of *C*-CH_3 moves significantly to high frequency on complexation (from 141.6 to 147.5 ppm) while that for *C*-CF_3 is virtually unchanged (from 142.9 to 142.2 ppm). We suggest that these data clearly point to F as the structure for **4**, i.e., the isomer in which the methyl substituent in each heterocyclic unit is closest to Pt.

Conclusion

The observations reported herein offer an interesting insight into the chemistry of MTMP. It seems likely that the molecule exists predominantly, if not exclusively, as 3-(trifluoromethyl)-5-methylpyrazole in solution, i.e., with the proton attached to the nitrogen center nearest to the inductive influence of the methyl group and furthest from the electron-withdrawing trifluoromethyl substituent, and that accordingly its coordination properties as a neutral species will center around ligation through N^2. The corresponding pyrazolyl (pyrazolide) anion complexes via M–N bond formation to the other nitrogen atom N^1, which is the more basic atom when it becomes available through deprotonation.

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Registry No. **1**, 84049-91-2; **2**, 84056-83-7; **3**, 84056-84-8; **4**, 84049-92-3; **5**, 84049-93-4; $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$, 19394-82-2; *cis*-$PtCl_2(PEt_3)_2$, 15692-07-6.

Supplementary Material Available: Listings of thermal parameters, least-squares planes, and observed and calculated structure factors for **1** and **3** (35 pages). Ordering information is given on any current masthead page.

Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Kinetics of the Oxidation of Chromium(II) by Hydrogen Peroxide: Flash-Photolytic and Stopped-Flow Studies Based on Radical-Trapping Reactions

ANDREJA BAKAČ* and JAMES H. ESPENSON*

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Thermally stable organochromium complexes such as $CrCHCl_2^{2+}$ and $CrCH_2OCH_3^{2+}$ undergo homolytic Cr–C bond cleavage upon irradiation with unfiltered light from xenon flash lamps: $CrR^{2+} \xrightarrow{h\nu} Cr^{2+} + R\cdot$. This enables determination of the rate constant k_1 for the reaction $Cr^{2+} + H_2O_2 \rightarrow CrOH^{2+} + \cdot OH$, because this is the rate-limiting step in a sequence of reactions. The hydroxyl radicals react very rapidly with organic and inorganic solutes to yield radicals that in turn react rapidly with Cr^{2+}, producing intensely colored chromium complexes. The formation of these species was monitored spectrophotometrically. Some experiments were also done by the stopped-flow technique using solutions of Cr^{2+} and H_2O_2 in the presence of an organic solute or KI. The two techniques yielded identical results. In aqueous solution at 25 °C and 1.0 M ionic strength ($HClO_4 + LiClO_4$), with methanol, ethanol, 2-propanol, dimethyl ether, diethyl ether, dimethyl sulfoxide, and potassium iodide as solutes, the value of the rate constant k_1 is $(7.06 \pm 0.04) \times 10^4\ M^{-1}\ s^{-1}$.

Introduction

The reaction of H_2O_2 with Cr^{2+} has been studied extensively.[1,2] It was shown that the reaction proceeds mainly via a one-electron-transfer mechanism[1a,b] according to eq 1–3.

$$Cr^{2+} + H_2O_2 \xrightarrow{k_1} CrOH^{2+} + \cdot OH \qquad (1)$$

$$Cr^{2+} + \cdot OH \xrightarrow{\text{fast}} CrOH^{2+} \qquad (2)$$

$$2Cr^{2+} + H_2O_2 = 2CrOH^{2+} \qquad (3)$$

This particular reaction was briefly addressed as part of a study[2] of the kinetics of reactions between hydrogen peroxide and metal complexes. Side reactions complicated the kinetics when H_2O_2 was used in excess over Cr^{2+}; thus the reported rate constant $k_1 = (2.8 \pm 0.7) \times 10^4\ M^{-1}\ s^{-1}$ was obtained with Cr^{2+} in excess. (As we point out later, the value reported in the literature[2] was calculated incorrectly and is too low by a factor of 2.) The rather large error is due to small absorbance changes in the stopped-flow experiments and to high reaction rates.

Owing to the formation of the OH radicals in reaction 1, the Cr^{2+}–H_2O_2 reaction proved to have a valuable synthetic utility in the preparation of various cationic organochromium complexes,[3-5] reactions 4 and 5, where R, R^1, R^2 = alkyl or

$$HCR^1R^2OR + \cdot OH \rightarrow \cdot CR^1R^2OR + H_2O \qquad (4)$$

$$\cdot CR^1R^2OR + Cr^{2+} \rightarrow CrCR^1R^2OR^{2+} \qquad (5)$$

hydrogen. The organochromium complexes produced have characteristic strong absorption bands at ~400 and ~300 nm with molar absorptivities ($M^{-1}\ cm^{-1}$) ranging from several hundred at the first maximum to ~2500 at the second.[3-5] This property of the organochromium complexes greatly enhances the absorbance change in the overall reaction, thus permitting an accurate measurement of the rate constant for reaction 1. In addition to large absorbance changes, this approach has the advantage in that the scavenging of the OH radicals (eq 4) eliminates side reactions and either reagent can be used in excess. This enabled us to generate low concentrations of Cr^{2+} (~3×10^{-5} M) flash photolytically from the thermally stable organochromium complexes $CrCHCl_2^{2+}$ and $CrCH_2OCH_3^{2+}$. Handling of low concentrations of Cr^{2+} in the stopped-flow apparatus could thus be avoided.

