

Photochemical Generation of the Acid-Labile (β -Hydroxyethyl)pentaquochromium(III) Ion¹

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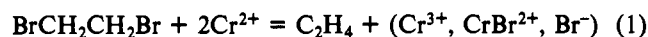
Received May 20, 1981

The complex $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CH}_2\text{OH}^{2+}$ was formed in dilute aqueous HClO_4 by the anaerobic reaction of $\text{Cr}^{2+}(\text{aq})$ and $\cdot\text{CH}_2\text{CH}_2\text{OH}$. The latter was generated photochemically from three independent sources by using flash photolysis of (1) $\text{Cr}^{2+}(\text{aq})$ in solutions containing nitrous oxide and ethylene, (2) $\text{HOCH}_2\text{CH}_2\text{Co}(\text{dmgBF}_2)_2\text{py}$, and (3) $(\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{CH}_2\text{OH}^{2+}$, each in the presence of Cr^{2+} . The complex $\text{CrCH}_2\text{CH}_2\text{OH}^{2+}$ is characterized by an absorption maximum at $390 \pm 5 \text{ nm}$ ($\epsilon 450 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$). The complex reacts rapidly with H_3O^+ to form $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and ethylene, with a pseudo-first-order rate constant dependent upon $[\text{H}^+]$ according to the equation $k_{\text{obs}} = k_0 + k[\text{H}^+]$. The acid-independent rate constant k_0 is barely discernible above zero. The value of k from the three systems listed above is (1) $(1.43 \pm 0.02) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 24.1°C and $\mu = 0.05 \text{ M}$, (2) $(1.5 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C and $\mu = 0.01 \text{ M}$, and (3) $(3.6 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 24.8°C and $\mu = 0.50 \text{ M}$. Studies of system 1 were made as a function of temperature ($\Delta H^\ddagger = 15.8 \pm 0.8 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 13.8 \pm 2.5 \text{ cal mol}^{-1} \text{ K}^{-1}$) and ionic strength. A mechanism is proposed in which the rate-limiting step is dissociation of a water molecule by the proton-assisted cleavage of a carbon-oxygen bond in the parent complex, followed by rapid dissociation of ethylene from what may be a π -bonded $\text{Cr}(\text{III})\text{-C}_2\text{H}_4$ intermediate.

Introduction

Although a great variety of complexes having the general formula $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ are now known, hardly any of these contain electronegative substituents such as a halogen, amine, or hydroxyl on the β carbon. The reason for their scarcity is surely the inherent instability of this particular group of compounds toward reaction with acid in solution, this being the only medium in which such organochromium complexes can be prepared. Two β -substituted complexes, $(\text{H}_2\text{O})_5\text{CrCH}_2\text{C}(\text{CH}_3)_2\text{OH}^{2+}$ and $(\text{H}_2\text{O})_5\text{CrCH}(\text{OH})\text{CH}_2\text{OH}^{2+}$ (or $\text{CrCH}_2\text{CHO}^{2+}$), were detected in pulse radiolysis experiments.² As expected, their lifetimes are very short, ~ 5 and $\sim 25 \text{ ms}$ at 0.1 M H^+ and 25°C . In this regard they are unlike the similarly prepared, analogous long-lived organochromium complexes that lack the β -OH group. The kinetic data for the decomposition of these two complexes were interpreted by a mechanism involving a π -bonded intermediate, formed in a proton-assisted elimination of the β -hydroxyl group. The immediate product was a σ -alkenyl complex,³ which ultimately formed Cr^{3+} and, presumably, 1-butene via protonolysis of the chromium-carbon bond. These reactions are shown in Scheme I.

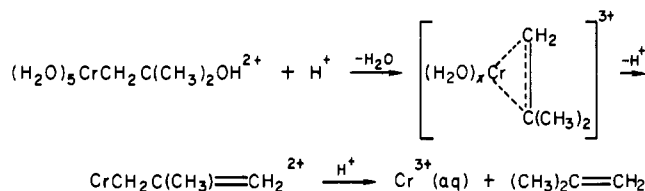
Reactions of β -hydroxyalkyl compounds find numerous literature precedent. Those most pertinent to the present work appear to be the acid cleavage reactions of β -hydroxyalkyl complexes of $\text{Co}(\text{III})$ and $\text{Cu}(\text{II})$ and the decomposition of β -haloalkyl complexes believed to be formed by reactions of vicinal dihalides and Cr^{2+} . A reductive elimination reaction occurs, eq 1, which has been shown⁴ to be a multistep process



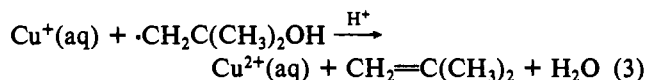
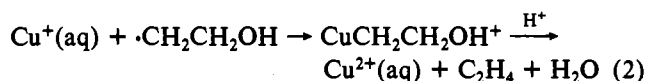
involving sequential halogen removal. Halide ion and $\text{Cr}(\text{III})$ are released during decomposition of a postulated intermediate, the (β -bromoalkyl)chromium complex.

