

calculations have been described previously.³⁹ Due to the low absorption coefficient ($\mu = 23 \text{ cm}^{-1}$), the small size (approximately $0.23 \times 0.40 \times 0.20 \text{ mm}$), and the very irregular shape of the data collection crystal, no absorption correction was performed.

The positions of the palladium atoms were assigned from Harker sections of the Patterson map and confirmed by direct methods (MULTAN 78). Initial positions for all nonhydrogen atoms were then obtained from Fourier syntheses phased by the metal atoms. Scattering factors for palladium, chlorine, nitrogen, and carbon were taken from ref 40, as were the correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to palladium. Disorder was detected in the dimethylene bridge of the TMEDA ligand (C8-C9), and attempts were made to model this disorder by including four fractional carbon atoms. This model proved to be unsatisfactory, and the dimethylene bridge of TMEDA was best modeled by two whole carbon atoms. Refinement was continued, with anisotropic thermal parameters for all atoms, until all shifts in parameters, both

thermal and positional, were less than 15% of the estimated standard deviation for that parameter.

The final R value was 0.063 (unobserved reflections not included), while the final R_w was 0.077. The error in an observation of unit weight was 2.24. The calculated and observed intensities of the 25 most intense reflections were examined, and correction for secondary extinction was not deemed necessary. In the final difference Fourier map, peaks with intensities of 1.2, 1.1, and $1.0 \text{ e} \text{ \AA}^{-3}$ were associated with Pd1. A peak of intensity of $0.8 \text{ e} \text{ \AA}^{-3}$ was associated with C2, while two peaks of $0.8 \text{ e} \text{ \AA}^{-3}$ were associated with Pd2 and Pd1, respectively. All other peaks were less than $0.7 \text{ e} \text{ \AA}^{-3}$. Final atomic positional and anisotropic thermal parameters are listed in Tables VIII and IX.

Acknowledgment. This work was supported under Grant No. CHE 80-19573 from the National Science Foundation (L.S.H.) and by the Swedish National Science Research Council and the Swedish Board for Industrial Development (B.Å.). High-field and ^{13}C NMR spectra were run by the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. CHE 78-18581. Computer funds for the X-ray structure determination were supplied by Colorado State University.

Supplementary Material Available: A list of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

(39) The following programs were used in structure determination: Zalkin's FORDAP Fourier program; Ibers' NUCL, a group-nongroup least-squares version of the Busing-Levy ORFLS program; Ibers' CELREF for least-squares refinement of cell parameters; ORFFE, Busing and Levy's function and error program; ORTEP, C. K. Johnson's thermal ellipsoid plotting program. The program for data reduction and L_p correction was locally written. MULTAN 78 (P. Main and M. Woolfson) was obtained from G. J. B. Williams (Brookhaven National Laboratory).

(40) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1969.

Reaction of Isopropyl(pentaaquo)chromium(III) Ion with Molecular Oxygen in Aqueous Solution: Kinetics of the Chain Reaction and Effects of Chain-Breaking Reagents and of Variable Ionic Strength¹

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Abstract: The reaction referred to in the title occurs according to the idealized stoichiometry $(\text{H}_2\text{O})_5\text{CrCH}(\text{CH}_3)_2^{2+} + \text{O}_2 + \text{H}^+ = \text{Cr}(\text{H}_2\text{O})_6^{3+} + (\text{CH}_3)_2\text{CO}$, although smaller amounts of HCrO_4^- , $\text{Cr}_2(\text{OH})_2^{4+}$, and $(\text{CH}_3)_2\text{CHOH}$ are also formed. The rate of reaction is given by $-\text{d}[\text{CrCH}(\text{CH}_3)_2^{2+}]/\text{d}t = k[\text{CrCH}(\text{CH}_3)_2^{2+}]^{3/2}$, with $k = 0.49 \pm 0.06 \text{ M}^{-1/2} \text{ s}^{-1}$ at 25.0°C and 1.0 M ionic strength, independent of $[\text{O}_2]$ and $[\text{H}^+]$ ($0.003\text{--}0.1 \text{ M}$). The kinetics are consistent with a chain mechanism initiated by unimolecular homolysis of $\text{CrCH}(\text{CH}_3)_2^{2+}$ ($k_H = (1.78 \pm 0.11) \times 10^{-4} \text{ s}^{-1}$). The preferred mechanism is the one consistent with the striking inhibition by Fe^{2+} or high concentrations of Cu^{2+} , $0.02\text{--}0.40 \text{ M}$; in the latter case the rate law for the chain reaction becomes $-\text{d}[\text{CrCH}(\text{CH}_3)_2^{2+}]/\text{d}t = k_{\text{Cu}}[\text{CrCH}(\text{CH}_3)_2^{2+}][\text{O}_2][\text{Cu}^{2+}]^{-1}$. In this chain mechanism, $(\text{CH}_3)_2\dot{\text{C}}\text{H}(\text{R}\cdot)$ and $(\text{CH}_3)_2\text{CHOO}(\text{ROO}\cdot)$ are the chain-carrying intermediates. One propagation step is the bimolecular ($\text{S}_{\text{H}2}$) displacement of $\dot{\text{R}}$ by ROO through attack at the metal center of the organochromium complex. The rate of reaction is unchanged by addition of the inert electrolytes lithium perchlorate or perchloric acid in the range of ionic strength $0.0033\text{--}0.043 \text{ M}$. This effect, which is diagnostic of mechanism in a chain reaction, unlike the situation with nonchain reactions, supports the mechanism above and rules out a kinetically equivalent mechanism in which the chain-carrying intermediates are Cr^{2+} and CrO_2^{2+} . The latter mechanism can also be ruled out on other grounds, including the failure of the independently prepared CrO_2^{2+} to react with Cu^{2+} .

Metal salts often function as catalysts for the oxidation of organic compounds in processes of considerable commercial importance,^{2a} accounting for the continuing interest given to the ability of soluble metal complexes to activate molecular oxygen.^{2b} Although complexes between the metal and molecular oxygen do

not appear to be involved in the major reaction pathways for hydrocarbon autoxidation,^{2a} reactions of organometals with molecular oxygen may play an important role. The reactions of main group organometallic complexes^{3a} have been studied much more thoroughly than have reactions of transition-metal complexes. Detailed studies of the kinetics and mechanisms of reactions of metal alkyls with O_2 are limited indeed, but it is well established

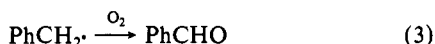
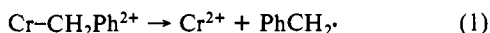
(1) Based in part on the Ph.D. thesis of D.A.R., Iowa State University, 1981.

(2) (a) Parshall, G. W. "Homogeneous Catalysis", Wiley: New York, 1980; Chapter 10. (b) Khan, M. M. J. T.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974; Vol. I, Chapter 2.

(3) (a) Razuvaev, G. A.; Brilkina, T. G. *Russ. Chem. Rev. (Engl. Trans.)* **1976**, *45*, 1135 (translated from *Usp. Khim.* **1976**, *45*, 2196). (b) Brilkina, T. G.; Shushunov, V. A. "Reactions of Organometallic Compounds with Oxygen and Peroxides"; Iliffe: London, 1969.

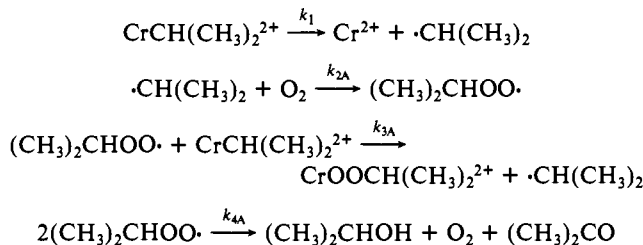
that, like the reactions of hydrocarbons with O₂, free-radical intermediates and chain mechanisms are often involved.^{3b}

The prospect of an informative study appeared to us when we noted^{4a} that secondary organochromium cations of the general series (H₂O)₅CrR²⁺ required anaerobic conditions for their stability and for a study of their electrophilic reactions with Hg²⁺; in contrast, the primary alkyl-chromium complexes appear to be unaffected by dissolved oxygen within their lifetimes in solution (in both cases a slow acidolysis or protonolysis reaction occurs, CrR²⁺ + H₃O⁺ = Cr³⁺(aq) + RH, which usually requires many hours to go to completion for R = a primary or secondary alkyl). A plausible explanation for the reaction of CrCH(CH₃)₂²⁺ with O₂ was that it occurred by the same mechanism as the benzylchromium ion:^{4b} the rate-limiting step is homolysis of the metal-carbon bond (eq 1), followed by the rapid oxidation of Cr²⁺ and benzyl radicals (eq 2 and 3).

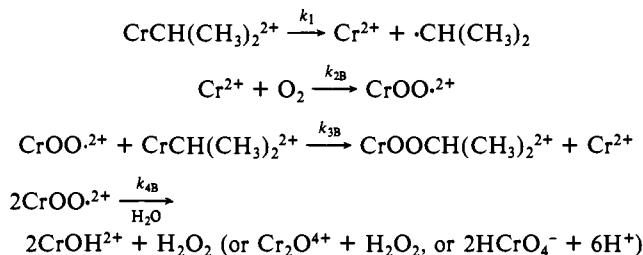


We showed, in results already reported in preliminary form,⁵ that this mechanism did not apply. Indeed, although the homolysis of CrCH(CH₃)₂²⁺ as well as reactions of O₂ with Cr²⁺ and (CH₃)₂CH might well be expected to play a role in the reaction, the actual sequence of events is more complex. The kinetic data support a chain mechanism such as that originally proposed,⁵ shown in mechanism A. A very real alternative is given in mechanism B. In this paper we give the results of our studies and consider specific experiments designed to distinguish between these mechanisms.⁶

Mechanism A



Mechanism B

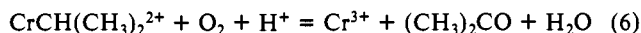
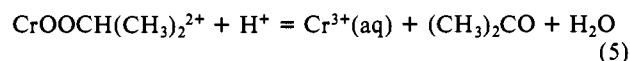
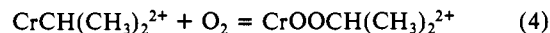


(4) (a) Leslie, J. P., II; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4839. (b) Nohr, R. S.; Espenson, J. H. *Ibid.* **1975**, *97*, 3392.