Results and Discussion

Flash-Photolytic Experiments. When a solution of $\geq 1 \times 10^{-4}$ M $CrCHCl_2^{2+}$ is exposed to a 50-J flash, the absorbance

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[1] (a) Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197. (b) Anderson, L. B.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 1470. (c) Cahill, A. C.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 2312.

[2] Samuni, A.; Meisel, D.; Czapski, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1273.

[3] Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.

[4] Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

[5] Kirker, G. W.; Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

0020-1669/83/1322-0779$01.50/0

at its 396-nm absorption maximum decreased by an amount corresponding to 3.0×10^{-5} M $CrCHCl_2^{2+}$. Similarly, 2.9×10^{-5} M $CrCH_2OCH_3^{2+}$ decomposes upon flashing a $\geq 1 \times 10^{-4}$ M solution. In the presence of H_2O_2 and an organic solute such as an alcohol or ether, the instantaneous absorbance decrease is followed by an absorbance increase due to the formation of a new organochromium complex, which occurs at a measurable rate with reaction 1 as the rate-limiting step. On the basis of these observations, we conclude that the photolytic process corresponds to reaction 6, where R = $CHCl_2$

$$CrR^{2+} \xrightarrow{h\nu} Cr^{2+} + R \qquad (6)$$

and CH_2OCH_3. It is analogous to the known photohomolysis reaction of organocobaloximes.[6,7] Subsequent reaction of Cr^{2+} with excess H_2O_2[8] in the presence of an organic solute produces the corresponding organochromium complex by reactions 1, 4, and 5. On the basis of this scheme, one derives a rate law of eq 7.

$$Cr^{2+} + H_2O_2 \rightarrow CrOH^{2+} + \cdot OH \qquad (1)$$

$$\cdot OH + HCR^1R^2OR \rightarrow \cdot CR^1R^2OR + H_2O \qquad (4)$$

$$Cr^{2+} + \cdot CR^1R^2OR \rightarrow CrCR^1R^2OR^{2+} \qquad (5)$$

$$-\frac{1}{2}\frac{d[Cr^{2+}]}{dt} = -\frac{d[H_2O_2]}{dt} = \frac{d[CrCR^1R^2OR^{2+}]}{dt} = k_1[Cr^{2+}][H_2O_2] \qquad (7)$$

The kinetic experiments were done with an excess of H_2O_2, $(0.19\text{–}2.58) \times 10^{-3}$ M, and methanol, ethanol, 2-propanol, dimethyl ether, and diethyl ether as sources of organic radicals. In most of the experiments $CrCHCl_2^{2+}$ was used as a source of Cr^{2+}, since it is more easily handled than $CrCH_2OCH_3^{2+}$. The latter complex is somewhat oxygen sensitive,[9] and its molar absorptivity at ~400 nm is higher, which increases the background absorbance in the kinetic experiments. The kinetic runs using $CrCHCl_2^{2+}$ and $CrCH_2OCH_3^{2+}$ as sources of Cr^{2+} yielded identical rate constants within the experimental error. A plot of the pseudo-first-order rate constants against $[H_2O_2]_{av}$ for all the alcohols and ethers, along with the rate constants measured in the stopped-flow experiments with H_2O_2 in excess, is a single straight line as expected. The slope of the line gives $2k_1 = (1.41 \pm 0.01) \times 10^5$ M^{-1} s^{-1}. The concentration of alcohols was usually 1.0 M, although it was varied in some experiments between 0.1 and 2.0 M without any effect on the rate constant. The concentration of ethers was kept constant in all the experiments at the saturation level (~1 M for $(CH_3)_2O$ and ~0.5 M for $(C_2H_5)_2O$). Variation of the hydrogen ion concentration between 0.05 and 1.0 M had no effect on the rate constant.

Stopped-Flow Experiments. In most of the experiments Cr^{2+} was used in a pseudo-first-order excess over H_2O_2, although a few check points with H_2O_2 in excess were also done. In addition to the alcohols and ethers, dimethyl sulfoxide[10] and potassium iodide were used as sources of radicals. A plot of the pseudo-first-order rate constants obtained with Cr^{2+} in excess against $[Cr^{2+}]_{av}$ is a straight line, the slope of which gives $k_1 = (7.10 \pm 0.08) \times 10^4$ M^{-1} s^{-1}.