In the case of bis(dimethylglyoximate)cobalt(III) complexes, so-called cobaloximes, several β -hydroxyalkyl complexes were isolated as pure, crystalline compounds. They, too, are unstable in acidic solution toward reactions in which an olefin is formed. Good evidence has been obtained for a mechanism

Scheme I

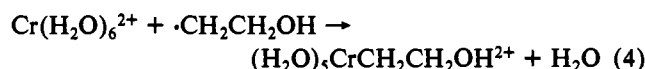


similar to that in Scheme I involving a π -bonded intermediate.⁵⁻⁸ Generation of the β -hydroxyethyl radical in the presence of $\text{Cu}^+(\text{aq})$ leads, by way of an organocopper(II) intermediate, to ethylene (eq 2);^{9,10} the carbon-centered radical



derived from *tert*-butyl alcohol reacts similarly (eq 3).^{9,10} Reactions similar to eq 3 have been proposed for the oxidation of Ni^{+11} and Cd^{+12} by $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$.

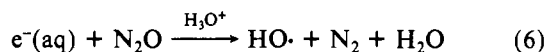
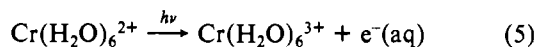
Photochemical routes to (β -hydroxyethyl)chromium(III) ion have been developed during this research, and a study has been made of the kinetics and mechanism of the β -elimination reaction in acidic solution. Flash photolysis of three chemical systems was used to generate the radical $\cdot\text{CH}_2\text{CH}_2\text{OH}$ in the presence of $\text{Cr}^{2+}(\text{aq})$, with each relying upon the fast reaction (eq 4) between these species to produce the desired product.



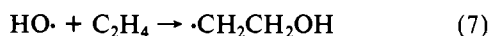
(1) Based on the Ph.D. thesis of D.A.R., Iowa State University, 1981.
(2) Cohen, H.; Meyerstein, D. *Inorg. Chem.* 1974, 13, 2434.
(3) The σ -alkenyl complex shown in Scheme I is suggested to be $\text{CrCH}_2\text{C}(\text{CH}_3)=\text{CH}_2^{2+}$, but its formulation as a substituted vinylchromium ion, $\text{CrCH}=\text{C}(\text{CH}_3)_2^{2+}$, is also a possibility.
(4) Singleton, D. M.; Kochi, J. K. *J. Am. Chem. Soc.* 1967, 89, 6547.

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(6) Brown, K. L.; Ingraham, L. L. *J. Am. Chem. Soc.* 1974, 96, 7681.
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(8) Brown, K. L.; Ramamurthy, S., private communication.
(9) (a) Buxton, G. V.; Green, J. C.; Higgins, R.; Kanji, S. *J. Chem. Soc., Chem. Commun.* 1976, 158. (b) Buxton, G. V.; Green, J. C. *J. Chem. Soc., Faraday Trans. 1* 1978, 74, 697.
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The main system employed for the photochemical production of the β -hydroxyethyl radical consists of the UV photolysis^{13a-c} of Cr^{2+} in solutions containing both nitrous oxide and ethylene. The reactions occurring are shown in eq 5-7. To

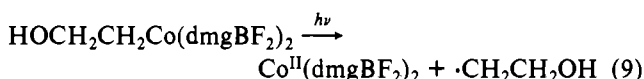
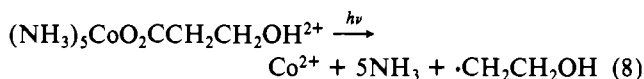


$$k = 8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (13d)$$

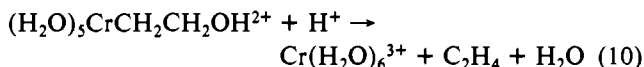


$$k = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (13e)$$

supplement these results, two other photochemical routes were used: UV photolysis of $(\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{CH}_2\text{OH}^{2+}$ ¹⁴ (eq 8) and visible photolysis of a cobaloxime analogue,¹⁵



$\text{HOCH}_2\text{CH}_2\text{Co}(\text{dmgBF}_2)_2\text{py}$ (eq 9), both in the presence of $\text{Cr}^{2+}(\text{aq})$. This publication describes the observations made in each system and the resulting reaction of the organochromium ion with H^+ (eq 10).