(5) Ryan, D. A.; Espenson, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 2488. It should be noted that the value cited for k_1 or k_H in this article is incorrect. As shown here the correct value is $1.8 \times 10^{-4} \text{ s}^{-1}$ not $<10^{-6} \text{ s}^{-1}$. This alters certain other calculated values given in that reference, such as k_{3A} and the chain lengths.

(6) The chain mechanisms shown appear incomplete in that they do not specify the fates of the minor intermediates which are not chain-carrying. In these cases where the kinetic chains are long, of course, very little of the net chemical reaction is accounted for by their subsequent reactions. In the mechanism shown, these include Cr²⁺ in mechanism A, which can be assumed to be oxidized to Cr(III) complexes via CrO₂²⁺, and ·CH(CH₃)₂ in mechanism B, which is oxidized via reactions 2A and 4A. It should be noted that self-reaction of two alkyl radicals is never important in these mechanisms since reactions with O₂ or Cr²⁺ always dominate at the very low steady-state concentrations of ·CH(CH₃)₂. Mechanisms analogous to A and B, but involving termination by reaction between CrO₂²⁺ and (CH₃)₂CHOO·, or Cr²⁺ and (CH₃)₂CHOO·, are not considered here because they lead to different rate laws.

An alkylperoxochromium ion is postulated to be the immediate product of the reaction. Other alkylperoxo complexes are formed in "oxygen insertion" reactions, including the large and extensively studied series of stable alkylperoxocobaloximes⁷ as well as unstable compounds derived from the alkyls of titanium, zirconium, molybdenum, and tungsten.⁸ The proposed mechanisms, in the limit where the chain length is high, would correspond to the stoichiometric reaction of eq 4. By postulating that CrOOCH(CH₃)₂²⁺, like the cobaloximes,^{9,10} is unstable in acid solution (eq 5), then the final reaction products are accounted for by the net stoichiometric reaction of eq 6. The latter is really only an approximation of the mixture of products formed, as considered subsequently.



Experimental Section

Materials. Solutions containing the complex (H₂O)₅CrCH(CH₃)₂²⁺ were prepared by reaction of aqueous chromium(II) perchlorate and 2,3-dimethyl-2-butyl hydroperoxide¹¹ as previously described.^{4a} The complex was separated by ion-exchange chromatography on a column of Sephadex C-25 resin in the Na⁺ or H⁺ form. The column was carefully deoxygenated and was chilled by circulation of water at 0 °C through an external jacket. After exhaustive washing to remove any unreacted hydroperoxide, elution with anaerobic sodium perchlorate (0.2–0.5 M containing 0.01 M perchloric acid) caused four bands to separate. The first was the yellow-to-brown band of the dipoisitive organochromium complex, followed by blue-grey Cr(H₂O)₆³⁺ and two smaller bands of dinuclear Cr(III) species, one blue-green, the other dark green. The band containing CrCH(CH₃)₂²⁺ was collected under nitrogen at 0 °C and stored in a freezer at –10 °C to slow decomposition. Depending on the nature of the experiments, the stored solutions were used 1–4 days after preparation. The UV-vis spectrum of the purest solutions of the complex shows the following absorption maxima: 560 nm (ε 10 M⁻¹ cm⁻¹), 400 (488), and 290 (2330). These values compare reasonably well to those found previously:^{4a} 560 (10), 399 (366), and 290 (1880); the lower values in the latter can be attributed to the presence of some Cr(H₂O)₆³⁺, a species which contributes to the total chromium analysis but only in a minor way to the absorption spectrum.

Solutions of CrO₂²⁺ were prepared¹² by slowly delivering 25 mL of 2 × 10⁻⁴ M Cr²⁺, in 0.1 M perchloric acid, below the surface of 75 mL of water into which a vigorous stream of oxygen was bubbling. This resulted in 1–2 × 10⁻⁵ M CrO₂²⁺, based on λ_{max} 290 nm (ε 3.0 × 10³ M⁻¹ cm⁻¹); the balance consisted of dinuclear Cr(III) complexes.

Nitrogen was purified by Cr²⁺ scrubbing towers. Oxygen (99.6%) was obtained from a lecture bottle (Matheson Gas Products), 52.5% O₂ (balance of N₂) from a Calibration Standard Grade cylinder (Union Carbide Corp.), and 21% O₂ from compressed air, purified before use. Other reagents were prepared as before,^{4,13} including Fe(ClO₄)₃, Cu(ClO₄)₂, [Co(NH₃)₅X](ClO₄)₂ (X = Cl, Br), LiClO₄, and Cr(ClO₄)₃, or were purchased as reagent grade chemicals.

Kinetic Experiments. Most of the kinetic determinations were made spectrophotometrically in the range 290–400 nm where the organochromium ion is the major light-absorbing species in solution. A few used an oxygen-sensing electrode. The concentration of O₂ was maintained constant throughout the former set of kinetic runs by gently bubbling the gas through the 2-cm or 5-cm cylindrical quartz cell. In numerous instances the oxygen concentration in spent reaction solutions was de-

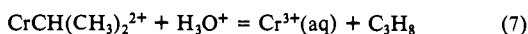
(7) (a) Giannotti, C.; Gaudemer, A.; Fontaine, C. *Tetrahedron Lett.* **1970**, 3209. (b) Duong, K. N. V.; Fontaine, C.; Giannotti, C.; Gaudemer, A. *Ibid.* **1971**, 1187. (c) Fontaine, C.; Duong, K. N. V.; Merienne, C.; Gaudemer, A.; Giannotti, C. *J. Organomet. Chem.* **1972**, *38*, 167. (d) Giannotti, C.; Fontaine, C.; Gaudemer, A. *Ibid.* **1972**, *39*, 381. (e) Giannotti, C.; Septe, B. *Ibid.* **1973**, *52*, C45. (f) Merienne, C.; Giannotti, C.; Gaudemer, A. *Ibid.* **1973**, *54*, 281. (g) Giannotti, C.; Fontaine, C.; Septe, B. *Ibid.* **1974**, *71*, 107. (h) Bied-Charreton, C.; Gaudemer, A. *Ibid.* **1977**, 299.

(8) Brindley, P. B.; Hodgson, J. C. *J. Organomet. Chem.* **1974**, *65*, 57. (9) Bied-Charreton, C.; Gaudemer, A. *Tetrahedron Lett.* **1976**, 4153. (10) Espenson, J. H.; Chen, J.-T. *J. Am. Chem. Soc.* **1981**, *103*, 2036. (11) Hedaya, E.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 1661. (12) Ilan, Y. A.; Czapski, G.; Ardon, M. *Isr. J. Chem.* **1975**, *13*, 15. (13) Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2721.

terminated directly. To do that, we transferred an aliquot of the solution into a solution containing excess Cr^{2+} , followed by addition of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, which was converted to $\text{Co}^{2+}(\text{aq})$ by reaction with Cr^{2+} . The Co^{2+} produced was determined spectrophotometrically as $\text{Co}(\text{NCS})_4^{2-}$ in aqueous acetone,¹⁴ the original concentration of O_2 being calculated with the assumption that its reaction with Cr^{2+} has a 1:4 stoichiometry. The value found at 25.0 °C in 0.1 M perchloric acid maintained at ionic strength 1.00 M by addition of lithium perchlorate in O_2 -saturated solutions was $[\text{O}_2] = (1.05 \pm 0.11) \times 10^{-3}$ M, the average of 26 determinations. The concentration of O_2 in solutions saturated with O_2 - N_2 mixtures was calculated from Henry's law. Under many conditions (but not all) the reaction rate is independent of $[\text{O}_2]$, so that a precise value is often not required.

A few kinetic experiments were conducted by use of an oxygen-sensing electrode, the Hach Oxygen Meter Model 16046. Since its response time is relatively slow (15–30 s), only low concentrations (1×10^{-4} M) of the organochromium complex could be used to keep the rate within the capabilities of the electrode system. The data using this method were determined in runs having $[\text{H}^+] = 0.010$ M and $\mu \sim 0.01$ M because of the sensitivity of the electrode to vibrations at higher concentrations of electrolyte. The reaction solution was isolated from the atmosphere and stirred continuously during the reaction. The depletion of oxygen concentration with time was displayed by use of an x-y recorder.

Kinetic data for the very slow anaerobic decomposition of $\text{CrCH}(\text{CH}_3)_2^{2+}$ were obtained by using a Cary Model 219 spectrophotometer equipped with an automated rotating turret. When Cr^{2+} is added ($\sim 3 \times 10^{-3}$ M) and neither oxygen nor other oxidizing agent is present, only acidolysis (eq 7) occurs. When an oxidizing agent other than O_2 is



present, acidolysis (eq 7) and homolysis occur concurrently. Further details have been given elsewhere.¹⁵

Kinetic Data. The decomposition of $\text{CrCH}(\text{CH}_3)_2^{2+}$ in the absence of O_2 followed first-order kinetics, and its reaction with O_2 in the presence of a high concentration of Cu^{2+} was pseudo-first-order with respect to $[\text{CrCH}(\text{CH}_3)_2^{2+}]$. In such cases k_{obsd} was computed as the slope of a plot of $\ln(D_t - D_\infty)$ vs. time, where D = absorbance.

Most kinetic runs concerned the reaction between $\text{CrCH}(\text{CH}_3)_2^{2+}$ and O_2 under conditions where it follows a three-halves-order rate law, eq 8. Integration of that equation and expression in terms of absorbance values (D) afford an expression, eq 9, which suggests that a plot of $(D_t - D_\infty)^{1/2}$

$$-d[\text{CrCH}(\text{CH}_3)_2^{2+}]/dt = k_8[\text{CrCH}(\text{CH}_3)_2^{2+}]^{3/2} \quad (8)$$

$$(D_t - D_\infty)^{1/2} = (D_0 - D_\infty)^{1/2} - (k_8/2)(D_t - D_\infty)^{1/2}[\text{CrCH}(\text{CH}_3)_2^{2+}]_0^{1/2} \quad (9)$$

vs. $t(D_t - D_\infty)^{1/2}$ will be linear. The rate constant was calculated by using eq 10; the accuracy of the determination is limited by the uncertainty in

$$k_8 = 2 \times \text{slope} \times [\text{CrCH}(\text{CH}_3)_2^{2+}]_0^{-1/2} \quad (10)$$

the initial concentration of the slowly decomposing organochromium complex.