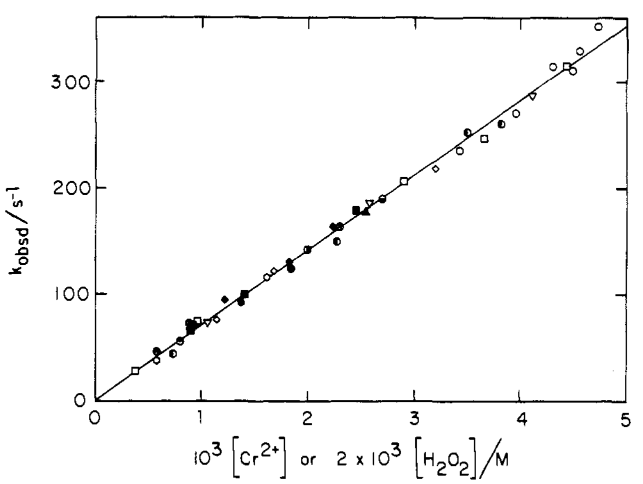

Figure 1. Plot of the first-order rate constants for the reaction of H_2O_2 with Cr^{2+} against the concentration of the reagent in excess. The concentration of H_2O_2 was multiplied by 2 to account for the stoichiometry, eq 3. Rate constants were determined by the stopped-flow technique *in the presence of different solutes with an excess of* Cr^{2+} (●, MeOH; ◒, EtOH; ■, 2-PrOH; ◓, Et_2O; ▲, Me_2SO; ♦, KI) or H_2O_2 (⊗, MeOH; ◑, 2-PrOH) and by flash photolysis using H_2O_2 in excess and either $CrCHCl_2^{2+}$ (○, MeOH; ◐, EtOH; □, 2-PrOH; ▽, Me_2O; ◇, Et_2O) or $CrCH_2OCH_3^{2+}$ (○, MeOH; ⬢, EtOH; ⊕, Et_2O) as a source of Cr^{2+}.

There are two possible mechanisms for the CrI^{2+} formation when the reaction is done in the presence of iodide: a Fenton-type reaction where eq 4a and 5a now replace eq 4 and

$$I^- + \cdot OH \rightarrow I\cdot + OH^- \qquad I\cdot + I^- \rightleftharpoons I_2^- \qquad (4a)$$
$$k = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}\ {}^{11}$$

$$I_2^- + Cr^{2+} \rightarrow CrI^{2+} + I^- \qquad (5a)$$

5 and a mechanism whereby Cr^{2+} is first complexed by iodide to produce CrI^+, which is then oxidized by H_2O_2 to CrI^{2+}, eq 8 and 9. The latter mechanism can be discarded on the basis

$$Cr^{2+} + I^- \rightleftharpoons CrI^+ \qquad (8)$$

$$CrI^+ + 0.5H_2O_2 \xrightarrow{H^+} CrI^{2+} + H_2O \qquad (9)$$

of the following considerations. Within the limited range of concentrations studied, the yield of CrI^{2+} was always ~90% of the initial concentration of H_2O_2, i.e., ~45% of the Cr(II) used in the reaction, regardless of the iodide concentration ($(1.0\text{–}2.2) \times 10^{-2}$ M).[12] The rate constant measured was in each case identical with the one obtained with all the other solutes used. If the complexation mechanism applied, the rate law for the disappearance of H_2O_2 (limiting reagent) would be defined by eq 10, where k_{CrI} denotes the rate constant for

$$-\frac{d[H_2O_2]}{dt} = \left(\frac{k_{CrI}K_8[I^-]}{1 + K_8[I^-]} + \frac{k_1}{1 + K_8[I^-]}\right)[Cr(II)]_T[H_2O_2] \qquad (10)$$

reaction 9 and $[Cr(II)]_T$ is the total concentration of Cr(II). The rate constant measured would be equal to k_1 only if $k_{CrI} = k_1$, which is unlikely. Even if this were the case, the yields of CrI^{2+} would have to show a dependence on $[I^-]$, contrary

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(6) Cobaloxime is a trivial name for bis(dimethylglyoximato)cobalt complexes (Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97).

(7) Golding, B. T.; Kemp, T. J.; Sheena, H. H. *J. Chem. Res., Miniprint* **1981**, 334.

(8) No complications attributable to the organic radicals were encountered. Most likely, they disappear via dimerization and/or disproportionation: $2R\cdot \rightarrow$ nonradical products, $k \sim 10^9$ M^{-1} s^{-1}.

(9) Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2721.

(10) The reaction of dimethyl sulfoxide with OH radicals produces $\cdot CH_3$, so that the final product of the reaction is $CrCH_3^{2+}$ (Gold, V.; Wood, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 2462).