Experimental Section

Materials. Several routes to the synthesis of the perchlorate salt of the previously unknown (β -hydroxypropionato)pentaamminecobalt(III) ion, $[(\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{CH}_2\text{OH}](\text{ClO}_4)_2$, were attempted based on methods published for similar complexes.¹ The most satisfactory method consisted of heating an excess of the half-neutralized carboxylic acid¹⁶ with a solution of $[(\text{NH}_3)_5\text{CoOH}_2](\text{ClO}_4)_3$. The latter compound was obtained as a crystalline substance by addition of an equivalent amount of perchloric acid to $[(\text{NH}_3)_5\text{CoCO}_3] \cdot \text{NO}_3 \cdot 1/2\text{H}_2\text{O}$.¹⁷ A sample of $\text{HOCH}_2\text{CH}_2\text{CO}_2\text{H}$ (0.9 g, 10 mmol)¹⁶ in 5 mL of H_2O was mixed with 0.2 g of sodium hydroxide, added to 2.0 mmol of $[(\text{NH}_3)_5\text{CoOH}_2](\text{ClO}_4)_3$ in 20 mL of H_2O , and stirred for 20 h at 45 °C. The cooled solution was loaded onto a 25-cm column of Sephadex SP C-25 cation exchange resin. Elution with 0.01 M perchloric acid removed a small quantity of a pink complex. With 0.25 or 0.50 M acid a larger, cherry-red band eluted. It was judged by its elution pattern to be the desired 2+ ion, leaving at the top of the column an orange-red band shown to be the unreacted tripositive parent aquo complex. The solution containing $(\text{NH}_3)_5\text{CoO}_2\text{CH}_2\text{CH}_2\text{OH}^{2+}$ was evaporated at 40-45 °C under reduced pressure to a wet precipitate, which after further drying yielded a pink powder. The ¹H and ¹³C NMR spectra¹ supported the formula assigned, although suggesting also that the sample was contaminated with some free carboxylic acid. In keeping with this, the % Co, 9-12%

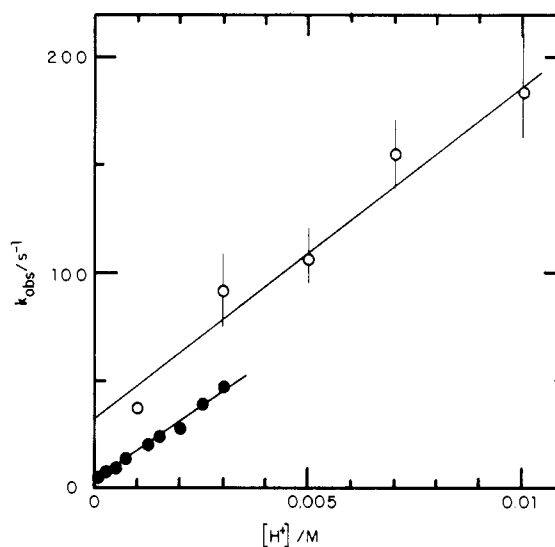


Figure 1. Illustration of the linear dependence of k_{obs} on $[\text{H}^+]$ for the β -elimination reaction of $\text{CrCH}_2\text{CH}_2\text{OH}^{2+}$ prepared by photolysis of (1) Cr^{2+} , N_2O , and C_2H_4 at 24.1 °C and $\mu = 0.010 \text{ M}$ (filled circles) and (2) $\text{HOCH}_2\text{CH}_2\text{Co}(\text{dmgBF}_2)_2\text{OH}_2$ in the presence of Cr^{2+} at 25 °C and $\mu = 0.050 \text{ M}$ (open circles).

in various samples, was less than 13.64% calculated for $[(\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{CH}_2\text{OH}](\text{ClO}_4)_2$. The UV-visible spectrum, with due allowance for the % Co, was the same for all samples and agreed with that expected for a (carboxylato)pentaamminecobalt(III) complex, $\lambda_{\text{max}} 502 \text{ nm}$ ($\epsilon 70.4 \text{ M}^{-1} \text{ cm}^{-1}$) and 351 (57.7).