Although eq 8 applies under most conditions, at very low concentrations of $\text{CrCH}(\text{CH}_3)_2^{2+}$ ($< 10^{-4}$ M), the rates of homolysis (k_{H}) and acidolysis (k_{A}) are comparable to those of the oxygenation reaction and can no longer be ignored. The complete rate law is thus given by

$$-d[\text{CrCH}(\text{CH}_3)_2^{2+}]/dt = (k_{\text{A}} + k_{\text{H}})[\text{CrCH}(\text{CH}_3)_2^{2+}] + k_8[\text{CrCH}(\text{CH}_3)_2^{2+}]^{3/2} \quad (11)$$

Integration of this equation and conversion to an absorbance basis give the following expression for the absorbance at time t :

$$D_t = D_\infty + (D_0 - D_\infty)/\alpha^2 \quad (12)$$

where α is given by

$$\alpha = [k_8[\text{CrCH}(\text{CH}_3)_2^{2+}]_0^{1/2}/(k_{\text{H}} + k_{\text{A}})] \exp[(k_{\text{H}} + k_{\text{A}})t/2] - 1 + \exp[(k_{\text{H}} + k_{\text{A}})t/2] \quad (13)$$

The value of k_8 was obtained from a nonlinear least-squares computer program,¹⁶ using $(k_{\text{H}} + k_{\text{A}}) = 2.85 \times 10^{-4} \text{ s}^{-1}$ and the appropriate value of $[\text{CrCH}(\text{CH}_3)_2^{2+}]_0$.

(14) (a) Kitson, R. E. *Anal. Chem.* **1950**, *22*, 664. (b) Espenson, J. H.; Parker, O. J. *J. Am. Chem. Soc.* **1968**, *90*, 3868.

(15) Kirker, G. W.; Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.*, in press.

(16) We are grateful to Dr. R. B. Pfaff for implementation of this program.

Kinetic determinations, using the oxygen electrode, were also made under conditions where eq 8 applies. Data from these runs can be analyzed by rewriting the rate law of eq 8 in the form

$$-d[\text{O}_2]/dt = k_8([\text{O}_2]_t - \Delta)^{3/2} \quad (14)$$

where $\Delta = [\text{O}_2]_0 - [\text{CrCH}(\text{CH}_3)_2^{2+}]_0$. Integration and rearrangement yield an expression

$$[(\text{O}_2)_t - \Delta]/([\text{O}_2]_0 - \Delta)^{1/2} = 1 - (k_8/2)([\text{O}_2]_t - \Delta)^{1/2}t \quad (15)$$

such that a plot of the left-hand side vs. the product $([\text{O}_2]_t - \Delta)^{1/2}t$ is linear with a slope of $-k_8/2$.

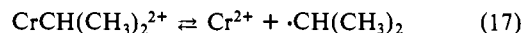
Products and Analyses. Acetone and 2-propanol were determined by gas chromatography with appropriate calibration. Samples of the aqueous product solution were injected directly onto a Tenax or 10%-FFAP column at 100 or 150 °C. Experiments to detect the possible formation of peroxides were based on the oxidation of iodide and the spectrophotometric determination of iodine.¹⁷ The cationic Cr(III) species $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and $\text{Cr}_2(\text{OH})_2^{4+}$ were identified by their visible spectra after separation by ion-exchange chromatography on Sephadex C-25 resin. Chromium(VI) was determined spectrophotometrically under conditions where the predominant species is HCrO_4^- , with λ_{max} 350 nm (ϵ $1.53 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁸ Propane, the only organic product of the anaerobic acidolysis reaction, was swept from the solution by a stream of nitrogen, condensed in a liquid nitrogen trap, and detected by mass spectrometry.

Results

The Acidolysis Reaction. In the absence of O_2 or other oxidizing agents, and in the presence of Cr^{2+} , solutions of $\text{CrCH}(\text{CH}_3)_2^{2+}$ in dilute perchloric acid slowly decompose in a first-order reaction according to eq 7. Typical conditions for kinetics experiments were 1×10^{-3} M $\text{CrCH}(\text{CH}_3)_2^{2+}$, 3.8×10^{-3} M Cr^{2+} , 0.050–0.17 M H^+ , at 25.0 °C, and $\mu = 1.00$ M. At 0.050 M H^+ k_{obsd} is $(1.07 \pm 0.01) \times 10^{-4} \text{ s}^{-1}$, and at 0.170 M H^+ , $1.04 \times 10^{-4} \text{ s}^{-1}$. The rate law, with $k_{\text{A}} = 1.05 \pm 0.02 \times 10^{-4} \text{ s}^{-1}$, is given by

$$-d[\text{CrCH}(\text{CH}_3)_2^{2+}]/dt = k_{\text{A}}[\text{CrCH}(\text{CH}_3)_2^{2+}] \quad (16)$$

The Homolysis Reaction. This process, given by eq 17, is known for many other organochromium cations to occur reversibly.^{4b,15,19}

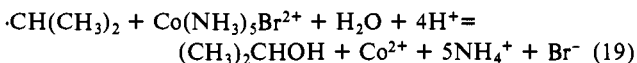


Experiments with Cu^{2+} and $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ give $k_{\text{obsd}} = (2.85 \pm 0.10) \times 10^{-4} \text{ s}^{-1}$. Determinations using Fe^{3+} were complicated by a direct reaction pathway.¹⁹ Extrapolation to $[\text{Fe}^{3+}] = 0$ gave the rate constant $(3.4 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$. The reaction rate under these conditions is given by eq 18. The rate constant for hom-

$$-d[\text{CrCH}(\text{CH}_3)_2^{2+}]/dt = (k_{\text{A}} + k_{\text{H}})[\text{CrCH}(\text{CH}_3)_2^{2+}] \quad (18)$$

olysis, obtained by difference, is $k_{\text{H}} = (1.78 \pm 0.11) \times 10^{-4} \text{ s}^{-1}$. Although these determinations were done only at 0.1 M H^+ , it can be safely assumed that the value is independent of $[\text{H}^+]$, since that was the case for 12 other complexes.^{4b,15}

Anaerobic decomposition of $\text{CrCH}(\text{CH}_3)_2^{2+}$ in the presence of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ produced²⁰ $(\text{H}_2\text{O})_5\text{CrX}^{2+}$ and $\text{Co}^{2+}(\text{aq})$. The yield of the latter was 2.11 ± 0.20 mol of $\text{Co}^{2+}(\text{aq})$ per mol of $\text{CrCH}(\text{CH}_3)_2^{2+}$ decomposed by homolysis (the fraction of the decomposition occurring homolytically being $k_{\text{H}}/(k_{\text{A}} + k_{\text{H}})$ or 0.624 ± 0.060). This establishes that $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ is reduced not only by Cr^{2+} , but also, like $\cdot\text{C}(\text{CH}_3)_2\text{OH}$ and similar radicals¹⁵ and unlike the benzyl radical,^{4b,19} by the 2-propyl radical (eq 19).



(17) Banerjee, D. K.; Budke, C. C. *Anal. Chem.* **1964**, *36*, 792.

(18) Tong, J. Y.; King, E. L. *J. Am. Chem. Soc.* **1953**, *75*, 6180.

(19) (a) Pohl, M. C.; Espenson, J. H. *Inorg. Chem.* **1980**, *19*, 235. (b) Marty, W.; Espenson, J. H. *Ibid.* **1979**, *18*, 1246.

(20) The chloro complex rather than the faster-aquating bromo complex was used to permit detection of the halochromium(III) ion at the completion of the experiment. The green CrCl^{2+} product was identified by its visible absorption spectrum, λ_{max} 609 and 428 nm. The yield was not determined in this instance because of its competing aquation, although it was found to be formed in quantitative yield in studies of the homolysis of other, faster-reacting CrR^{2+} complexes.^{4b,15}

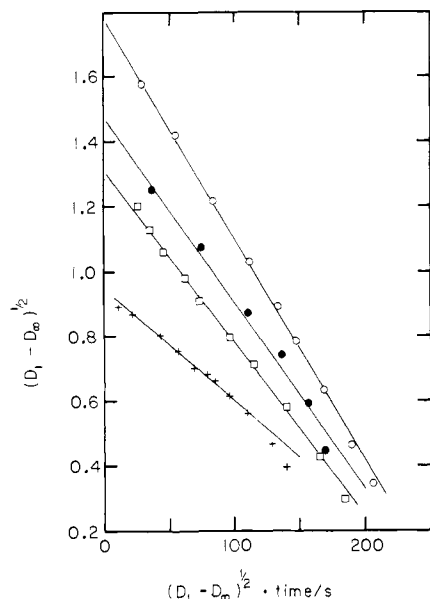


Figure 1. Kinetic plots of the integrated 3/2-order rate law given by eq 9. The runs had $[O_2] = 1.05 \times 10^{-3}$ M and $10^3[CrCH(CH_3)_2^{2+}]_0$ (reading downward) = 0.71, 0.51, 0.35, and 0.20 M. The rate constants for these runs are 0.511, 0.508, 0.571, and $0.459 \text{ M}^{-1/2} \text{ s}^{-1}$.

Table I. Kinetics of Decomposition of $CrCH(CH_3)_2^{2+}$ in the Presence of Oxidizing Agents^a

| $10^3 \times [CrCH(CH_3)_2^{2+}]_0$, M | ox. agent | [ox. agent], M | $10^4(k_A + k_H)$, s^{-1} |
|---|---------------------|----------------------|------------------------------|
| 0.93 | Cu^{2+} | 0.10 | 2.91 ± 0.21 (2) |
| 1.10 | $Co(NH_3)_5Br^{2+}$ | 2.4×10^{-3} | 3.17 ± 0.02 (4) |
| 0.88 | $Co(NH_3)_5Br^{2+}$ | 3.7×10^{-3} | 2.87 (1) |
| 0.88 | $Co(NH_3)_5Br^{2+}$ | 4.8×10^{-3} | 2.80 ± 0.13 (3) |
| 0.93 | $Co(NH_3)_5Br^{2+}$ | 9.6×10^{-3} | 2.86 ± 0.01 (4) |
| 0.98 | Fe^{3+} | 0.050–0.10 | 3.4 ± 0.3^b |

^a Conditions: 25.0 °C, $[H_3O^+] = 0.10$ M, 1.0 M ionic strength maintained with $LiClO_4$. ^b Extrapolated to $[Fe^{3+}] = 0$ from k_{obsd} at 0.05 M ($3.98 \pm 0.02 \times 10^{-4} \text{ s}^{-1}$) and 0.10 M ($4.56 \pm 0.26 \times 10^{-4} \text{ s}^{-1}$).