(11) Farhataziz; Ross, A. B. *Natl. Stand. Ref. Ser. (U.S., Natl. Bur. Stand.)* **1977**, *NSRDS-NBS 59*.

(12) The important requirement here is that $[I^-] \geq 10[Cr^{2+}]$, due to the competition between Cr^{2+} and I^- for the OH radicals, eq 2 and 4a ($k_2 = 4.8 \times 10^9$ M^{-1} s^{-1} [11] and $k_{4a} = 1.2 \times 10^{10}$ M^{-1} s^{-1} [11]).

to our observations. A Fenton-type reaction, on the other hand, requires that the rate constant k_1 be measured at all iodide concentrations and that the yields approach $[H_2O_2]_0$ when Cr^{2+} is in excess.

Excellent agreement between the rate constants obtained with the two techniques and either reagent in excess ($2k_1 = (1.41 \pm 0.01) \times 10^5$ M^{-1} s^{-1}, H_2O_2 in excess, and $k_1 = (7.10 \pm 0.08) \times 10^4$ M^{-1} s^{-1}, Cr^{2+} in excess) permits us to calculate the best value for the rate constant k_1 by using all the data. Figure 1 shows a plot of the observed pseudo-first-order rate constants against the average concentration of the reagent in excess. The stoichiometric factor of 2 was taken into account by multiplying the H_2O_2 concentration by 2. A linear least-squares analysis of the data yields $k_1 = (7.06 \pm 0.04) \times 10^4$ M^{-1} s^{-1}. This rate constant is rather different from the reported value[2] of $(2.8 \pm 0.7) \times 10^4$ M^{-1} s^{-1}. The latter was obtained from an experiment using Cr^{2+} in excess over H_2O_2. However, the authors calculated the second-order rate constant by dividing the pseudo-first-order rate constant by *twice* the initial concentration of Cr^{2+}, thus introducing an incorrect and artificial factor of 2. From the available experimental data in ref 2 and with use of the average concentration of Cr^{2+} rather than the initial value, we calculate $k_1 = (6.0 \pm 1.5) \times 10^4$ M^{-1} s^{-1}, which is within the experimental error identical with the value obtained in this work. We believe our value is more accurate due to the choice of methods used in this study. The correct relationship among reaction rate, rate constant, and stoichiometric factors is given by eq 7, which thereby provide the definition for k_1. This relationship also provides the basis for showing in Figure 1 both sets of data on a single ordinate by incorporation of the stoichiometric factor in the concentration plotted. It should be noted that in every case the observed pseudo-first-order rate constant (k_{obsd}) necessarily corresponds to $-d \ln [\text{limiting reagent}]/dt$. The experimental value of k_1 includes, of course, any contribution from the two-electron pathway.

Yields of Chromium Complexes in the Kinetic Experiments. The theoretical yields of α-hydroxylalkyl and α-alkoxyalkyl complexes produced in the reaction of Cr^{2+} with H_2O_2 in the presence of different alcohols and ethers can be calculated on the basis of 2:1 Cr^{2+}:H_2O_2 stoichiometry and the known percentage of the α-hydrogen abstraction[13,14] by OH radicals.[15] With iodide, reaction 4a should account for all the OH radicals. Also, a minor part of the Cr^{2+}–H_2O_2 reaction ($\lesssim 7\%$) is probably occurring by a two-electron pathway.[1b] This conclusion is corroborated by the fact that there is always some $Cr(OH)_2Cr^{4+}$ [16] found in solutions of organochromium complexes produced in the Fenton-type reactions. In the study by Anderson and Plane,[1b] 14% of the chromium(III) product was found in the form of the dimer. Since no scavengers for the OH radicals were used in that study, the dimer could be formed partly in the reaction of Cr^{2+} with O_2, the latter being produced in the side reactions.[1b] The two-electron pathway was therefore not taken into account in calculating the theoretical yields in this work. All the calculated yields throughout the rest of the paper are based only on the 2:1 stoichiometry and the percentage of the α-hydrogen abstraction.

With the exception of $CrCH(CH_3)OC_2H_5^{2+}$ (see below), the yields of the chromium complexes in the stopped-flow experiments were usually ~75–88% of the theoretical ones, regardless of which reagent was used in excess. The yields of α-hydroxyalkyl complexes were calculated by using published values of molar absorptivities, which were determined pulse radiolytically with an accuracy of ±15%.[4] The α-alkoxyalkyls are thermally quite stable,[3,4,9] and the molar absorptivities were determined on solutions purified by ion exchange.[9] The error is thus lower for the latter complexes. In view of the uncertainty in the molar absorptivities (at least for the α-hydroxyalkyl complexes) and the occurrence of the minor two-electron pathway, the yields of the organochromium complexes produced in the stopped-flow experiments are considered quantitative within the errors involved.

