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Reactions of Hydroxyl and Other Free Radicals with Organopentaaquochromium(2+) Ions

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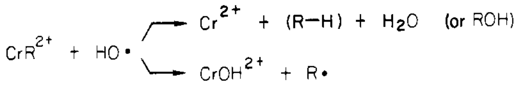
Complexes of the family $(H_2O)_5CrR^{2+}$ (R = CH_2OCH_3, $CH(CH_3)OC_2H_5$, $CH(CH_3)_2$, and $CH_2C_6H_5$) react with hydroxyl radicals, with accompanying cleavage of the chromium–carbon bond. Decomposition of the CrR^{2+} complexes in the presence of H_2O_2 occurs by self-sustaining chain reactions, because the reactive intermediates from the HO· reactions, Cr^{2+} and R·, react with H_2O_2 to form HO· again. The overall chain length is not high because of efficient chain-terminating reactions. An estimate of $\sim 1.6 \times 10^9$ M^{-1} s^{-1} is made for the total rate constant representing the reactions of HO· with CrR^{2+}. Less detailed studies show that Br_2^- reacts with $CrCH(CH_3)OC_2H_5^{2+}$ and $CrCH(CH_3)_2^{2+}$ and that R· also reacts with the latter.

Introduction

This paper concerns the cleavage of the carbon–chromium σ bond in complexes[1] of the general family $(H_2O)_5CrR^{2+}$ by free radicals, especially HO·. The hydroxyl radical is notorious for its high reactivity and low selectivity.[2-4] It is thus reasonable to consider alternative reactions such as hydrogen atom abstraction (or other processes) at the aliphatic group R itself, so as to liberate Cr^{2+} (eq 1A), or direct attack at the metal center (eq 1B).



$$CrR^{2+} + HO\cdot \rightarrow Cr^{2+} + (R{-}H) + H_2O \text{ (or ROH)} \quad (1A)$$

$$CrR^{2+} + HO\cdot \rightarrow CrOH^{2+} + R\cdot \quad (1B)$$

Many routes for the synthesis of organochromium complexes utilize reactions of hydrogen peroxide in which HO· is a reactive intermediate, although usually under conditions where reactions such as those shown in eq 1 will not be very important.[5-10] Nonetheless, such reactions may be among those responsible for yields of CrR^{2+} complexes that quite often are lower than theoretical. Furthermore, there is some precedent for suggesting that free radicals may react with complexes containing metal–carbon σ bonds in view of several other examples that now are known.[1,11-14] It is particularly suitable to consider that the indicated reactions might be found for CrR^{2+} complexes because many of them are subject to ready chromium–carbon bond homolysis reactions (eq 2).[1,6,7,15-18]

$$CrR^{2+} \rightleftarrows Cr^{2+} + R\cdot \qquad (2)$$

We report here studies primarily related to the question of whether and how hydroxyl radicals react with selected CrR^{2+} complexes. The numerous chemical reactions involved and their rate constants are summarized for easy reference in Table I.

Results and Interpretation

The homolytic cleavage of chromium–carbon bonds is a thermodynamically unfavorable reaction.[6] The kinetics of the forward reaction (chromium–carbon bond dissociation) can be studied by adding a reagent that reacts rapidly with either Cr^{2+} or R·, thereby drawing the reaction to the right. In the case where H_2O_2 is the reagent used, hydroxyl radicals will be involved. They are produced in the reactions that immediately follow homolysis, these being (a) the reaction of chromium(II) ions and hydrogen peroxide (eq 3)[8,19-21] and (b) in some cases the oxidation of the aliphatic radical by hydrogen peroxide (eq 4 for R = $\cdot C(CH_3)_2OH$).[22-24]

$$Cr^{2+} + H_2O_2 \rightarrow CrOH^{2+} + HO\cdot \qquad (3)$$

$$\cdot C(CH_3)_2OH + H_2O_2 \rightarrow (CH_3)_2CO + H_2O + HO\cdot \qquad (4)$$

The question is whether the hydroxyl radicals will then undergo reactions with the organochromium complexes such as those represented by eq 1. If not, then the decomposition of CrR^{2+} run in the presence of H_2O_2 will be characterized by k_2, the same rate constant as it is when other oxidants are used. On the other hand, if HO· radicals react as in eq 1 to cleave the carbon–chromium bond, then decomposition will be accelerated; indeed, either of the sequences (3) + (1A) or (4) + (1B) constitutes a chain path for the oxidation of CrR^{2+} by hydrogen peroxide.