The Co^{2+} yield substantiates the correctness of the procedure by which the observed rate constant in the presence of such oxidants was divided into its components of acidolysis and homolysis.

Reaction with O_2 : Variation of $[CrCH(CH_3)_2^{2+}]$. Considerable effort was expended to verify that the reaction order is really 3/2 and that this unusual order is not (for example) an artifact due to curvature in first-order plots such as might result from unrecognized complications or from the occurrence of parallel reactions (or reaction pathways) following first- and second-order kinetics. The order was established (a) from the "reaction-order plots" of $\log(\text{rate})$ vs. $\log([CrCH(CH_3)_2^{2+}]_{av})$, examples of which are given in Figure 1 of ref 5, (b) from the linearity to >75% reaction of the 3/2-order kinetic plots made according to eq 9, as shown in Figure 1, and (c) from the constancy of the 3/2-order rate constant (denoted as k_8) when determined over a substantial range of initial concentration, 1×10^{-4} to 1×10^{-3} M $CrCH(CH_3)_2^{2+}$.

It is the latter which is particularly convincing in establishing the fact the kinetic data require a fractional-order dependence. These data are summarized in Table I. The scatter among multiple determinations is somewhat higher than usually found, due in part to the chain mechanism which makes the rate somewhat sensitive to trace impurities and due also to an appreciable difference in values determined at different wavelengths. At wavelengths such as 330 and 400 nm where the byproduct $HCrO_4^-$ absorbs comparably to $CrCH(CH_3)_2^{2+}$, higher apparent rates were found as a result of partially offsetting absorbance changes. In comparison, at $\lambda = 290$ nm, where $CrCH(CH_3)_2^{2+}$ dominates, the rate constant will more accurately reflect the

Table II. 3/2-Order Rate Constants for the Reaction of $CrCH(CH_3)_2^{2+}$ with O_2 ^a

| range ^b $10^3[CrCH(CH_3)_2^{2+}]_0$ | $10^3[O_2]^c$ | $k_8 \pm 1\sigma$, $M^{-1/2} \text{ s}^{-1}$ (No.) ^d | |
|---|---------------|--|------------------------------------|
| | | λ 290 nm | λ 320, 330 nm ^e |
| 0.20–0.23 | 1.05 | 0.46 ± 0.04 (3) | |
| 0.30–0.40 | 1.05 | 0.55 ± 0.03 (5) | |
| 0.43 | 1.05 | | 0.57 (1) |
| 0.50–0.58 | 1.05 | 0.46 ± 0.06 (5) | 0.72 ± 0.09 (4) |
| 0.70–0.71 | 1.05 | 0.52 (1) | 0.84 ± 0.01 (2) |
| 0.78–0.84 | 1.05 | | 0.72 ± 0.09 (5) |
| 0.97–1.0 | 1.05 | 0.40 (1) | 0.70 (1) |
| 0.10 | 0.54 | 0.55 (1) ^f | |
| 0.30 | 0.54 | 0.50 ± 0.09 (2) | 0.64 ± 0.04 (2) |
| 0.50 | 0.54 | | 0.65 (1) |
| 1.0 | 0.54 | | 0.60 ± 0.05 (2) ^g |
| 0.10 | 0.19 | 0.83 (1) | |
| 0.30 | 0.19 | 0.43 ± 0.07 (2) | |
| 0.50 | 0.19 | | 0.54 (1) |
| 1.0 | 0.19 | | 0.55 (1) ^g |

^a Conditions: 25 °C at 0.10 M H^+ and 1.00 M ionic strength.

^b Ranges are given because individual runs were grouped into sets covering a narrow range of initial concentrations to consolidate a large number of determinations. ^c $[O_2]$ remains constant because of continuous saturation. ^d The number of experiments in the particular group. ^e At 320–330 nm except as noted. ^f Followed using the O_2 -sensing electrode; $[O_2]$ is not sustained at a constant values in these experiments. ^g λ 400 nm.

Table III. Rate Constants for the Reaction of $CrCH(CH_3)_2^{2+}$ with O_2 as a Function of $[H^+]$ at Constant Ionic Strength^a

| $10^3 \times [CrCH(CH_3)_2^{2+}]_0$, M | $[H^+]$, M | μ , M | k , $M^{-1/2} \text{ s}^{-1}$ |
|---|----------------------|-----------|---------------------------------|
| 0.58 | 3.0×10^{-3} | 0.042 | 0.276 |
| 0.56 | 3.2×10^{-3} | 0.043 | 0.313 |
| 0.68 | 6.7×10^{-3} | 0.043 | 0.310 |
| 0.75 | 6.8×10^{-3} | 0.043 | 0.314 |
| 0.72 | 7.0×10^{-3} | 0.044 | 0.306 |
| 0.58 | 3.7×10^{-2} | 0.041 | 0.297 |
| 0.74 | 0.0117 | 1.07 | 0.530 |
| 0.70 | 0.0846 | 0.98 | 0.521 |
| 0.35 | 0.0972 | 1.07 | 0.577 |
| 0.1–1.0 | 0.100 | 1.00 | 0.49 ± 0.06^b |

^a At 25.1 °C, $[O_2] = 1.05 \times 10^{-3}$ M. Spectrophotometric determinations at 290 nm. ^b Average of 15 corresponding values from Table II.

oxygen reaction alone. The "best value" is $k_8 = 0.49 \pm 0.06 \text{ M}^{-1/2} \text{ s}^{-1}$ at 25.0 °C, $\mu = 1.00$ M.

Values of k_8 were determined at lower initial concentrations after due allowance for the concurrent first-order term, as in eq 11. An average value of $k_8 = 0.43 \pm 0.05 \text{ M}^{-1/2} \text{ s}^{-1}$ was obtained for runs at 290 nm having $[CrCH(CH_3)_2^{2+}]_0 = 4 \times 10^{-5}$ to 2×10^{-4} M at $[O_2] = 1.05 \times 10^{-3}$ M, 0.10 M H^+ ($\mu = 1.0$ M, $T = 25$ °C).

Variation of $[O_2]$ and $[H_3O^+]$. The 3/2-order kinetic plots at two lower concentrations of O_2 were again linear and k_8 was independent of $[CrCH(CH_3)_2^{2+}]_0$. The rate constants obtained also are listed in Table II. Although the scatter (especially in one determination) is fairly large, it is clear that the rate constant is independent of $[O_2]$ over the fivefold variation employed and is also independent of $[H^+]$ (Table III). The less precise determinations using the oxygen-sensing electrode are included simply to confirm that both reactants are consumed at the same rate.

Effect of Fe^{2+} . Even very low concentrations of Fe^{2+} produced a remarkable inhibition of the reaction. Contrast the initial rate of reaction in a pair of experiments otherwise identical (1×10^{-3} M $CrCH(CH_3)_2^{2+}$, 1.05×10^{-3} M O_2 , $[H^+] = 0.10$ M, 25 °C, $\mu = 1.0$ M) except that one contained Fe^{2+} ($\sim 3 \times 10^{-4}$ M) and the other did not. The former had an initial rate estimated as $4.3 \times 10^{-7} \text{ M s}^{-1}$, the latter nearly 50 times higher, $\sim 2 \times 10^{-5} \text{ M s}^{-1}$.

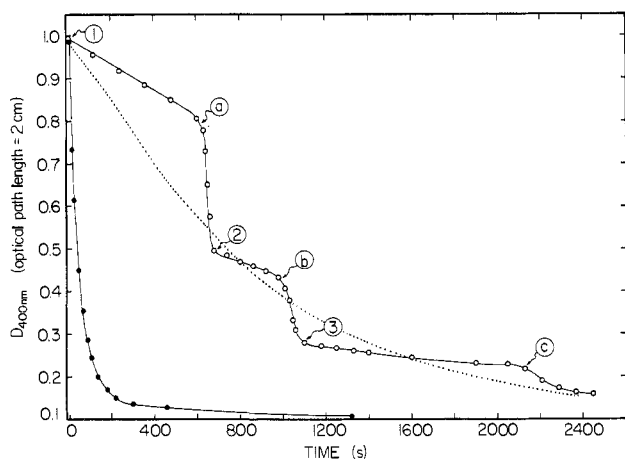
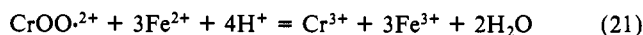
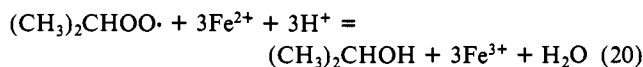


Figure 2. The results of experiments to illustrate the chain-breaking effect of added Fe^{2+} and Cu^{2+} by tracings of absorbance (at λ 400 nm) vs. time for three identical experiments ($[\text{CrCH}(\text{CH}_3)_2^{2+}]_0 = 1 \times 10^{-3}$ M, $[\text{O}_2]$ constant at 1.05×10^{-3} M, $[\text{H}^+] = 0.10$ M, 1.00 M ionic strength, 25 °C) with Fe^{2+} (open circles), 0.105 M Cu^{2+} (dots), and without either (filled circles). In the run with Fe^{2+} , a smaller amount was present initially, and additional small amounts were added by syringe injection at the points labeled 2 and 3. The points marked a, b, and c are the times at which the chain reaction resumes, presumably after consumption of Fe^{2+} by reaction with the chain-carrying intermediate $(\text{CH}_3)_2\text{CHOO}\cdot$ as in eq 20. The dotted line illustrates the kinetic trace for the same reaction conditions in the presence of 0.10 M Cu^{2+} (entry 6, Table IV) where a pseudo-first-order equation applies.

The effect of a small concentration of Fe^{2+} is depicted in Figure 2. This graph shows two tracings of the recording of absorbance at the 400 nm peak of $\text{CrCH}(\text{CH}_3)_2^{2+}$ vs. time. In the experiment lacking Fe^{2+} , the absorbance decreased rapidly but measurably, the reaction reaching completion within a few minutes. In the experiment with added Fe^{2+} there was a slow, first-order decrease in $[\text{CrCH}(\text{CH}_3)_2^{2+}]$ with $k = 4.3 \times 10^{-4} \text{ s}^{-1}$. Provided Fe^{2+} was not present in excess over the organochromium ion, a point was reached (point a in Figure 2) at which the reaction rate abruptly increased to the same value it had in an experiment lacking Fe^{2+} . The length of the inhibition period increased with the concentration of Fe^{2+} added but was not sufficiently reproducible to quantify. The effect could be repeated: Addition of more Fe^{2+} (points 2 and 3) inhibited the chain reaction. As before, however, the inhibition disappeared after a time (points b and c), evidently when Fe^{2+} was depleted.