The samples of (β -hydroxyethyl)(pyridine)bis(dimethylglyoximate)cobalt(III) and of its previously unreported analogue $\text{HOCH}_2\text{CH}_2\text{Co}(\text{dmgBF}_2)_2\text{py}$ were prepared by standard procedures⁴⁻⁷ and gave good elemental analyses and NMR spectra. Aqueous solutions of $\text{Cr}(\text{ClO}_4)_2$ were prepared by dissolving an excess of the metal in oxygen-free perchloric acid. Nitrogen and nitrous oxide were purified by passage through Cr^{2+} scrubbing towers. Ethylene, 99.98% purity, was used as received. Other reagents such as perchloric acid, sodium hydroxide, and lithium perchlorate were prepared and standardized by accepted methods.

Techniques. The flash photolysis experiments were done by using a Xenon Corporation Model 710 system equipped with FP-5-100C fast-extinguishing flash tubes. A solution of the desired starting materials other than Cr^{2+} was made up in a cylindrical spectrophotometer cell of 10-cm optical path length constructed entirely of quartz and sealed with a rubber septum wired in place. The solution was thoroughly purged of air with nitrogen or, in some experiments, nitrous oxide and brought to the (approximate) reaction temperature. Photolysis of Cr^{2+} and $(\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{CH}_2\text{OH}^{2+}$ was accomplished by using unfiltered radiation. Photolysis of $\text{HOCH}_2\text{CH}_2\text{Co}(\text{dmgBF}_2)_2\text{py}$ was restricted to visible light either with a cell in which the outer jacket contained 0.1 M sodium nitrite ($\lambda > 380 \text{ nm}$) or, with equivalent results, by slipping a Pyrex tube over each flashlamp. The temperature of each solution was determined immediately after photolysis by using a miniature thermistor probe and digital thermometer.

The transient absorption that was produced as a result of flash photolysis was evident at several wavelengths. The kinetic monitoring was done by use of an oscilloscope, most often following the transmittance at 380-390 nm, the region where all Cr^{2+} complexes have an absorption maximum. Other wavelengths were studied as needed to determine the absorption spectrum of $\text{CrCH}_2\text{CH}_2\text{OH}^{2+}$. Kinetic data were analyzed by standard methods, usually as simple pseudo-first-order kinetics, but in one case for a mixture of two transient components.

Results

Photolysis of $\text{Cr}^{2+}(\text{aq})$.^{13a-c} The most extensive set of determinations was carried out on the system consisting of Cr^{2+} , N_2O , and C_2H_4 because fewer complicating reactions need be considered. Typical concentrations were $5.0 \times 10^{-4} \text{ M}$ Cr^{2+} , $2.0 \times 10^{-2} \text{ M}$ N_2O , and $8.8 \times 10^{-4} \text{ M}$ C_2H_4 . Ionic strength was maintained at 0.050 M by addition of lithium perchlorate,

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- (14) (a) Campano, D. D.; Kantrowitz, E. R.; Hoffman, M. Z.; Weinberg, M. S. *J. Phys. Chem.* **1974**, *78*, 686. (b) Kantrowitz, E. R.; Hoffman, M. Z.; Endicott, J. F. *Ibid.* **1971**, *75*, 1914.
- (15) Maillard, P.; Gianotti, C. *J. Organomet. Chem.* **1979**, *182*, 225.
- (16) Read, R. R. *Org. Synth.* **1927**, *7*, 54.
- (17) Basolo, F.; Murmann, R. K. *Inorg. Synth.* **1953**, *4*, 171.

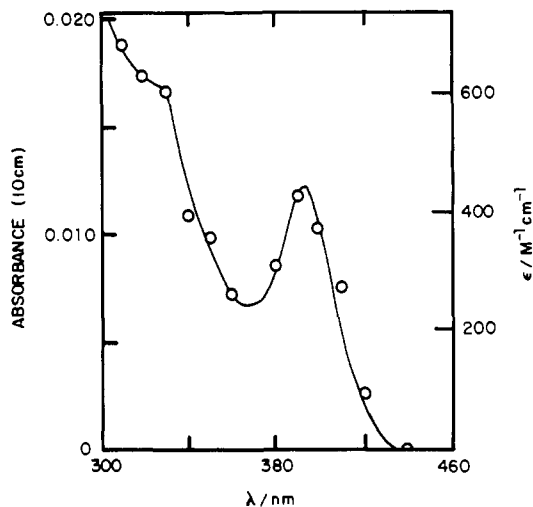


Figure 2. The UV-visible spectrum of the chemical transient identified as $\text{CrCH}_2\text{CH}_2\text{OH}^{2+}$.