Preliminary Observations. The results of several experiments can be cited that clearly implicate HO· as being the species responsible for the accelerated decomposition of CrR^{2+} complexes. It is convenient to consider both organochromium complexes such as $CrCH(CH_3)_2^{2+}$ and $CrCH(CH_3)OC_2H_5^{2+}$ (derived from diethyl ether), which are themselves susceptible

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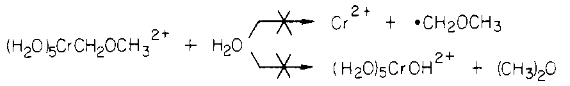
Table I. Summary of Chemical Reactions and Rate Constants at 25 °C, $[H^+] = 0.05–0.10$ M

eq no.	reacn	rate constant[a] k_f $[k_r]$	ref
1	(A) $CrR^{2+} + HO\cdot \rightarrow Cr^{2+} +$ "ROH"	$\sim 8 \times 10^8$ [c]	this work
	(B) $CrR^{2+} + HO\cdot \rightarrow CrOH^{2+} + R\cdot$	$\sim 8 \times 10^8$ [c]	this work
2 $R = \cdot C(CH_3)_2OH$	$CrR^{2+} \rightleftarrows Cr^{2+} + R\cdot$	0.127 $[5.1 \times 10^7]$	6, 28
$R = \cdot CH(CH_3)OC_2H_5$		2.0×10^{-3} $[3.4 \times 10^7]$	6, 28
$R = \cdot CH(CH_3)_2$		1.8×10^{-4} [a] $[8 \times 10^7]$[b]	17, 18
$R = \cdot CH_2OCH_3$		$<10^{-6}$	6
$R = \cdot CH_2Ph$		2.6×10^{-3}	15
3	$Cr^{2+} + H_2O_2 \rightarrow CrOH^{2+} + HO\cdot$	7.0×10^4	8
4 $R = \cdot C(CH_3)_2OH$	$H_2O_2 + R\cdot \rightarrow (CH_3)_2CO + H_2O + HO\cdot$	5×10^5	22
$R = \cdot CH(CH_3)OC_2H_5$	$H_2O_2 + R\cdot \rightarrow C_2H_5OH + CH_3CHO + HO\cdot$	5.5×10^4	23
$R = \cdot CH(CH_3)_2$	$H_2O_2 + R\cdot \rightarrow ROH + HO\cdot$	(4.6×10^4)[b]	24
$R = \cdot CH_2OCH_3$	$H_2O_2 + R\cdot \rightarrow CH_3OH + HCHO + HO\cdot$		
5	$2R\cdot \rightarrow R_2$ $(\rightarrow RH + (R\text{-}H))$	$\sim(1–2) \times 10^9$	2, 25
6	$Cr^{2+} + HO\cdot \rightarrow CrOH^{2+}$	4.8×10^9	21, 26
7	$H_2O_2 + HO\cdot \rightarrow H_2O + HO_2\cdot$	4.5×10^7	4, 27

[a] Units M^{-1} s^{-1} except k_{2f}, s^{-1}. [b] The value given is for the closely related c-C_5H_9. [c] $R = CH(CH_3)OC_2H_5$.

to homolytic decomposition as in eq 2, and another such as $CrCH_2OCH_3^{2+}$ (derived from dimethyl ether), which is kinetically stable for long periods of time under all the reaction conditions considered.

$CrCH_2OCH_3^{2+}$. Anaerobically maintained solutions of this complex are kinetically stable for hours or longer toward decomposition by either homolysis or acidolysis reactions:



Despite that, a portion of the organochromium complex is lost "instantaneously" when a solution is treated first with Cr^{2+} and then with a comparable quantity of H_2O_2. The phenomenon can be repeated again and again. When displayed by the stripchart recorder of a spectrophotometer with the wavelength set at 385 nm (an absorption maximum of $CrCH_2OCH_3^{2+}$, $\epsilon = 404$ M^{-1} cm^{-1}), this gives rise to a staircaselike drop of absorbance as each increment of Cr^{2+} or H_2O_2 is added.