The dramatic inhibition of the reaction is strong evidence for a chain mechanism involving free-radical intermediates. This is not sufficient to distinguish between mechanisms A and B, however, since both alkylperoxy radicals such as $(\text{CH}_3)_2\text{CHOO}\cdot$ of Mechanism A and CrO_2^{2+} (a "metalloperoxy radical") of Mechanism B might be expected to react with Fe^{2+} . For example, regardless of mechanism (and plausible ones could be suggested for either net process), one might attribute the chain-breaking effect of Fe^{2+} to either of the following reactions (eq 20, 21).



It is known²¹ that alkylperoxy radicals can oxidize both Co^{2+} ($E^0 = 1.81$ V) and Mn^{2+} (1.51 V), so eq 20 for Fe^{2+} (0.77 V) is plausible. When the reaction of $\text{CrCH}(\text{CH}_3)_2^{2+}$ with O_2 is run with added Fe^{2+} , some 3–4 mol of Fe^{2+} are consumed per mol of $\text{CrCH}(\text{CH}_3)_2^{2+}$ initially present. It was found that independently prepared CrO_2^{2+} rapidly oxidizes Fe^{2+} to Fe^{3+} ; about 3.2 mol of Fe^{2+} are consumed per mol of CrO_2^{2+} .

Effect of High $[\text{Cu}^{2+}]$. No changes in the kinetics were found upon addition of Cu^{2+} , Mn^{2+} , or Co^{2+} at a concentration comparable to that of the organochromium cation, $\sim 10^{-3}$ M. That

Table IV. Rate Constants^a for the Reaction between $\text{CrCH}(\text{CH}_3)_2^{2+}$ and O_2 in the Presence of High Concentrations of Cu^{2+}

| $10^3[\text{O}_2]$, M | $[\text{Cu}^{2+}]$, M | 10^3k_{Cu} , s^{-1} |
|------------------------|------------------------|---------------------------------------|
| 1.05 | 0.020 | 2.89 ± 0.23 |
| 1.05 | 0.025 | 2.78 ± 0.20 |
| 1.05 | 0.033 | 2.15 |
| 1.05 | 0.038 | 1.97 |
| 1.05 | 0.050 | 1.50 ± 0.04 |
| 1.05 | 0.10 | 1.26 ± 0.07 |
| 1.05 | 0.20 | 0.89 ± 0.03 |
| 1.05 | 0.30 | 0.728 ± 0.020 |
| 1.05 | 0.40 | 0.727 ± 0.010 |
| 0.54 | 0.050 | 1.03 |
| 0.54 | 0.10 | 0.80 ± 0.02 |
| 0.19 | 0.050 | 0.78 |
| 0.19 | 0.10 | 0.68 ± 0.04 |
| 0.19 | 0.20 | 0.59 ± 0.01 |
| 0.19 | 0.30 | 0.65 ± 0.08 |
| 0 ^b | 0 | 0.291 ± 0.021 ^b |

^a Conditions: $[\text{H}^+] = 0.10$ M, (25.0 ± 0.1) °C, ionic strength 1.0 M except at $[\text{Cu}^{2+}] = 0.40$ M where $\mu = 1.3$ M. ^b Under nitrogen, see Table I; this entry represents $k_A + k_H$.

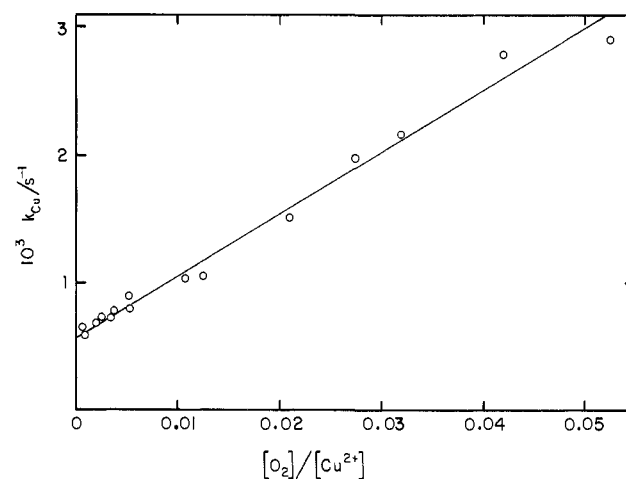
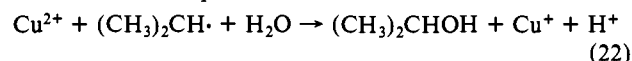


Figure 3. Illustrating the linear dependence of k_{Cu} (the pseudo-first-order rate constant in the presence of high concentrations of Cu^{2+}) on the ratio $[\text{O}_2]/[\text{Cu}^{2+}]$, in experiments where $[\text{O}_2]$ is maintained constant in each run, according to eq 23.

was the case despite the fact that Cu^{2+} is well-known²² to oxidize alkyl radicals rapidly, and might thus have been expected to exert a chain-breaking effect²³ if mechanism A were operative, by virtue of the reaction of eq 22.



The kinetics in the presence of higher concentrations of Cu^{2+} (0.020–0.40 M) were studied by monitoring the decrease in

(22) (a) Kochl, J. K.; Subramanian, R. V. *J. Am. Chem. Soc.* **1965**, *87*, 4855. (b) Kochl, J. K.; Bemis, A.; Jenkins, C. T. *Ibid.* **1968**, *90*, 4616.

(23) Certain other radical scavengers were examined. Galvinoxyl, an efficient scavenger for alkyl and alkylperoxy radicals,^{24,25} was examined (in aqueous acetone, for solubility). Galvinoxyl was "instantly" decolorized when added to $\text{CrCH}(\text{CH}_3)_2^{2+}$, however, after which the reaction continued its normal course with 3/2-order kinetics. Titrations in the absence of O_2 showed that substantial amounts of galvinoxyl are consumed by such direct reaction with $\text{CrCH}(\text{CH}_3)_2^{2+}$. Diphenylamine, a scavenger for alkylperoxy radicals,²⁶ was also investigated, now in aqueous methanol at $[\text{Ph}_2\text{NH}]_0 \sim [\text{Cr}(\text{CH}_3)_2^{2+}] \sim 10^{-3}$ M. In this case the course of reaction was altered entirely, with an unidentified blue coloration (λ_{max} 630 nm) and a cloudy solution slowly developing.

(24) Bartlett, P. D.; Funahashi, T. *J. Am. Chem. Soc.* **1962**, *84*, 2596.

(25) Ingold, K. U. In "Free Radicals"; Kochl, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, Chapter 2, pp 65–66.

(26) Howard, J. A. In "Free Radicals"; Kochl, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. II, Chapter 12, pp 43–47.

Table V. The Rate Constants for the Reaction between $(\text{H}_2\text{O})_5\text{CrCH}(\text{CH}_3)_2^{2+}$ and O_2 at $(25.1 \pm 0.1)^\circ\text{C}$ under Conditions of Variable Ionic Strength^a

| range, $\text{M} \times 10^3$ | | | | |
|-------------------------------|--------------|----------------|---------------------------------------|--|
| μ_0 | μ_∞ | $[\text{H}^+]$ | $[\text{CrCH}(\text{CH}_3)_2^{2+}]_0$ | $k_8 \pm 1\sigma, \text{M}^{-1/2} \text{s}^{-1}$ (No.) |
| 3.3-3.6 | 4.0-4.4 | 1.4-1.6 | 0.40 | 0.258 ± 0.004 (2) |
| 5.8-8.1 | 6.7-9.4 | 3.4-6.0 | 0.48-0.79 | 0.259 ± 0.013 (7) |
| 11.1-11.5 | 12.3-12.8 | 8.6-8.9 | 0.59-0.74 | 0.257 ± 0.008 (3) |
| 15.8-15.9 | 17.4 | 11.5-11.6 | 0.80-0.88 | 0.249 ± 0.008 (3) |
| 23.9-25.4 | 24.7-26.2 | 22.3-23.6 | 0.44-0.47 | 0.264 ± 0.012 (2) |
| 32.0-32.9 | 33.0-33.6 | 29.7-30.0 | 0.41-0.56 | 0.262 ± 0.007 (2) |
| 40.2-43.1 | 41.2-44.4 | 3.0-37.0 | 0.56-0.75 | 0.303 ± 0.014 (6) |
| 75 | 76 | 2.9-7.0 | 0.56-0.78 | 0.335 ± 0.010 (4) |
| 107 | 108 | 9.5-11.5 | 0.69-0.74 | 0.340 ± 0.002 (2) |
| 210 | 211 | 7.4 | 0.53-0.54 | 0.375 ± 0.006 (2) |
| 254 | 255 | 32.2 | 0.75 | 0.353 (1) |
| 317 | 318 | 11.6 | 0.70 | 0.396 (1) |
| 565 | 568 | 9.5 | 0.69-0.71 | 0.440 ± 0.015 (2) |
| 764 | 766 | 9.5-9.6 | 0.72 | 0.505 ± 0.025 (2) |
| 977 | 978 | 84.6 | 0.70 | 0.521 (1) |
| 1070 | 1070 | 11.7-97.2 | 0.20-1.0 | 0.49 ± 0.06 (15) |

^a Individual runs, all from determination at 290 nm, have been grouped in sets within narrow ranges of ionic strength (μ), which changes slightly from the start of the run (μ_0) to completion (μ_∞). The uncertainty cited for each rate constant represents one standard deviation from the mean of the individual determinations, the number of individual runs in each set being given in parentheses.

$[\text{CrCH}(\text{CH}_3)_2^{2+}]$ at 400 nm, where Cu^{2+} does not absorb. Three concentrations of oxygen were used, with $[\text{CrCH}(\text{CH}_3)_2^{2+}]_0 = (0.6-1.0) \times 10^{-3} \text{ M}$ and 0.1 M H^+ . Ionic strength was maintained at 1.0 M by addition of lithium perchlorate except at the highest $[\text{Cu}^{2+}]$ where, by necessity, it was 1.3 M .

The order with respect to $[\text{CrCH}(\text{CH}_3)_2^{2+}]$ in these experiments is unity. The values of the pseudo-first-order rate constant (k_{Cu}) at various concentrations of O_2 and Cu^{2+} are given in Table IV.