and temperature was kept at 24.1 ± 0.5 °C. Concentrations of H^+ were varied in the range 1.0×10^{-4} to 3.0×10^{-3} M. A transient was detected by its absorbance at 390 nm, which decayed rapidly with time by pseudo-first-order kinetics. A plot of k_{obsd} vs. $[\text{H}^+]$ is linear (Figure 1), suggesting the rate equation

$$-d[\text{CrCH}_2\text{CH}_2\text{OH}^{2+}]/dt = (k_0 + k[\text{H}^+])[\text{CrCH}_2\text{CH}_2\text{OH}^{2+}] \quad (11)$$

A least-squares fit of the data gives $k_0 = 2.9 \pm 0.4 \text{ s}^{-1}$ and $k = (1.43 \pm 0.02) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. We express some doubt, however, whether the acid-independent term is real. It is difficult to determine the precise concentration of perchloric acid remaining in solutions of $\text{Cr}(\text{ClO}_4)_2$ prepared by dissolving the metal in insufficient acid. An uncertainty in $[\text{H}^+]$ that would shift its value as little as 2×10^{-4} M in the runs would cause the line in Figure 1 to pass through the origin.

The spectrum of the transient was determined on a point-by-point basis in the region 310–440 nm and is shown in Figure 2. It is characterized by a maximum at 390 ± 5 nm and a minimum at 365 ± 10 nm. The calculation of molar absorptivities requires knowledge of the concentration of the transient, which can be indirectly estimated from the yield of $e^-(\text{aq})$ from eq 5. In the absence of N_2O , $e^-(\text{aq})$ forms H atoms and ultimately $(\text{H}_2\text{O})_5\text{CrH}^{2+}$, which has a well-characterized spectrum.^{18,19} The independently determined yield of CrH^{2+} permits calculation of the yield of $e^-(\text{aq})$, which, after due allowance for its competing reaction with H_3O^+ , can be converted to the concentration of $\text{HO}\cdot$ formed in a solution having $[\text{N}_2\text{O}] = 0.020$ M. The fraction of $\text{HO}\cdot$ that adds to ethylene (eq 6) in competition with Cr^{2+} oxidation can be calculated from the known rate constants. On the basis of all of these considerations,²⁰ the concentration of $\cdot\text{CH}_2\text{CH}_2\text{OH}$ in an experiment having 5×10^{-4} M Cr^{2+} , 2.0×10^{-2} M N_2O , 8.8×10^{-4} M C_2H_4 , and 1.0×10^{-4} M H_3O^+ is $(2.6 \pm 0.4) \times 10^{-6}$

M. From the measured absorbance change at 390 nm, 0.0117 ± 0.0006 in a 10-cm cell, the molar absorptivity is estimated to be $(4.5 \pm 1.0) \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$. Although the uncertainty is quite substantial, the value is consistent with those for other CrR^{2+} cations, all of which have a maximum in this region and a similar molar absorptivity value.

Photolysis of Cobalt Complexes. Although Cr^{2+} reacts too rapidly with the organocobaloxime for use here, Cr^{2+} and $\text{HOCH}_2\text{CH}_2\text{Co}(\text{dmgBF}_2)_2\text{py}$ are thermally stable for short times.²¹ Visible flash photolysis¹⁵ of solutions containing the cobalt complex, $\sim 2 \times 10^{-5}$ M, and Cr^{2+} , 1×10^{-3} M, produced a short-lived transient, which absorbed more than the reactants at 390 nm. The permanent spectral change corresponded to the conversion of the spectrum of $\text{HOCH}_2\text{CH}_2\text{Co}(\text{dmgBF}_2)_2\text{py}$ (λ_{max} 442 and 380 nm) to one having a more intense maximum at 456 nm. The latter corresponds to the independently prepared cobalt(II) complex $(\text{H}_2\text{O})_2\text{Co}(\text{dmgBF}_2)_2$, which, unlike the rapidly decomposed²² pseudomacrocyclic complex $(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2$, reacts only slowly with H_3O^+ .

Flash photolysis conducted in the presence of 2–5 M CH_3OH did not affect the yield or rate constant of the transient. No $\text{CrCH}_2\text{OH}^{2+}$, which would remain detectable for hours under these conditions, was formed. These observations rule out any role of hydrogen atoms in the generation of the transient and substantiate that it is not CrH^{2+} , a species of similar absorption spectrum^{18,19} and lifetime.