That this experiment does not lead to complete consumption of $CrCH_2OCH_3^{2+}$ in a single injection implies that certain fairly efficient termination reactions occur.[24] These include (see Table I) self-reaction between aliphatic radicals (eq 5)[2,25] and the reaction of hydroxyl radical with Cr^{2+} (eq 6)[21,26] and with H_2O_2 (eq 7),[4,27] as well as the recombination reaction between R· and Cr^{2+} (reverse of eq 2).[18,28]

$$2R\cdot \rightarrow R_2 \text{ (and } RH + (R\text{–}H)) \tag{5}$$

$$Cr^{2+} + HO\cdot \rightarrow CrOH^{2+} \tag{6}$$

$$H_2O_2 + HO\cdot \rightarrow H_2O + HO_2\cdot \tag{7}$$

When the same injections, or series of injections, are made into solutions of $CrCH_2OCH_3^{2+}$ containing *tert*-butyl alcohol (0.1–1 M), there is recorded no absorbance decrease signaling the partial decay of the organochromium complex. Instead, the absorbance increases slightly each time, to a stable value, the increase being simply that from the overall formation of Cr^{3+} as in reaction 3. The reactions of hydroxyl radicals with $CrCH_2OCH_3^{2+}$ are prevented completely by virtue of the very rapid scavenging of HO· by the alcohol (eq 8; $k_8 = 4.3 \times 10^8$

$$HO\cdot + (CH_3)_3COH \rightarrow H_2O + \cdot CH_2C(CH_3)_2OH \tag{8}$$

M^{-1} s^{-1}).[29] The aliphatic radical so formed will, under these circumstances, most likely react with Cr^{2+}, but the resulting organochromium complex has a β-OH group and so decomposes within the mixing time (eq 9).[28]

$$Cr^{2+} + \cdot CH_2C(CH_3)_2OH \rightarrow CrCH_2C(CH_3)_2OH^{2+} \tag{9A}$$

$$CrCH_2C(CH_3)_2OH^{2+} + H^+ \rightarrow Cr^{3+} + (CH_3)_2CCH_2 + H_2O \qquad (9B)^{28b}$$

If a solution of $CrCH_2OCH_3^{2+}$ (10^{-4}–10^{-3} M; again, as always, maintained in the strict exclusion of oxygen) is treated with H_2O_2 alone (10^{-3}–10^{-2} M), decomposition occurs gradually. Over some 10–30 min, an appreciable quantity (10–50%) of the organochromium complex is lost, but the rate is not reproducible. The decomposition is not simply homolytic cleavage of $CrCH_2OCH_3^{2+}$ being drawn to completion, however, since oxidizing agents other than H_2O_2 leave $[CrCH_2OCH_3^{2+}]$ essentially unchanged (<0.2% decomposition) over the same period. Moreover, addition of *tert*-butyl alcohol virtually halts the decomposition, as does addition of a reagent such as $Co(NH_3)_5Cl^{2+}$, which prevents the potential chain from being sustained efficiently because of its reactions with Cr^{2+} (eq 10, $k_{10} = 2.6 \times 10^6$ M^{-1} s^{-1})[30] and with $\cdot CH_2OCH_3$ (eq 11, $k_{11} \approx 1.4 \times 10^7$ M^{-1} s^{-1}).[31,32]

$$Cr^{2+} + Co(NH_3)_5Cl^{2+} \xrightarrow{+5H^+} CrCl^{2+} + Co^{2+} + 5NH_4^+ \tag{10}$$

$$\cdot CH_2OCH_3 + Co(NH_3)_5Cl^{2+} \xrightarrow{+H_2O,\ +4H^+} CH_3OH + HCHO + Co^{2+} + Cl^- + 5NH_4^+ \tag{11}$$

These observations are easily attributed to the reactions shown earlier, with the steps critical for sustaining the loss of $CrCH_2OCH_3^{2+}$ over some period of time being the cyclically recurring pairs such as (3) + (1A) and/or (4) + (1B). The poor reproducibility of the phenomenon probably indicates only that the initiating species (which may be Cr^{2+}, HO·, or $\cdot CH_2OCH_3$, any of which will serve to start the chain process) are present at variable concentration levels in solution or that these species are initially made from very minor side reactions. Consistent with the chemical equations written (eq 1 and 4),

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(29) Walling, C.; Kato, S. *J. Am. Chem. Soc.* **1971**, *93*, 4275.