Hydrogen peroxide was used in excess over Cr^{2+} in all the flash-photolytic experiments. With $CrCH_2OCH_3^{2+}$ as a source of Cr^{2+}, the yields of organochromium complexes were identical with the ones obtained in the stopped-flow experiments. When $CrCHCl_2^{2+}$ was flashed, the amounts of organochromiums produced were somewhat lower, typically ~ 50–75% of the calculated. The kinetics were however unaffected; the rate constants measured were identical with the ones obtained with $CrCH_2OCH_3^{2+}$. The reason for this behavior is probably the more complicated photochemistry of $CrCHCl_2^{2+}$. In addition to reaction 6, there appears to exist a minor pathway ($\lesssim 20\%$) that destroys $CrCHCl_2^{2+}$ but does not produce Cr^{2+}. This additional pathway may be a photochemical process involving the chlorine–carbon bond. The excited state could be subject to a different mode of the chromium–carbon bond cleavage such as rapid acidolysis, producing Cr^{3+} and CH_2Cl_2 (eq 11).

$$CrCHCl_2^{2+} \xrightarrow{h\nu} CrCHCl_2^{2+*} \xrightarrow{H^+} Cr^{3+} + CH_2Cl_2 \qquad (11)$$

The yields of the organochromium complexes produced from $CrCHCl_2^{2+}$ also showed a minor dependence on the hydrogen peroxide concentration (this was not verified for the experiments using $CrCH_2OCH_3^{2+}$, where low concentrations ($\leq 8 \times 10^{-4}$ M) of H_2O_2 were always used). The kinetics were once again unaffected. The likely reason for this behavior is that H_2O_2, when present at higher concentrations, absorbs some of the unfiltered UV–visible light. This will not only diminish the yield of Cr^{2+} in the flash but will also consume some additional Cr^{2+} via reactions 12, 4, and 5. Some Cr^{2+} is thus used up on the time scale of the flash, and consequently less is available for the reaction with H_2O_2.

$$H_2O_2 \xrightarrow{h\nu} 2{\cdot}OH \qquad (12)$$

If the sequence of reactions 12, 4, and 5 applies, small amounts of the organochromium complexes are produced on the time scale of the flash, and the total yields are higher than those calculated from the absorbance changes in the kinetic experiments. Since the amounts of the organochromium cations produced in these experiments are rather small ($\leq 1 \times 10^{-5}$ M) and their spectra are masked by the remaining $CrCHCl_2^{2+}$ ($\sim 1 \times 10^{-4}$ M), the total yields cannot be determined accurately. It was noticed however that in experiments using high $[H_2O_2]$ ($\geq 2 \times 10^{-3}$ M) the kinetic traces were displaced upward as expected if some absorbing species such as an organochromium was formed in the flash. Also, the yields were diminished when solutions of $\geq 2 \times 10^{-3}$ M H_2O_2 were used as flash filters, again pointing to the photochemistry of H_2O_2 as the most likely explanation for the low kinetic yields (~50%) of the organochromiums at high $[H_2O_2]$.

The $CrCH(CH_3)OC_2H_5^{2+}$ Case. The yields of this complex in both stopped-flow and flash-photolysis experiments were

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(13) Swallow, A. J. *Prog. React. Kinet.* **1978**, *9*, 195.

(14) Anbar, M.; Meyerstein, D.; Neta, P. *J. Chem. Soc. B* **1966**, 742.

(15) (a) The abstraction of β and hydroxyl hydrogens will not alter the overall stoichiometry, since the radicals produced in these cases also react with Cr^{2+}, producing Cr(III) complexes. However, both kinds of complexes will escape detection. β-Hydroxyalkyl complexes of chromium(III) undergo rapid acidolysis

$$CrCR^1R^2CH_2OH^{2+} \xrightarrow{H^+} Cr^{3+} + R^1R^2C{=}CH_2 + H_2O$$

and cannot be observed under the present experimental conditions.[4,15b] The alkoxy complexes absorb negligibly in comparison with α-hydroxylalkyl complexes. (b) Ryan, D. A.; Espenson, J. H. *Inorg. Chem.* **1982**, *21*, 527.