The transient absorption, monitored at 390 nm, decayed with time in a process following precise pseudo-first-order kinetics. Values of k_{obsd} were determined as a function of $[\text{H}_3\text{O}^+]$, 0.0010–0.010 M, at 0.01 M ionic strength and 25 °C. The plot of k_{obsd} vs. $[\text{H}^+]$ is linear, as shown in Figure 1. A least-squares analysis according to eq 12 gives $k_0 = 33 \pm 12 \text{ s}^{-1}$ and $k = (1.5 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The uncertainty in the former is, again, too large to permit its being identified as indicative of an authentic reaction pathway.

The third system, examined only briefly, consists of photolysis of (β -hydroxypropionato)pentaamminecobalt(III) ion²³ in the presence of Cr^{2+} ,²⁴ according to eq 8 and 9. A transient was seen at 380–390 nm that was absent if Cr^{2+} was not present. Saturation of the solution with N_2O rather than N_2 did not affect the concentration or lifetime of the transient, showing²⁵ again that it cannot be CrH^{2+} . The kinetics of the transient decay are not as clean in this system as in the other

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 (19) Ryan, D. A.; Espenson, J. H. *Inorg. Chem.* **1981**, *20*, 4401.
 (20) Details of the calculation are as follows: The same experiment in the absence of N_2O and C_2H_4 gives $[\text{CrH}^{2+}] = (1.17 \pm 0.21) \times 10^{-5}$ M, calculated from $\epsilon = 190 \pm 20 \text{ M}^{-1} \text{ cm}^{-1}$ at 380 nm.²¹ The yield of $e^-(\text{aq})$ is $[\text{CrH}^{2+}]/0.94 = (1.24 \pm 0.22) \times 10^{-5}$ M, the fraction 0.94 accounting for the reaction with H_3O^+ to form $\text{H}\cdot$ ($k = 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) as opposed to reducing Cr^{2+} ($k = 1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). At $[\text{Cr}^{2+}] = 5 \times 10^{-4}$ M, $[e^-(\text{aq})]$ is calculated to be 6.2×10^{-6} M for a flash of the same intensity. The fraction of $e^-(\text{aq})$ converted to $\text{HO}\cdot$ by reaction with 0.020 M N_2O ($k = 8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) is 0.949 at $[\text{H}^+] = 1 \times 10^{-4}$ M or $[\text{HO}\cdot] = 5.9 \times 10^{-6}$ M. Hydroxyl radicals react with Cr^{2+} ($k = 4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) or produce the desired radical (eq 7). The fraction of the latter is 0.44, giving $[\cdot\text{CH}_2\text{CH}_2\text{OH}] = (2.6 \pm 0.4) \times 10^{-6}$ M.

(21) Samples of $\text{HOCH}_2\text{CH}_2\text{Co}(\text{dmgBF}_2)_2\text{py}$ contained a minor contaminant that we could not remove, which reacts on mixing with Cr^{2+} . The subsequent photochemistry and chemistry are quite clean, however, suggesting that this did not interfere. It is presumed that this complex rapidly loses pyridine in dilute perchloric acid, like the organo(pyridine)cobaloximes do, although that point is immaterial here.
 (22) The cobalt complex $\text{Co}^{\text{II}}(\text{dmgBF}_2)_2$ contains an authentic macrocyclic ligand and in the $\text{Co}(\text{II})$ state is only slowly converted to $\text{Co}^{2+}(\text{aq})$. This contrasts with the cobalt(II) cobaloxime, $\text{Co}(\text{dmgH})_2$, which is destroyed by reaction with H^+ nearly instantaneously.
 (23) It is the cobalt complex and not Cr^{2+} that is photolyzed under these conditions. At λ 270 nm, for example, the molar absorptivities are $\epsilon_{\text{Co}} = 6.5 \times 10^2$ and $\epsilon_{\text{Cr}(\text{II})} = 1.5 \times 10^1 \text{ M}^{-1} \text{ cm}^{-1}$. Thus >95% of the light is absorbed by the cobalt complex, which is the species whose photolysis is desired. The UV photolysis of Cr^{2+} is unimportant under these conditions.
 (24) The thermal reaction between (carboxylato)pentaamminecobalt(III) and Cr^{2+} is, as expected, slow. The rate constant for $(\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{OH}^{2+} + \text{Cr}^{2+}$ is $3.06 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and $\mu = 1.0$ M: Butler, R. D.; Taube, H. *J. Am. Chem. Soc.* **1965**, *85*, 5597. The present reaction was found to have $k = 0.9 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$. In addition to the absorbance change corresponding to reduction of the $\text{Co}(\text{III})$ complex, there is a second reaction, which is much slower than the first and may be catalyzed by Cr^{2+} . Although it was not investigated in any detail, that reaction may be the aquation or inner-sphere isomerization of the $\text{Cr}(\text{III})$ complex $\text{CrO}_2\text{CCH}_2\text{OH}^{2+}$, since similar processes are known: Gould, E. S. *J. Am. Chem. Soc.* **1965**, *87*, 4730.
 (25) Use of nitrous oxide rather than nitrogen does not affect the yield of the transient whereas $e^-(\text{aq})$, the precursor to the $\text{H}\cdot$ needed to form CrH^{2+} , is efficiently scavenged by N_2O .