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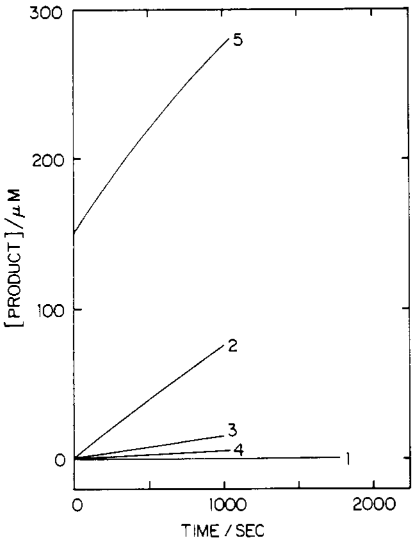

Figure 1. Initial rate of decomposition of anaerobic solutions of $CrCH_2OCH_3^{2+}$, 100 mM, under various conditions: (1) by itself; (2) with 0.010 M H_2O_2; (3) with 0.010 M H_2O_2 + 50 μM $Co(NH_3)_5Br^{2+}$; (4) with 0.010 M H_2O_2 + 1 M *tert*-butyl alcohol + 2.0 mM Cr^{2+}; (5) with 0.010 M H_2O_2 + 2.0 mM Cr^{2+}. The notation "product" refers to the composite loss of $CrCH_2OCH_3^{2+}$ by all reactions occurring under the given conditions. The unhindered reaction of HO· with $CrCH_2OCH_3^{2+}$ is indicated by the initial burst of decomposition in experiment 5 as well as by the accelerated ongoing loss (see text).

Cr^{3+} (~100%) and HCHO (86%) are the final products detected.

The results of several such experiments are depicted in Figure 1. This shows not only decomposition reactions of $CrCH_2OCH_3^{2+}$ that are proceeding successfully in the presence of H_2O_2 but also those that have been halted by addition of *tert*-butyl alcohol or $Co(NH_3)_5Cl^{2+}$.

$CrCH(CH_3)OC_2H_5^{2+}$. This complex is subject to only a very slow acidolysis reaction ($k_A \approx 10^{-6.2}$ s^{-1} at 0.1 M H^+).[5] Homolysis occurs readily,[6] however ($k_H = 2 \times 10^{-3}$ s^{-1}),[6] and the reactions of HO· are seen on top of the homolytic reaction since both require oxidizing conditions. We review first the homolytic phenomenon by itself: When a reagent such as $Co(NH_3)_5X^{2+}$ (X = F, Cl, Br) is added, decomposition proceeds smoothly. The reaction rate under such conditions follows a first-order kinetic equation

$$-d[CrCH(CH_3)OC_2H_5^{2+}]/dt = k_{12}[CrCH(CH_3)OC_2H_5^{2+}] \quad (12)$$

where $k_{12} = k_A + k_H$, but for this particular system $k_H >> k_A$, so that $k_{12} \approx k_H$. The rate is independent of the identity and of the concentration of $Co(NH_3)_5X^{2+}$ or other oxidant added.[6] When H_2O_2 is the oxidant employed, however, irregular kinetic profiles are found unless *tert*-butyl alcohol or $Co(NH_3)_5X^{2+}$ is also added. That implicates the involvement of HO·, a species such as Cr^{2+} or R· that generate HO·, in the decay scheme.