The effects of concentration on k_{Cu} suggest a rate-law term varying directly with $[\text{O}_2]$ and inversely with $[\text{Cu}^{2+}]$. A graph illustrating the validity of eq 23 is shown in Figure 3; a least-squares analysis affords, with a correlation coefficient of 0.988, the values of $k_d = (5.67 \pm 0.41) \times 10^{-4} \text{ s}^{-1}$ and $k' = (4.83 \pm 0.20) \times 10^{-2} \text{ s}^{-1}$.

$$k_{\text{Cu}} = k_d + k'[\text{O}_2]/[\text{Cu}^{2+}] \quad (23)$$

No reaction occurred upon mixing CrO_2^{2+} and Cu^{2+} at 0.01 M H^+ ; the resulting UV spectrum was simply the sum of the individual contributions of the two. The slow subsequent decay of CrO_2^{2+} was noted, the same as in the absence of Cu^{2+} .

Variation of Ionic Strength. Salt effects on the reaction of $\text{CrCH}(\text{CH}_3)_2^{2+}$ were examined in some 25 determinations in the ionic strength range $0.004-0.044 \text{ M}$. In these experiments the perchloric acid concentration was low but variable $[(1.4-3.7) \times 10^{-3} \text{ M}]$, as was the initial concentration of $\text{CrCH}(\text{CH}_3)_2^{2+}$ $[(4.0-8.8) \times 10^{-4} \text{ M}]$. On the basis of the results of experiments already referred to, the latter variations were immaterial since the invariance of k_8 both with $[\text{H}^+]$ and with $[\text{CrCH}(\text{CH}_3)_2^{2+}]$ has been established. The reaction rate followed the 3/2-order rate law of eq 8 under these conditions, just as it did at $\mu = 1.0 \text{ M}$. The value of k_8 remained unchanged, within the experimental error, as ionic strength was varied over the range referred to. These results are given in summary form in Table V, in which the results for experiments under similar but not quite identical conditions are listed as a single entry to conserve space, especially because the individual values do not show discernible variation from one run to the next in this region of "low" ionic strength.

At higher ionic strengths, however, one must expect deviations from ideal behavior. The ionic strength at which such effects become appreciable is not known in advance of experimental measurements, however, because the deviations are expected to arise from specific properties of individual ions, molecules, and activated complexes. It would appear on the basis of the data summarized in Table V that effects of nonideality begin to become appreciable above $\mu \sim 0.04 \text{ M}$.

Products of the Reaction with O_2 . Acetone and 2-propanol were the only organic products detected from oxygenation reactions. A slight dependence on acidity is seen (Table VI), acetone ac-

Table VI. Products and Yields in the Reaction^a of $(\text{H}_2\text{O})_5\text{CrCH}(\text{CH}_3)_2^{2+}$ and O_2

| $[\text{H}_3\text{O}^+], \text{M}$ | % yield based on $[\text{CrCH}(\text{CH}_3)_2^{2+}]_0$ | | | |
|------------------------------------|--|------------------------------|-------------------|--------------------|
| | $(\text{CH}_3)_2\text{CO}$ | $(\text{CH}_3)_2\text{CHOH}$ | HCrO_4^- | Cr(III)^b |
| ~ 0.002 | 57.7 ± 1.4 | 28.3 ± 1.6 | | |
| 0.01-0.011 | 66.8 ± 0.4 | 24.1 ± 0.1 | 12.9 | |
| 0.10 | 71.8 ± 2.5 | 18.9 | 12.6 ± 2.6 | 82.1 ± 9.5^b |
| 0.50-0.90 | | | 9.3-10.0 | |

^a Conditions: $[\text{CrCH}(\text{CH}_3)_2^{2+}]_0 = (5-20) \times 10^{-3} \text{ M}$; $[\text{O}_2]$ constant at $1 \times 10^{-3} \text{ M}$, $\mu \approx 0.5 + [\text{H}_3\text{O}^+]$, ambient temperature.

^b This is the sum of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $70.1 \pm 8.3\%$, and $\text{Cr}_2(\text{OH})_4^{4+}$, $10.1 \pm 1.2\%$.

counting for 58% of the products at $0.002 \text{ M H}_3\text{O}^+$, and 72% at 0.1 M . At the same time, the yield of 2-propanol dropped from 28 to 19%. Tests for "active oxygen" showed no hydroperoxide was present at the end of the reaction.

Although Cr(III) species, both monomeric $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and dimeric species such as Cr_2O^{4+} (and its hydrates), were the major products, an appreciable and reproducible quantity of Cr(VI) was formed. The yield of HCrO_4^- was some 9-13%, decreasing with increasing $[\text{H}_3\text{O}^+]$.

Discussion

Spontaneous Decomposition of $\text{CrCH}(\text{CH}_3)_2^{2+}$. The reactions characteristic of the various members of the general family of organometallic complexes $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ are well exemplified by $\text{CrCH}(\text{CH}_3)_2^{2+}$. In this case, as it happens, the competing modes of spontaneous decomposition both occur to appreciable extents.

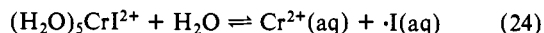
The homolysis reaction occurs by the $\text{S}_{\text{H}}1$ mechanism. The factors inherent in the structure of R which affect the value of k_{H} have been considered before in the context of studies concerned with a large number of such complexes. It was shown¹⁵ that the rate constant for homolysis of $\text{CrCH}(\text{CH}_3)_2^{2+}$ is very much what is expected if one considers the steric strain in the chromium-carbon bond as measured by the strain enthalpy of substituted ethanes according to Rüdhardt.²⁷

The rate constant for the bond-forming reaction between Cr^{2+} and $\cdot\text{CH}(\text{CH}_3)_2$ can be estimated from values determined²⁸ for other carbon-centered free radicals. A value $k_{-17} = (5 \pm 3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ is reasonable. The equilibrium constant for the homolytic dissociation equilibrium of eq 17 is thus $K_{17} = k_{\text{H}}/k_{-17} \sim 3 \times 10^{-12} \text{ M}$. This gives a clear indication of the magnitude

(27) Rüdhardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 429-440.

(28) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

of the strength of the chromium-carbon bond in the alkyl complexes. In comparison, homolysis of the chromium-iodine bond in the iodo complex according to the reaction



is much less favorable with $K_{24} \sim 10^{-27}$ M.²⁹ It should thus come as no surprise that experiments³⁰ designed to detect homolysis of CrI^{2+} in competition with its heterolysis (i.e., aquation to $\text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{I}^-$) were unsuccessful. Even if the reverse of eq 24 occurred at the diffusion-controlled rate (and it is likely that it does, or nearly so),³¹ the homolysis rate constant (k_{24}) could be no larger than K_{24}/k_{-24} or $<10^{-17}$ s⁻¹.

Chain Mechanisms for the Reaction of $\text{CrCH}(\text{CH}_3)_2^{2+}$ and O_2 . Consider the rate expressions associated with mechanisms A and B. If it is assumed that the reactive intermediates of both follow the steady-state approximation, then the rate law applicable to either is

$$-d[\text{CrR}^{2+}]/dt = k_d[\text{CrR}^{2+}] + k_{\text{O}_2}[\text{CrR}^{2+}]^{3/2} \quad (25)$$

where k_d is related to k_A and k_H (see below), and $k_{\text{O}_2} = (k_1/2k_{4A})^{1/2}k_{3A}$ or $(k_1/2k_{4B})^{1/2}k_{3B}$ for mechanisms A and B, respectively. This expression agrees with that found in eq 8 and 11 and accounts for the kinetic data in runs having low initial concentrations of complex.

The general form of eq 25 reduces to the simpler 3/2-order expression of eq 8 at higher concentrations of $\text{CrCH}(\text{CH}_3)_2^{2+}$. This is equivalent to stating that the kinetic chain length becomes sufficiently greater under those concentration conditions that it is feasible to approximate the rate of loss of reactant by the rate of the chain-propagating steps.

The kinetic chain length, defined as the rate of the net reaction compared to the rate of initiation, is thus $k_d[\text{CrR}^{2+}]^{3/2}/k_H[\text{CrR}^{2+}]$, which simplifies to $(2.8 \times 10^3)[\text{CrR}^{2+}]^{1/2}$. Typical values are 86 in a run having $[\text{CrR}^{2+}]_0 = 10^{-3}$ M and 61 at $[\text{CrR}^{2+}]_0 = 5 \times 10^{-4}$ M. This justifies the long-chain approximation, although by but a small margin, at these concentrations. At lower concentrations of CrR^{2+} , however, the chain length drops substantially. The inclusion of the first-order term in eq 25 is thus justified by the known rate constants as well as by the kinetic data in the individual experiments.

Although we shall subsequently present evidence to rule out mechanism B and to substantiate A, it should be noted that the kinetic data themselves do not. Moreover, the various reactions proposed as propagation and termination steps in the two mechanisms appear to be reasonable ones, having valid precedents in the literature.

Consider the first of the two propagation steps as given by the alternatives of mechanisms A and B. Both homolysis products are known independently to react rapidly with O_2 in solution. The formation of CrO_2^{2+} occurs^{12,32} with $k_{2B} = 1.6 \times 10^8$ M⁻¹ s⁻¹, and the isopropylperoxy radical is formed with $k_{2A} \sim 10^9$ M⁻¹ s⁻¹.³³ The termination steps are proposed to be the bimolecular reactions of two alkylperoxy radicals (A) or of two peroxochromium radicals (B). The former is believed³⁴ to occur via decomposition of a tetroxide formed in a cyclic transition state and has $2k_{4A} = 3 \times 10^6$ M⁻¹ s⁻¹ in hydrocarbon solvents.³⁵ It has also been shown^{12,36}

(29) The value of K_{24} was calculated from the known stability constant $K = 7.0 \times 10^{-5}$ M⁻¹ (25 °C) for the reaction $\text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{I}^- = (\text{H}_2\text{O})_5\text{CrI}^{2+} + \text{H}_2\text{O}$ [Swaddle, T. W.; Guastalla, G. *Inorg. Chem.* **1968**, *7*, 1915], and from the standard reduction potentials of $\cdot\text{I}(\text{aq})$ [Woodruff, W. H.; Margerum, D. W. *Inorg. Chem.* **1973**, *12*, 963] and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$.

(30) Schmidt, A. R.; Swaddle, T. W. *J. Chem. Soc. A* **1970**, 1927.