two in that two components having decay times that vary differently with $[H^+]$ could be resolved from the kinetic analyses. The smaller and slower reacting transient probably arises from an impurity in the cobalt(III) complex, whereas the faster reacting of the two appears to be the desired complex $CrCH_2CH_2OH^{2+}$. The pseudo-first-order rate constant for its reaction with H^+ varies linearly with $[H^+]$ from 0.0025 to 0.04 M. The plot has $k_0 \approx 0$ and k (eq 11) $= (3.6 \pm 0.4) \times 10^4 M^{-1} s^{-1}$ at 24.8 °C and $\mu = 0.50$ M. The increase in k as compared to that in the two preceding cases can be accounted for by the kinetic salt effect at higher ionic strength.

The gaseous products from photolysis of $(NH_3)_5CoO_2CCH_2CH_2OH^{2+}$ in the presence of Cr^{2+} were swept from the solution by a stream of nitrogen and condensed into a cold trap carefully protected from atmospheric CO_2 . The products, determined mass spectrometrically, consisted only of C_2H_4 and CO_2 .

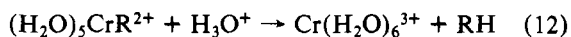
Effects of Temperature and Ionic Strength. Rate constants for the system consisting of Cr^{2+} , N_2O , and C_2H_4 were determined as a function of temperature (13.2–42.6 °C) at $\mu = 0.05$ M. The nominal $[H^+]$ in each case was 1.0×10^{-4} M, and the value of k_{obsd} increases from 1.38 to 24.9 s^{-1} over this range. As discussed earlier, however, there are reasons for believing that unaccounted acid from the chromium(II) perchlorate solution may raise the real $[H^+]$ closer to 3×10^{-4} M. If the latter value is used and k_0 of eq 11 is set to zero, the activation parameters are $\Delta H^\ddagger = 15.8 \pm 0.8$ kcal mol $^{-1}$ and $\Delta S^\ddagger = 13.8 \pm 2.5$ cal mol $^{-1}$ K $^{-1}$. On the other hand, a treatment that would formulate both rate constants as contributing would give different values.²⁶ The positive value of ΔS^\ddagger under the former interpretation agrees with results from (β -hydroxyalkyl)cobaloximes⁷ and is consistent with the β -elimination mechanism given in Scheme II.

The rate constant for the same system was determined as a function of ionic strength ($\mu = 0.002$ – 0.10 M) at constant $[H^+]$, nominally 1×10^{-4} M. There is a small but steady increase in k_{obsd} with μ throughout this range, from 3.5 to 4.4 s^{-1} . The increase is consistent with the transient being positively charged. The low precision of the data, the previously mentioned uncertainty in $[H^+]$, and the questions regarding the origin (and reality) of the k_0 term of eq 11 preclude a quantitative interpretation of the ionic strength effect.

Discussion

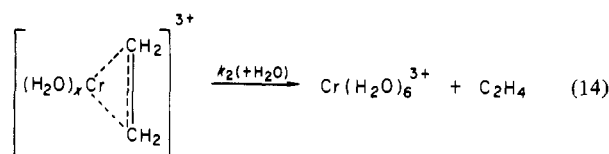
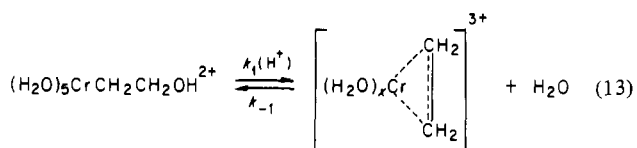
The methods chosen to generate $CrCH_2CH_2OH^{2+}$ were based on known photochemical processes followed by established thermal reactions. By the correct choice of reaction conditions and concentrations, the effects of undesired side reactions can be minimized. It is expected from the rate constants for the reaction between Cr^{2+} and other carbon-centered radicals, which range² from 3.4×10^7 to 3.5×10^8 $M^{-1} s^{-1}$, that formation of $CrCH_2CH_2OH^{2+}$ according to eq 4 will have $t_{1/2} \approx 15$ μs and will therefore be complete within the period of the flash itself. Consequently, we did not expect to be able to measure the rate of eq 4 and were thus not surprised that the transient was completely formed by the time of the first absorbance measurement.