Different results were obtained from experiments on the decomposition of $CrCH(CH_3)OC_2H_5^{2+}$ in solutions containing hydrogen peroxide but lacking the radical scavengers mentioned. The decomposition rate was considerably higher (roughly, by factors of 2–10) than the rate of homolysis alone, such that the concentration of the CrR^{2+} complex declined more sharply during each run than a first-order dependence would have done. The kinetic data during any such run do not conform to a simple expression because (a) the rates of the chain components do not exceed that of the initiation step by an amount so great that the latter can be neglected, (b) there are competing propagating steps (eq 1), which continue parallel chain paths propagated by Cr^{2+} (eq 3) and by R· (eq 4), qualitative evidence for which will be given, and (c) under different conditions the form of the kinetic equation will change, even during a single run, as different termination steps (eq 5–7) assume different degrees of relative importance. Rather than attempting to fit the data to a multiparameter relation, we chose to express the results in a semiquantative manner in terms of apparent first-order rate constants for one or more particular segments of the run. The ratios of such approximate k_{obsd} values for the earliest stages of reaction to the authentic first-order rate constant for homolysis, k_H of eq 2 and 12, are designated *R*.

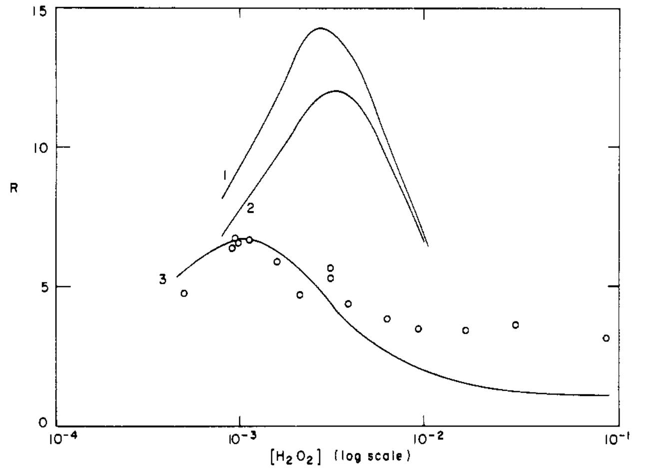

Figure 2. Rate of decomposition of $CrCH(CH_3)OC_2H_5^{2+}$ enhanced, as compared to its homolysis rate, by an amount dependent on $[H_2O_2]$ ($R = k_{dec}/k_H$). The solid curves show calculated values based on the model given in Table I for three combinations of rate constants, $10^{-9}k$/M^{-1} s^{-1} values for k_{1A}, k_{1B}, and $2k_5$ being as follows: (1) 4, 4, and 1; (2) 4, 4, and 2; (3) 0.8, 0.8, and 1. Other rate constants are as in Table I.

Values of *R* typically fall in the range 2–7. They do vary regularly with the concentration of hydrogen peroxide, as expected from the mechanism shown, because the steady-state concentrations and the relative importance of different termination steps vary with $[H_2O_2]$. Our approach to the approximate kinetic analysis is to simulate values of the initial reaction rate with use of the full steady-state solution to the set of differential equations implied by the elementary reactions shown in Table I. Except for k_{1A} and k_{1B} (for which various choices were attempted), all of the rate constants are known independently. This affords calculated values of *R* that can then be compared with the experimental data. The procedure is moderately sensitive to variation of k_1, although a further assumption was made, namely that $k_{1A} \approx k_{1B}$. Evidence that both chain-propagating steps are important will be given, but it is clearly a rough approximation to equate them. In any event, with that approximation, a reasonably good fit (Figure 2) is obtained by taking $k_{1A} \approx k_{1B} \approx 8 \times 10^8$ M^{-1} s^{-1}, with the radical–radical self-reaction rate constant taken[33] as $2k_5 = 1 \times 10^9$ M^{-1} s^{-1}. Agreement is poorest at high $[H_2O_2]$, which is also the condition under which the reaction of eq 7 becomes the major termination step. In that event appreciable quantities of the hydroperoxyl radicals are formed. It is assumed HO_2 does not enter the chain sequence itself, but its rapid disproportionation reaction (eq 13, $k = 7.6 \times 10^5$ M^{-1}

$$2HO_2\cdot \rightarrow O_2 + H_2O_2 \quad (13)$$

$$Cr^{2+} + O_2 \rightarrow CrOO^{2+} \quad (14)$$

s^{-1})[34] produces oxygen, which will intervene, most likely by

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[33] The value for R = $\cdot CH(CH_3)OC_2H_5$ has not been determined, but the estimate shown is within the narrow range found for similar aliphatic radicals.[2,25]

reaction with Cr^{2+} (eq 14, $k = 1.6 \times 10^8$ M^{-1} s^{-1}).[35] Such reactions were not brought into the modeling.