(16) (a) Kolaczkowski, R. W.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 322. (b) Thompson, M.; Connick, R. E. *Ibid.* **1981**, *20*, 2279.

usually ~140% of the calculated (~110% in the $CrCHCl_2^{2+}$ experiments). The calculated[14] theoretical yield of the α radical produced in reaction 13 is only 72%, the remaining 28%

$$CH_3CH_2OCH_2CH_3 + \cdot OH \xrightarrow{72\%} CH_3\dot{C}HOCH_2CH_3 \quad \xrightarrow{28\%} \cdot CH_2CH_2OCH_2CH_3 \qquad (13)$$

of the reaction producing the β radical, $\cdot CH_2CH_2OC_2H_5$. To explain the yields higher than calculated, one has to assume either that the yield of the α radical is much higher (~100%) or that the complex produced from the β radical, $CrCH_2CH_2OC_2H_5^{2+}$, is stable under the experimental conditions with a molar absorptivity similar to that of the α isomer. As far as the spectrum is concerned, the latter is a reasonable possibility, since most of the alkyl and substituted-alkyl complexes of chromium(III) exhibit similar spectral features. It is much more difficult to predict the stability of the β isomer. β-Hydroxyalkyl complexes of chromium(III) are highly unstable,[4,15b] and by analogy one might also expect the β-alkoxyalkyls to decompose quite rapidly. Similarly, both β-hydroxyalkyl and β-alkoxyalkyl complexes of some cobalt macrocycles are unstable toward acid.[17] On the other hand, the α-alkoxyalkyl complexes of chromium(III) are many orders of magnitude more stable than the hydroxyalkyl analogues. It is possible that qualitatively the same trend applies to the β isomers, so that the (β-ethoxyethyl)chromium ion was observed under our experimental conditions.

Effect of Radical Self-Reactions. In the stopped-flow experiments using excess Cr^{2+}, the calculated steady-state concentrations of the radicals are small compared to $[Cr^{2+}]$ and >99% of all the radicals formed should react with Cr^{2+} to produce CrR^{2+}. High experimental yields of CrR^{2+} are consistent with this calculation. In the experiments using excess H_2O_2 and small amounts of Cr^{2+} (all the flash-photolysis and some stopped-flow runs), the calculated steady-state concentrations of the radicals are such that substantial proportions of the radicals should dimerize and/or disproportionate.[18] This is especially true for the radicals that react slowly with Cr^{2+} (eq 5) such as $\cdot CMe_2OH$ ($k_5 = 5 \times 10^7$ M^{-1} s^{-1}). Using the model Runge–Kutta calculations,[19] we find that, in a typical flash-photolysis experiment ($[Cr^{2+}]_0 = 3 \times 10^{-5}$ M, $[H_2O_2] = 1 \times 10^{-3}$ M), ~50% of the radical should disproportionate, the remaining ~50% producing $CrCMe_2OH^{2+}$. On the basis of this calculation, less than quantitative experimental yields of $CrCMe_2OH^{2+}$ and other complexes could be in part attributed to the radical self-reactions. On the other hand, the yields of $CrCMe_2OH^{2+}$ were not significantly lower at higher $[H_2O_2]$ ($\geq 1 \times 10^{-3}$ M) than they were at low $[H_2O_2]$ ($\sim 2 \times 10^{-4}$ M), although the calculated steady-state concentration of the radicals is lower in the latter case and consequently self-reactions should be less prominent. In addition, the yields of $CrCMe_2OH^{2+}$ were not lower than the yields of, e.g., $CrCH_2OH^{2+}$ under identical conditions, although the rate constant for the reaction of $\cdot CH_2OH$ with Cr^{2+} is ~3 times higher than the corresponding rate constant for $\cdot CMe_2OH$. Also, one expects a significant effect on the overall kinetics of the radical self-reactions if they are appreciable. The 2:1 stoichiometry would no longer hold, and the observed rate constant would be up to a factor of 2 lower than predicted by the line in Figure 1. This has not been observed experimentally; within the experimental error all the points in Figure 1 lie on one straight line, even at concentrations of H_2O_2 as high as 2.2×10^{-3} M. In effect the system behaves as if additional reactions take place to keep the steady-state concentration of the free radicals much lower than calculated, thus preventing the self-reactions. There is at present no direct experimental evidence that would enable us to identify these reactions. We have given some consideration to the known reaction of eq 14, but it does not alter the

$$\cdot CMe_2OH + H_2O_2 \rightarrow Me_2CO + HO\cdot + H_2O \qquad k = 5 \times 10^5\ M^{-1}\ s^{-1}\,{}^{20} \qquad (14)$$

steady-state concentration of $\cdot CMe_2OH$, since the $HO\cdot$ produced in reaction 14 is instantaneously converted back to $\cdot CMe_2OH$ by reaction 4. Model Runge–Kutta calculations also showed that the concentration of H_2O_2 does not change appreciably by the involvement of reaction 14.

Table I. Summary of the Rate Constants for the Reaction of Cr^{2+} with Butyl Hydroperoxides and H_2O_2 at 25.0 °C and 1.0 M Ionic Strength

peroxide	$10^{-4}k/M^{-1}\ s^{-1}$	ref
t-BuOOH[a]	1.65	21
sec-BuOOH[a]	3.63	21
n-BuOOH[a]	5.77	21
H_2O_2	7.06 (3.53[b])	this work

[a] In 1:1 v/v CH_3OH/H_2O. [b] The rate constant given in parentheses is $k_1/2$ to account for the statistical factor of 2 for H_2O_2 compared to ROOH.

