce benzaldehyde.[2-4]
(14) The conclusion of a first-order dependence on [1] in the absence of oxidants is based only on the linearity of the rate plots; these measurements were all performed on solutions having very nearly the same initial concentration of **1**, in the range 2.7–5.1 × 10^{-5} M.
(15) Values of σ_p used are those given by H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). The correlation coefficient, r, is 0.996, and the expected standard deviation, s, is 0.0113. (For a definition of terms, see J. Shorter, "Correlation Analysis in Organic Chemistry", Oxford University Press, London, 1973, pp 103–105.)
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(17) The second-order rate constants (dm^3 mol^{-1} sec^{-1}) at 25° for Cr^{2+} oxidations are: (a) Fe^{3+}, 2.3 × 10^3 + 5.6 × 10^3 [H$^+$]$^{-1}$ (G. Dulz and N. Sutin, *J. Am. Chem. Soc.*, **86**, 829 (1964)); (b) O$_2$, >7 × 10^5 (A. G. Sykes, "Kinetics of Inorganic Reactions", Pergamon Press, London, 1966, p 213; see also R. W. Kalacykowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964)); (c) [Co(NH$_3$)$_5$Cl]$^{2+}$, 2.6 × 10^8 and [Co(NH$_3$)$_5$Br^{2+}], >3 × 10^6 (J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965)); (d) H$_2$O$_2$, 2.1 × 10^3 (G. Davies and N. Sutin, unpublished observations, as cited by G. Davies, N. Sutin, and K. O. Watkins, *J. Am. Chem. Soc.*, **92**, 1892 (1970)); (e) Cu^{2+}, 0.17 + 0.59 [H$^+$]$^{-1}$ (K. Shaw and J. H. Espenson, *Inorg. Chem.*, **7**, 1619 (1968)).
(18) The relatively slow reaction of Cu^{2+} with Cr^{2+} appears insufficient in itself to remove Cr^{2+} in competition with its recombination with C$_6$H$_5$CH$_2$·. The same kinetic effect in this case may result instead from the rapid oxidation of the benzyl radical by Cu^{2+}, which (as pointed out in the text) leads to the same kinetic situation.
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(21) Compare $\Delta H^\ddagger$ = 123 kJ mol^{-1} and $\Delta S^\ddagger$ = 47 J mol^{-1} K^{-1} for the SH1 dissociation of 4-pyridinomethylchromium(III) ion[9]

$$[(H_2O)_5CrCH_2\text{---}\langle\text{---}\rangle\text{NH}]^{3+} \longrightarrow Cr^{+}_{aq} + \cdot CH_2\text{---}\langle\text{---}\rangle\text{NH}^+$$
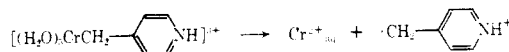
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(28) We are grateful to Professor J. S. Fritz for access to this equipment, and to Mr. Richard Chang for assistance with the operations.
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