Experiments were done to determine the stoichiometry of the reaction, expressed as S, the change in concentration of H_2O_2 per unit change in the concentration of $CrCH(CH_3)OC_2H_5^{2+}$, or $S = \Delta[H_2O_2]/\Delta[CrCH(CH_3)OC_2H_5^{2+}]$. Because this required an analysis of the final concentration of hydrogen peroxide, giving $\Delta[H_2O_2]$ by difference, the determinations were limited to runs at $[H_2O_2]_0/[CrR^{2+}]_0 \lesssim 50$. The experimental values were $S = 1.7 \pm 0.3$ over a range of 2.5–50 in initial concentration ratio; the scatter was appreciable but not systematic with concentration. In comparison, values of S would be 3.0 for homolysis alone[36] or 1.0 were the kinetic chains very long. An approximate value of S calculated by using the rate constants found from the kinetic simulation ($k_{1A} \approx k_{1B} \approx 8 \times 10^8$ M^{-1} s^{-1}) is $S = 1.6$, an average of values that increased (1.2 to 2.2) throughout the course of a simulated run as the ratio of $[H_2O_2]_t/[CrR^{2+}]_t$ increased.

$CrCH(CH_3)_2^{2+}$. The 2-propyl complex slowly decomposes by parallel acidolysis and homolysis reactions at a rate given by

$$-d[CrCH(CH_3)_2^{2+}]/dt = (k_A + k_H)[CrCH(CH_3)_2^{2+}] \tag{15}$$

with $k_A = 1.05 \times 10^{-4}$ s^{-1} and $k_H = 1.78 \times 10^{-4}$ s^{-1} at 25.0 °C.[17] Addition of hydrogen peroxide caused an increase in the rate constant for decomposition to $k_{obsd} = 9 \times 10^{-3}$ s^{-1}, much greater than $k_A + k_H$ yet independent of $[H_2O_2]$ in the range $(3–30) \times 10^{-3}$ M. The implication again is that HO· reacts with the 2-propyl complex in a chain sequence, so as to sustain a rate in excess of homolysis.

A second set of experiments was performed in which solutions of $CrCH(CH_3)_2^{2+}$ containing Cr^{2+} were treated with H_2O_2 and then with alternating injections of Cr^{2+} and H_2O_2. Each addition of Cr^{2+} and H_2O_2 causes a sudden loss of a substantial quantity of the organochromium ion, otherwise stable to decomposition during this brief time interval. For example, a solution having $[CrCH(CH_3)_2^{2+}]_0 = 7.4 \times 10^{-4}$ M and $[Cr^{2+}]_0 = 2 \times 10^{-3}$ M when treated with 1×10^{-3} M H_2O_2 undergoes a sudden drop of 1.1×10^{-4} M (or 15%) in $[CrCH(CH_3)_2^{2+}]$. Further addition of Cr^{2+} followed by H_2O_2 causes about half that drop in $[CrCH(CH_3)_2^{2+}]$ and subsequent additions even less. That is consistent with the growing importance of termination reactions, particularly the reaction of HO· with Cr^{2+} (eq 6).

Reaction of Cr^{2+} and H_2O_2 in the Presence of CrR^{2+}. The sequence of events represented by eq 3 and 6 represents the "normal" reaction between Cr^{2+} and H_2O_2, resulting in the net reaction $2Cr^{2+} + H_2O_2 + 2H^+ = 2Cr^{3+} + 2H_2O$. The most precise kinetic evaluation and the validation of the mechanism were based on the formation of equimolar concentrations of Cr^{3+} and CrR^{2+} in reactions run in solutions containing RH.[8] In such circumstances the hydroxyl radicals formed in eq 3 lead to aliphatic radicals (eq 16), rather than

$$HO\cdot + RH \rightarrow H_2O + R\cdot \tag{16}$$

to oxidation of Cr^{2+} via eq 6. The net reaction then becomes $2Cr^{2+} + H_2O_2 + H^+ + RH = Cr^{3+} + CrR^{2+} + 2H_2O$.