Comparison with Other Systems. The rate constant k_1 for the reaction of Cr^{2+} with H_2O_2 can now be compared with the rate constants for the reaction of Cr^{2+} with organic hydroperoxides, ROOH.[21] (The changes in solvent composition involved in this comparison are believed to be negligible on the basis of the lack of effect on k_1 in this study between different organic solutes and with their concentration, up to 2 M ethanol.) In the latter reaction the attack by Cr^{2+} takes place at the OH group of the hydroperoxide,[21] analogous to the reaction of H_2O_2.[1] It has been pointed out before[21] that the rate constant decreases as the steric crowding at the oxygen-bound carbon increases. For example, in the case of the butyl hydroperoxides the rate constant decreases in the order *n*-BuOOH, *sec*-BuOOH, *t*-BuOOH (Table I). For the purpose of comparing these rate constants with the rate constant for reaction 1, the latter has to be corrected for the statistical factor of 2, since there are two identical OH sites in the molecule where the attack can occur. This corrected rate constant, $k_1/2$, has a value of 3.5×10^4 M^{-1} s^{-1} and falls in the same range with the organic hydroperoxides. It is lower only than the rate constant for *n*-BuOOH. Apparently the weaker O–O bond in ROOH, as compared to HOOH,[22] and the greater stability of the radical produced (RO· vs. HO·) can have an appreciable effect on the kinetics only when steric effects become negligible, as in the case of *n*-BuOOH.

In the oxidations of transition-metal ions, hydrogen peroxide shows a strong preference for a one-electron transfer, as evidenced by the data in Table II. A minor two-electron pathway can be proved for the Cr^{2+} and V^{2+} reactions because kinetically inert dimeric products are formed—$Cr(OH)_2Cr^{4+}$ (~14%)[1] and VOV^{4+} or $V(OH)_2V^{4+}$ (~30%).[23] The rate constants for the octahedral aquo ions (first five entries of Table II) parallel their standard reduction potentials, so that the most reducing metal ion, Cr^{2+}, reacts most rapidly. The

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(17) See for example: (a) Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1. (b) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 143. (c) Espenson, J. H.; Wang, D. M. *Inorg. Chem.* **1979**, *18*, 2853. (d) Vickrey, T. M.; Katz, R. N.; Schrauzer, H. N. *J. Am. Chem. Soc.* **1975**, *97*, 7248.

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Table II. Summary of the Kinetic Data for the One-Electron Oxidation of Transition-Metal Complexes by Hydrogen Peroxide at 25 °C

reductant	k/M^{-1} s^{-1}	$E°$/J	ref
$Cr(H_2O)_6^{2+}$	7.06×10^4	−0.41	this work
$V(H_2O)_6^{2+}$	$>10^2$	−0.255	23
$Ti(H_2O)_6^{3+}$	5.40×10^2	0.10	2[a]
$Fe(H_2O)_6^{2+}$	57.8	0.77	[b]
$VO(H_2O)_5^{2+}$	~1	1.0	2[c]
TiF_2^+	80		[d]
$Co^{II}([14]aneN_4)^{2+}$	3.97×10^3	0.44	29
trans-$((H_2O)_2Co^{II}[N_4])^{n+}$	$(0.077–1.92) \times \times 10^3$	0.074–0.51	29[e]
$Cu(phen)_2^+$	3.91×10^3	0.174	31
$Cr(CN)_5H_2O^{3-}$	3.6×10^3		25
$Cr(CN)_6^{4-}$	3.3×10^2	−1.14	25
$Co(CN)_5^{3-}$	7.4×10^2	$\leqslant -0.81$[f]	28
$Ru(NH_3)_6^{2+}$	$<10^{-2}$	0.10	26

[a] The rate constant is pH dependent and varies between 540 M^{-1} s^{-1} at pH 0 (1.0 M $HClO_4$) and 920 M^{-1} s^{-1} at pH 1. The values from ref 2 were multiplied by 2, because the data were calculated erroneously in the original paper.[2] The rate constant in sulfuric acid is of the same order of magnitude and is independent of the acid concentration. Similar values were also obtained by other authors. [b] Po, H. N.; Sutin, N *Inorg. Chem.* **1968**, *7*, 621. Values reported earlier by other authors all fall into the same general range. [c] Estimated from the graph in ref 2 at pH 0. The reaction is pH dependent; k = 5.8 M^{-1} s^{-1} at pH 1. [d] Brooks, H. B.; Silicio, F. *J. Phys. Chem.* **1975**, *79*, 2544. The isomer, cis or trans, was not specified. The rate constant given represents the acid-independent term of the two-term rate law. [e] The assignment of a one-electron-oxidation mechanism to the reactions of the cobalt(II) macrocycles could not be confirmed experimentally;[29] see text. [f] Cited in ref 25.