(31) Laurence, G. S.; Thornton, A. T. *J. Chem. Soc., Dalton Trans.* **1974**, 1142. These authors find $k = 1.5 \times 10^7$ M⁻¹ s⁻¹ for the reaction of Cr^{2+} and I_2^- .

(32) Sellers, R. M.; Slmic, M. G. *J. Chem. Soc., Chem. Commun.* **1975**, 401; *J. Am. Chem. Soc.* **1976**, *98*, 6145.

(33) Ingold, K. U. *Acc. Chem. Res.* **1969**, *2*, 1.

(34) Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 3871.

(35) Howard, J. A. In "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, D.C., 1978; ACS Symp. Ser. No. 69, p 428.

that CrO_2^{2+} decomposes by a bimolecular pathway with $2k_{4B} = 2.4 \times 10^6$ M⁻¹ s⁻¹ (at pH 2 in water; the products were not determined but the possibilities suggested in mechanism B appear consistent with other observations).

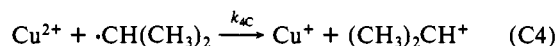
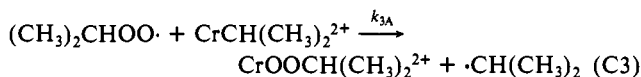
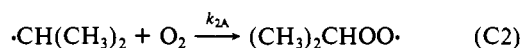
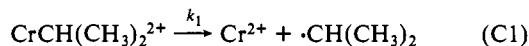
The second of the termination steps, those reactions represented as having rate constants symbolized k_{3A} and k_{3B} , are the least preceded in either case. Both are "radical displacement" processes, a mechanism sometimes referred to as an $\text{S}_{\text{H}}2$ mechanism (bimolecular homolytic substitution). The rate constant k_3 can be calculated from the experimental values of k_1 and k_8 determined here and the alternative values of $2k_{4A}$ and $2k_{4B}$ cited above. The values are $k_{3A} = 6.4 \times 10^4$ M⁻¹ s⁻¹, $k_{3B} = 5.7 \times 10^4$ M⁻¹ s⁻¹. The implications of these steps will be considered in a subsequent section.

Effects of Fe^{2+} and Cu^{2+} . The chain-breaking effect of Fe^{2+} has been described and illustrated in Figure 2. Equation 20 accounts for that effect under the assumption that mechanism A is the correct mechanism, and eq 21 does likewise for mechanism B.

During the inhibition one would assume, as implied by eq 11 and 25, that the only pathways for loss of $\text{CrCH}(\text{CH}_3)_2^{2+}$ are acidolysis and homolysis. An estimate of the rate constant during the Fe^{2+} -inhibited reaction of $\text{CrCH}(\text{CH}_3)_2^{2+}$ and O_2 was made, giving $k_d = (4.3 \pm 0.1) \times 10^{-4}$ s⁻¹.³⁷

The effect of Cu^{2+} on the rate is well accounted for by substitution of a new termination step, eq 22 in place of the final step of mechanism A. The resulting mechanism is shown in mechanism C. On the other hand, Cu^{2+} is known³⁸ to react with Cr^{2+} too slowly to play a role in the mechanism, and during the course of this work we used direct experiments to establish that Cu^{2+} and CrO_2^{2+} do not react. It is thus clear that neither of the chain-carrying intermediates of mechanism B reacts with Cu^{2+} , and therefore, that mechanism B fails to account for the data. This and the ionic-strength dependence, which also supports mechanism A over B, are the bases on which mechanism B is discarded.

Mechanism C



Mechanism C gives rise to the following expressions for the steady-state concentrations of the radical intermediates,

$$[\cdot\text{CH}(\text{CH}_3)_2]_{\text{ss}} = k_1[\text{CrCH}(\text{CH}_3)_2^{2+}]/k_{4C}[\text{Cu}^{2+}] \quad (26A)$$

$$[(\text{CH}_3)_2\text{CHOO}\cdot]_{\text{ss}} = k_1k_{2A}[\text{O}_2]/k_{3A}k_{4C}[\text{Cu}^{2+}] \quad (26B)$$

(36) There do appear to be some contradictions in the statements made¹² concerning the rate law for decomposition of CrO_2^{2+} . To quote two passages: "At pH ~ 2 , CrO_2^{2+} [prepared by pulse radiolysis and stable at pH 3] decayed apparently by a second order process with rate constant of $\sim 2.4 \times 10^6$ M⁻¹ s⁻¹", and "The decay of CrO_2^{2+} at pH 2 could be studied over a much longer time range when CrO_2^{2+} was generated by mixing Cr^{2+} with an excess of O_2 , than it was when it was generated by pulse radiolysis. These results indicate a slow first-order decay of CrO_2^{2+} with $t_{1/2} \sim 20$ min." This suggests to us that different species may be involved in the two types of experiments.

(37) One would have expected k_d to be equal to $k_A + k_H$ or $(2.9 \pm 0.2) \times 10^{-4}$ s⁻¹. The value found in the presence of Fe^{2+} is $(4.3 \pm 0.1) \times 10^{-4}$ s⁻¹, and at high $[\text{Cu}^{2+}]$, $5.7 \pm 0.4 \times 10^{-4}$ s⁻¹. Although the discrepancy is not large there is some suggestion in these results that k_d should be equal to $k_A + 2k_H$, or $(4.6 \pm 0.3) \times 10^{-4}$ s⁻¹. The latter would be the case if a second organochromium ion were consumed in a rapid step which was significant under these conditions. A possible explanation was sought in a reaction between CrO_2^{2+} and $\text{CrCH}(\text{CH}_3)_2^{2+}$, but direct tests (for which we thank R. C. McHatton) showed that no reaction occurred. It is possible that an intermediate formed during the reaction of eq 20 may consume the second $\text{CrCH}(\text{CH}_3)_2^{2+}$ in the former case. In the presence of Cu^{2+} , the Cu^+ produced in eq 22 is rapidly converted to CuO_2^+ ; it, or the HO_2 resulting from its reaction with H^+ , may produce the effect.

(38) Shaw, K.; Espenson, J. H. *Inorg. Chem.* **1968**, *7*, 1619.

The rate of reaction, at high concentration of Cu^{2+} , is

$$(-d[\text{CrCH}(\text{CH}_3)_2^{2+}]/dt) = \frac{[\text{CrCH}(\text{CH}_3)_2^{2+}](k_d + k_1 k_{2A}[\text{O}_2]/k_{4C}[\text{Cu}^{2+}])}{k_A + k_H} \quad (27)$$

where the nonchain reactions have been included, as necessary under these experimental conditions. This equation has the same form as the one found experimentally, eq 11 or 25. The value of k_d is $(5.67 \pm 0.41) \times 10^{-4} \text{ s}^{-1}$, and one would expect it to be $k_A + k_H$ or perhaps³⁷ $k_A + 2k_H$. The constant k' of eq 25 is, according to mechanism C and eq 27, $k_1 k_{2A}/k_{4C}$ where $k_1 = k_H$. Using the value³³ of $k_{2A} \approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (presumably) hydrocarbon solvents as valid in aqueous solution, we calculated k_{4C} as $k_{4C} = k_H k_{2A}/k' = 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. In comparison, the values in competition experiments for oxidation of the 2-propyl radical by copper(II) are $5.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (at 57 °C in 66% v/v acetic acid/water) and $5.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (at 25.5 °C in 44% v/v acetonitrile/acetic acid).²² The agreement, considering the large difference in conditions, lends support to the applicability of mechanism C under the conditions employed.

We noted earlier the lack of any kinetic effect arising from addition of Cu^{2+} at much lower concentrations comparable to those of $\text{CrCH}(\text{CH}_3)_2^{2+}$. This, too, is consistent with mechanisms A and C. The rate of reaction of the 2-propyl radical with oxygen as compared to its rate with Cu^{2+} is the point at issue. Thus we compare $k_{2A}[\text{O}_2]$ vs. $k_{4C}[\text{Cu}^{2+}]$. Under the conditions of the experiments at "high" $[\text{Cu}^{2+}]$, 0.020–0.40 M as in Table V, the values are comparable. On the other hand, at "low" concentrations of Cu^{2+} , say $1 \times 10^{-3} \text{ M}$, the former would predominate by a factor of $\sim 500:1$.

Mechanistic Implications of the Effect of Ionic Strength. The two mechanisms A and B are customarily termed "kinetically equivalent" because, as shown by eq 25, both lead to a rate law having the same algebraic dependence on concentrations. The primary kinetic salt effect on the value of the 3/2-order rate constant for the chain mechanism is expected³⁹ to be different for each, however, in contradistinction to the well-established principle for nonchain reactions according to which the magnitude of the ionic strength effect is determined by the rate law, not by the mechanism.

For mechanisms A and B, the expression for the 3/2-order rate constant k_8 is $k_{3A}(k_1/2k_{4A})^{1/2}$ or $k_{3B}(k_1/2k_{4B})^{1/2}$. Each rate constant for an elementary reaction will vary with ionic strength, in the limit of low ionic strengths where the activity coefficients are expected to obey a Brønsted–Debye–Hückel equation, according to the expression

$$\log k_1 = \log k_1^0 + \frac{A(\Delta Z^2)^* \mu^{1/2}}{1 + \mu^{1/2}} \quad (28)$$

where A is a constant ($A = 0.509$ in water at 25 °C), and $(\Delta Z^2)^*$ is the difference in the squares of the ionic charges between the activated complex and the reactants for the given elementary reaction. Each of the three constants in the expression for k_8 from mechanism A have $(\Delta Z^2)^* = 0$. Consequently the composite will, if this is the correct mechanism, be expected to be independent of ionic strength. The data (Table V) support this formulation.