If HO· does react with CrR^{2+}, as is claimed in eq 1, one must ask the following question: How can CrR^{2+} be produced from the "modified Fenton's reagent" combination, $Cr^{2+} + H_2O_2 + RH$? The answer lies simply in the relative concentrations and rate constants; under conditions used both for synthesis of CrR^{2+} complexes and for the precise measurement of k_3, the relative concentrations were always maintained such that $k_{16}[RH] >> k_1[CrR^{2+}]$.

Table II. Kinetic Data[a] Illustrating the Effect of Added $(H_2O)_5CrR^{2+}$ on the Kinetics of the Reaction between Cr^{2+} and H_2O_2

init concn/mol dm^{-3}			
$10^3 \times [H_2O_2]_0$	$10^3 \times [CrR^{2+}]_0$	k_{obsd}/s^{-1} [b]	$10^{-4}k_{17}$/M^{-1} s^{-1} [c]
1.01	0.50[d]	37	3.7
1.01	1.0[d]	33	3.3
2.03	1.0[d]	69	3.4
1.01	1.0[e]	34	3.4
0.1–5.0	0		14.1[f]

[a] Conditions: 25.0 °C, 0.30 M H^+, $\mu = 1.00$ M, $[Cr^{2+}]_0 \leqslant 1 \times 10^{-4}$ M. [b] $k_{obsd} = -d \ln [Cr^{2+}]/dt$. [c] $k_{17} = k_{obsd}/[H_2O_2]_0$. [d] $R = CH(CH_3)_2$. [e] $R = CH_2OCH_3$. [f] For reaction in the absence of added CrR^{2+}; this value represents $2k_3$.

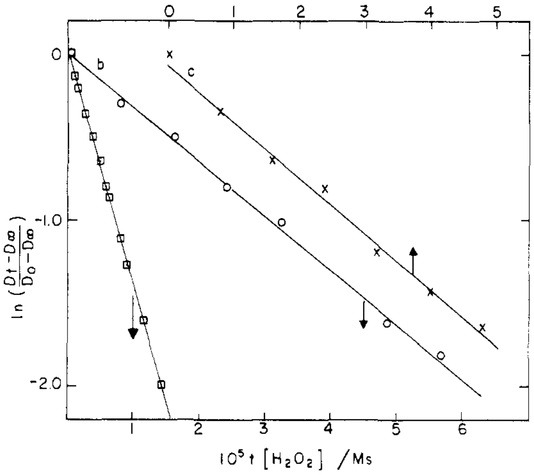

Figure 3. First-order kinetic plots illustrating the effect of added CrR^{2+} on the rate of oxidation of Cr^{2+} ($\leq 10^{-4}$ M) by an excess of H_2O_2 (D = absorbance; plots were normalized to the same hydrogen peroxide concentration). The experiments are as follows: (a) $[CrR^{2+}]_0 = 0$, 1.0 M $(CH_3)_2O$, and 5.3×10^{-4} M H_2O_2, *D increases* as CrR^{2+} forms; (b) 1.0×10^{-3} M $CrCH(CH_3)_2^{2+}$, 2.03×10^{-3} M H_2O_2; (c) 1.0×10^{-3} M $CrCH_2OCH_3^{2+}$, 1.01×10^{-3} M H_2O_2, this curve offset along the abscissa to separate it from (b). In (b) and (c) *D decreases* as CrR^{2+} reacts with HO·. The rate constant ratios for (a) as compared to (b) and (c) are 4.1, as compared to the theoretical 4.00 (see text).