only exception seems to be V^{2+}. Although the cited value represents the lower limit, the rate constant for the V^{2+}–H_2O_2 reaction is probably lower than expected on the basis of the standard reduction potential, −0.255 V, of the $V^{3+/2+}$ couple. Most likely, the reason is the substitutional inertness of V^{2+},[24] which limits the value of the second-order rate constant for inner-sphere reactions of V^{2+} to ~200 M^{-1} s^{-1}. Alternatively, the rate constant for the reaction with H_2O_2 could be much higher than the substitution limit, in which case one would have to assign an outer-sphere mechanism to the V^{2+} reaction. This however seems less likely owing to the known tendency of H_2O_2 to react by an inner-sphere mechanism,[25] as exemplified by the last three entries in Table II. Substitutionally inert complexes that cannot react by an inner-sphere mechanism ($Ru(NH_3)_6^{2+}$ [26] and $Cr(CN)_6^{4-}$ [25]) react quite slowly. Although $Cr(CN)_6^{4-}$ is a much more powerful reductant than V^{2+}, the rate constant for the reaction with H_2O_2 is only 330 M^{-1} s^{-1}.[25] Replacement of one coordinated cyanide group by H_2O results in a change of mechanism to inner sphere and an increase in the rate constant to $k = 3.6 \times 10^3$ M^{-1} s^{-1}.[25] The reaction of another outer-sphere reductant, $Ru(NH_3)_6^{2+}$, is imperceptibly slow.[26] A very potent reductant $Co(CN)_5^{3-}$ shows little tendency to add a sixth ligand.[25,27] This is again reflected in the low rate constant[28] for the inner-sphere reaction with H_2O_2.

A study of the reactions of H_2O_2 with a series of the cobalt(II) macrocyclic complexes of the general formula *trans*-$(H_2O)_2Co[N_4]^{n+}$ has been reported.[29,30] Of all the complexes studied, only $(H_2O)_2Co([14]aneN_4)^{2+}$ has been unequivocally shown to react by a one-electron pathway, producing free OH radicals. Other complexes most likely react by a mechanism similar to $(H_2O)_2Co([14]aneN_4)^{2+}$, but the OH radicals are not released into solution. Instead, they react with coordinated macrocyclic ligands.[29]

The reaction of H_2O_2 with coordinatively saturated $Cu(phen)_2^+$ [31] was proposed to occur by an inner-sphere mechanism. The change of the coordination number from 4 to 5 or 6 in oxidations of Cu(I) to Cu(II) is considered the greatest barrier in these reactions.[31,32] Since the change in the coordination number is required irrespective of the mechanism, an inner-sphere pathway with increased coordination number prior to electron transfer is quite facile in the oxidations of Cu(I) complexes.

Experimental Section

Kinetic Experiments. Flash photolysis[33] was conducted with unfiltered UV–visible radiation from fast-extinguishing xenon flash lamps in the Xenon Model 710 system. A flash energy of 50 J was used in all the experiments. A storage oscilloscope was used to record the transmittance change accompanying the formation of the α-hydroxyalkyl and α-alkoxyalkyl complexes of chromium(III). The reactions were monitored at the ~400-nm maximum of the organochromium complexes produced.

Some kinetic experiments were done with either a Durrum 110 or a Canterbury SF-3A stopped-flow spectrophotometer. The reactions were followed at either maximum of the organochromium complexes formed. The formation of CrI^{2+} was monitored at 280 nm (ε 3.4 × 10^3 M^{-1} cm^{-1}). The rate constants were evaluated by standard procedures.

Reactants and Materials. The dichloromethyl[34] and the methoxymethyl[9] complexes of chromium(III) were prepared and purified according to the published procedures. Reagent grade chemicals were used throughout. Solutions of chromium(II) perchlorate were prepared by the reduction of chromium(III) perchlorate using amalgamated zinc.

All the experiments were done at 25.0 °C and 1.0 M ionic strength ($HClO_4$ + $LiClO_4$) under rigorously air-free conditions using Cr^{2+}-scrubbed N_2 or Ar.

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Registry No. Cr, 7440-47-3; H_2O_2, 7722-84-1; $Cr(H_2O)_6^{2+}$, 20574-26-9.

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(30) Among the cobalt(II) complexes used were the following (trivial abbreviation, systematic name): $Co([14]aneN_4)^{2+}$, (1,4,8,11-tetraazacyclotetradecane)cobalt(II) ion; $Co(dmgH)_2$, bis(dimethylglyoximato)cobalt(II); $Co(dpnH)^+$, [3,3′-(trimethylenediimino)bis(butan-2-one oximato(1−))]cobalt(II) ion; $Co(tim)^{2+}$ or $Co(teteneN_4)^{2+}$, (2,3,9,11-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)cobalt(II) ion; Co^{II}(corrin), vitamin B_{12r}.

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