On the other hand, the values of $(\Delta Z^2)^*$ are not zero for the elementary reactions represented by rate constants k_{3B} and k_{4B} ; for each, $(\Delta Z^2)^* = 8$. As a consequence the composite rate constant k_8 for mechanism B would vary with ionic strength according to eq 29. There are no free parameters in the slope

$$\log k_{8B} = \log k_{8B}^0 + \frac{4A\mu^{1/2}}{1 + \mu^{1/2}} \quad (29)$$

of a plot of $\log k_8$ vs. $A\mu^{1/2}/(1 + \mu^{1/2})$. As shown in Figure 4 the magnitude of the experimental effects, which are inappreciable below $\mu = 0.04$ and rise only slowly beyond that, are very different than those required by eq 29. The disagreement of the data relating to the kinetic salt effect with the model implicit in

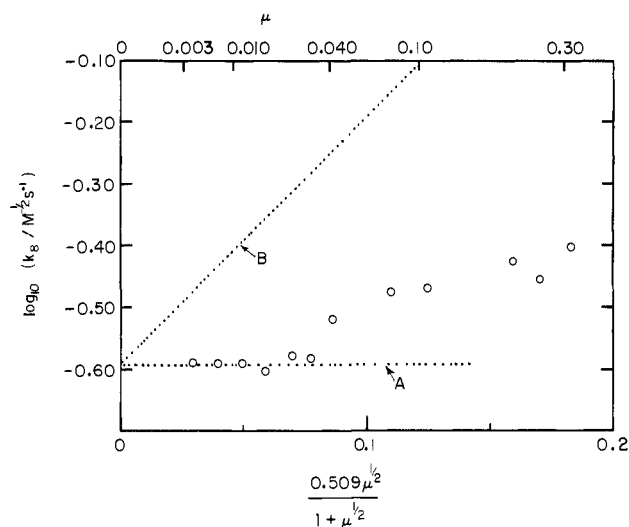


Figure 4. A plot showing the ionic strength dependence of the 3/2-order rate constant for the chain reaction of $\text{CrCH}(\text{CH}_3)_2^{2+}$ and O_2 by a plot of $\log k_8$ vs. $0.509 \mu^{1/2}/(1 + \mu^{1/2})$.

mechanism B constitutes another ground for discounting this mechanism.

Radical Displacement as a Chain-Propagation Step. The second propagating step of mechanism A is a process lacking abundant literature precedents. The reaction proposed accounts for the kinetic observations in that it provides a mechanism whereby the chain-carrying 2-propyl radical is regenerated to sustain the kinetic chains. In addition, it does so in a manner which produces a new complex, (2-propylperoxy)chromium(III) ion, for which analogues are known, as cited in the introduction.

Among the precedents which do exist are the reactions⁸ of eq 30 where R_nM = tetraalkyls of titanium and zirconium and hexaalkyls of dimolybdenum and ditungsten, and R represents such groups as benzyl and (trimethylsilyl)methyl. The authors



state, in reference to this proposed reaction, that it "would be the first example of a bimolecular homolytic substitution ($\text{S}_{\text{H}2}$) by peroxy radicals at an early transition metal center".⁸

The autoxidation of alkylboranes produces organoperoxyboranes. It is now widely held^{40–44} that these reactions proceed by a free radical chain mechanism in which one chain-propagating step is the $\text{S}_{\text{H}2}$ displacement of an alkyl radical from boron:



Evidence for this reaction is supported by stereochemical arguments, by the effects of inhibitors in scavenging radical intermediates, and by ESR studies. Rate constants have been determined for several alkyls, with values of k_{31} between 10^3 and $10^7 \text{ M}^{-1} \text{ s}^{-1}$. In comparison, the value calculated for k_{3A} is $6.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The autoxidations of Grignard reagents⁴⁵ and of alkyls of zinc, cadmium, aluminum, and tin⁴⁶ have also been explained in terms of an $\text{S}_{\text{H}2}$ attack of a peroxy radical at the metal.

It is necessary to consider, in the present instance, the process(es) leading up to the displacement itself; in particular, how does the 2-propylperoxy radical penetrate the coordination sphere

(40) Davies, A. G.; Roberts, B. P. *Chem. Commun.* **1966**, 298; *J. Chem. Soc.* **1962**, 17; *Chem. Commun.* **1969**, 699; *J. Chem. Soc.* **1969**, 311.

(41) Allies, P. G.; Brindley, P. B. *Chem. Ind. (London)* **1967**, 319; *J. Chem. Soc.* **1969**, 1126; *Chem. Ind. (London)* **1968**, 1439.

(42) Ingold, K. U. *Chem. Commun.* **1969**, 911.

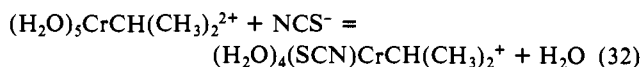
(43) Korcek, S.; Watts, G. B.; Ingold, K. U.; Roberts, B. P.; Tudor, R. J. *Chem. Soc. B* **1971**, 1968.

(44) Brindley, P. B.; Hodgson, J. C. *Chem. Commun.* **1972**, 202.

(45) Walling, C.; Cloffair, A. *J. Am. Chem. Soc.* **1970**, 92, 6609.

(46) Davies, A. G.; Roberts, B. P. *J. Chem. Soc. B* **1968**, 1074.

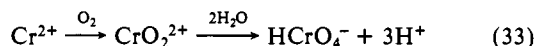
of the organochromium cation? The alkyl group of $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ complexes is known to labilize the trans water to a very substantial extent.⁴⁷ Experiments to determine directly the substitution rate were done using its anation reaction with NCS⁻:



The value⁴⁸ at 25.0 °C is $k_{32} = 1.25 \pm 0.02 \text{ M}^{-1} \text{ s}^{-1}$, far less than required ($k_{3A} = 6.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) to have the trans-accelerated ligand substitution reaction provide a pathway for $\text{S}_{\text{H}2}$ attack by $(\text{CH}_3)_2\text{COO}^\cdot$. (This argument presumes that the same limits found for nucleophilic substitution reactions such as eq 32 govern the rate constants for homolytic displacement, which is not necessarily the case.)

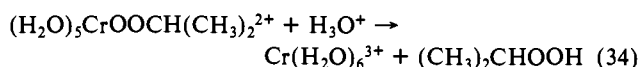
The homolytic displacement may instead occur by simultaneous displacement of the alkyl group by the entering peroxy. That is to say, the mechanism might be a bimolecular displacement process rather than the unimolecular reaction of an intermediate such as ROOCr^{2+} formed in a prior substitution step.

Products of Autoxidation. If we accept, on the basis of the arguments given above, that the chain-propagation steps produce the (alkylperoxy)chromium(III) ion, then its subsequent reactions account for all the products formed. The yields given in Table VI refer to experiments run under conditions where the chain process predominates. When that is the case, the appreciable yield of 2-propanol is not exclusively that produced by the termination step of mechanism A, since (given the chain length) only some 1-1.5% could be so produced. Likewise, of the 10% of so of chromium(VI) found, only a comparably small amount might be formed via eq 33 from oxidation of the Cr^{2+} (the product shown



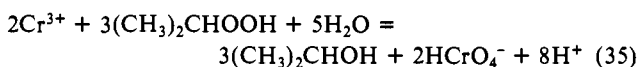
in eq 33 is a minor one in any case) which is a product of the homolysis reaction. The appreciable yields suggest another explanation must be sought.

We suggest that $\text{CrOOCH}(\text{CH}_3)_2^{2+}$ decomposes by reaction with H^+ to two independent products, acetone (eq 5) and 2-propyl hydroperoxide (eq 34). The analogous cobaloxime complex



$(\text{CH}_3)_2\text{CHOOCo}(\text{dmgH})_2\text{L}$ is known to react concurrently by two such independent processes.¹⁰ The relative importance of each depends, among other things, on the identity of the ligand L.

The hydroperoxide formed in eq 34 which is not found among the final products—although it has been shown¹⁰ to be stable in aqueous perchloric acid toward decomposition to acetone and water—evidently reacts further. It is likely that 2-propyl hydroperoxide oxidizes Cr(III) species $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ or $\text{Cr}_2\text{O}_4^{4+}$, accounting for the 2-propanol and HCrO_4^- formed. (The latter substances, although eventually reacting to form acetone and Cr(III), do so very slowly under these conditions.) It would be too tentative, on the basis of the data, for us to speculate as to the detailed steps involved, considering the reactions are undoubtedly quite complex, but the results are not inconsistent with the involvement of reactions such as that given by eq 35.



Some 10% of the chromium products are dimeric Cr(III) species such as $\text{Cr}_2\text{O}_4^{4+}$ or $\text{Cr}_2(\text{OH})_2^{4+}$ (Table VI). The reaction of Cr^{2+} and O_2 , although known to produce dimers, is probably not responsible under conditions where Cr^{2+} is produced slowly by homolysis in the presence of a large excess of O_2 . Under such conditions the CrO_2^{2+} so formed is unlikely to be further converted to CrOOCr^{4+} , the latter believed to be the precursor of the stable dimers. Instead, we suggest that reactions of intermediate oxidation states of chromium formed during its reaction with the peroxide as in eq 35 are a more likely source. The suggestion that HCrO_4^- formation largely occurs independently of the reaction with O_2 , although closely following it, accounts qualitatively for the wavelength dependence observed.

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 Drs. A. Bakač and M. D. Johnson and the assistance of the Ames Laboratory Analytical Services group for gas chromatographic (J. Richard) and mass spectrometric (G. J. Flesch) analyses.

(47) Bushey, W. R.; Espenson, J. H. *Inorg. Chem.* 1977, 16, 2772.
(48) Bakač, A., unpublished results.

Nitrous Acid Decomposition Catalyzed by an Iron(II) Complex: Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II)¹

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Abstract: In the presence of low concentrations of tris(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) ($\text{Fe}^{\text{II}}\text{TMP}$), nitrous acid decomposes to yield nitric oxide and nitrate. The kinetics of this two-stage reaction have been studied by using rapid-mixing techniques. During the first rapid phase, $\text{Fe}^{\text{II}}\text{TMP}$ is oxidized by HNO_2 and by NO_2^- to $\text{Fe}^{\text{III}}\text{TMP}$. The initial ferrous complex is then regenerated in a slower second phase dominated by the reaction of $\text{Fe}^{\text{III}}\text{TMP}$ with NO_2 . Rate constants for the reactions of $\text{Fe}^{\text{III}}\text{TMP}$ with nitrous acid and with nitrite were found to be $(7.26 \pm 0.07) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $(2.57 \pm 0.03) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, respectively, at 25 °C and ionic strength 0.5 M. Computer simulations have been carried out by using a mechanism developed for the hexaquoiron(II)-nitric acid system, with appropriate modification for the different kinetic properties of the iron species. Quantitative agreement between calculation and experiment is obtained for the first phase, and the model qualitatively predicts the observed regeneration of $\text{Fe}^{\text{II}}\text{TMP}$ in the second phase.

The surprisingly complex oxidation of aquoiron(II) ion by nitric acid has recently been the subject of a systematic kinetics study.²

The slow direct reaction between hexaquoiron(II) and nitrate was found to be of minor importance in that system. Once the