All organochromium complexes that have been examined are subject to a protonolysis (acidolysis) reaction which results in heterolytic cleavage of the chromium–carbon bond (eq 12).



Presumably $CrCH_2CH_2OH^{2+}$ would be subject to this reaction as well. That, however, is not the reaction we believe re-

Scheme II



sponsible for the kinetic results obtained here, despite the fact that the rate law of eq 11 has the same concentration dependences found for other organochromium ions in eq 12. For one thing, the organic product expected from acidolysis of $CrCH_2CH_2OH^{2+}$ is ethanol, not ethylene. For another, the rate constant for acidolysis would be expected to be much smaller. The comparison of $Cr-n-C_3H_7^{2+}$ (with $k_{12} = 3.0 \times 10^{-4} + 6.5 \times 10^{-5}[H^+]$)²⁷ to $CrCH_2CH_2OH^{2+}$ clearly suggests that the latter decomposes by a different reaction. Similar comparisons with $CrCH_2CH_3^{2+}$ or $CrCH_2OH^{2+}$ lead to the same conclusion.

In keeping with mechanistic studies of reactions similar to the present, we suggest that the steps of Scheme II comprise the mechanism of eq 10.

It is reasonable to propose that the π intermediate obeys the steady-state approximation, since the absorbance of the transient decays to that of $Cr(H_2O)_6^{3+}$ by a simple exponential function; that would not be the case if the intermediate attained an appreciable concentration. With that assumption the rate expression derived for eq 13 and 14 is

$$\frac{-d[CrCH_2CH_2OH^{2+}]}{dt} = \left(\frac{k_1 k_2}{k_2 + k_{-1}} \right) [CrCH_2CH_2OH^{2+}][H^+] \quad (15)$$

Based on comparisons with the data for the corresponding reaction of (β -hydroxyethyl)cobaloxime,⁷ it seems reasonable to propose that the first step, eq 13, is rate limiting. Indeed, the argument should apply even more strongly here since the d^3 chromium center is not capable of stabilizing such a π -bonded intermediate. If that is the case then the rate law of eq 15 reduces to the simpler form with $k = k_1$. This argument is consistent with the positive entropies of activation observed for this case (13.8 ± 2.5 cal mol $^{-1}$ K $^{-1}$) and for (β -hydroxyethyl)cobaloxime (29.9 ± 1.2 cal mol $^{-1}$ K $^{-1}$) in that one or more water molecules dissociate from the activated complex in this step during the course of forming the indicated π intermediate.

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 acknowledge the Chemistry Department Instrument Services Group (T. Lyttle, W. McGranahan) for ^{13}C NMR spectra and the Ames Laboratory Analytical Services Groups for mass spectrometric (G. J. Flesch) and elemental (R. J. Bachman) analyses.

Registry No. $(H_2O)_5CrCH_2CH_2OH^{2+}$, 79802-98-5; $(H_2O)_6Cr^{2+}$, 20574-26-9; N_2O , 10024-97-2; C_2H_4 , 74-85-1; $HOCH_2CH_2Co(dmgBF_2)_2py$, 26544-81-0; $[(NH_3)_5CoO_2CCH_2CH_2OH](ClO_4)_2$, 79803-00-2; $[(NH_3)_5CoOH_2](ClO_4)_3$, 36395-83-2.

(26) This would give, for k_0 , $\Delta H^\ddagger = 19.6 \pm 0.8$ kcal mol $^{-1}$ and $\Delta S^\ddagger = 9.4 \pm 2.6$ cal mol $^{-1}$ K $^{-1}$, and, for k , $\Delta H^\ddagger = 10.3 \pm 1.1$ kcal mol $^{-1}$ and $\Delta S^\ddagger = -5.0 \pm 3.9$ cal mol $^{-1}$ K $^{-1}$.

(27) Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463.