On the other hand, the analysis given above suggested additional experiments on the reaction of Cr^{2+} and H_2O_2 in solutions containing a relatively kinetically stable organochromium cation ($CrCH_2OCH_3^{2+}$ and $CrCH(CH_3)_2^{2+}$ were used) but lacking any organic solute RH. The mixing of solutions of Cr^{2+} containing CrR^{2+} with H_2O_2, both free of added solute RH, gave a timed *decrease* in absorbance at 400 nm (near λ_{max} for the CrR^{2+} complexes). The kinetic traces followed first-order kinetics and, in a series of experiments with varying $[H_2O_2]_0$, the excess reagent, showed a first-order dependence on $[H_2O_2]$. The rate of reaction (written, as it must be, in terms of the limiting reagent) is

$$\text{rate} = -d[Cr^{2+}]/dt = k_{17}[Cr^{2+}][H_2O_2] \tag{17}$$

The value of k_{17} is $(3.4 \pm 0.3) \times 10^4$ M^{-1} s^{-1}, independent of $[Cr^{2+}]_0$ and of the concentration *and identity* of the CrR^{2+} complex used as shown in Table II and illustrated in Figure 3.

The contrast with eq 3 is striking. The rate equations have the same form, yet the value of k_{17} is 4.1 ± 0.5 times smaller than that measured under the same conditions but in the absence of added CrR^{2+} (in the latter circumstances k_{obsd} =

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(34) Bielski, B. H. J. *Photochem. Photobiol.* **1978**, *28*, 645.

(35) Sellers, R. M.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6145.

(36) The calculation of S = 3.0 for homolysis alone applies only in the limiting case where O_2 produced in eq 13 consumes negligible amounts of Cr^{2+} and R·, which would be realized only at very high $[H_2O_2]/[Cr^{2+}]$ ratios ($>10^4$).

$2k_3 = 1.41 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$). This factor of 4 is explained by the reactions written before; in particular, if hydroxyl radicals react largely with CrR^{2+} (eq 1) rather than with Cr^{2+} (eq 6) at these relatively high concentrations, then the sequence of events (eq 3, 1A, 1B, 5) leads to a process (eq 18) having an

$$Cr^{2+} + 2H_2O_2 + 2CrR^{2+} + 3H^+ = 3Cr^{3+} + ROH + {}^1/_2R_2 + 3H_2O \quad (18)$$

overall stoichiometry Cr^{2+}:H_2O_2 = 1:2. The difference is, in effect, a factor of exactly 4 in the rate of disappearance of Cr^{2+}, the limiting reagent.

This interpretation is consistent with the value of k_6[21,26] and the estimates of k_1. It is based on $k_{1A} \cong k_{1B}$, a result also obtained earlier. The steady-state concentrations under the conditions prevailing during the kinetic experiments given in Table II are such that the primary fate of the aliphatic radical R· is to undergo self-reaction by eq 5. That is to say, the chain reaction is negligible under these circumstances.

Catalyzed Decomposition of H_2O_2. In several experiments involving $CrCH(CH_3)OC_2H_5^{2+}$ and H_2O_2, 2.0 M 2-propanol was used as a scavenger for HO· radicals. Despite a substantial excess of H_2O_2 over CrR^{2+} (2.9×10^{-3} and 7×10^{-4} M), the decomposition of CrR^{2+} (a first-order reaction with $k = 2.3 \times 10^{-3}\ \mathrm{s^{-1}}$, within 10% of k_H) stopped well before completion. This was because $[H_2O_2]$ had diminished nearly to zero during the partial decomposition of CrR^{2+}. With addition of more H_2O_2, the reaction resumed its course ($k = 2.3 \times 10^{-3}\ \mathrm{s^{-1}}$). These observations suggest that the catalytic decomposition of H_2O_2 is initiated by organochromium homolysis (eq 2) and HO· generation (eq 3). The reactions that, if they occur as a pair of chain propagation steps, will account for the catalytic process are two that are independently known

$$HO\cdot + (CH_3)_2CHOH \rightarrow H_2O + \cdot C(CH_3)_2OH \quad (19)$$

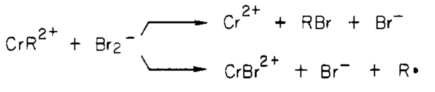
$$H_2O_2 + \cdot C(CH_3)_2OH \rightarrow (CH_3)_2CO + H_2O + HO\cdot \quad (4)$$

with $k_{19} = 2.2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$[4] with $k_4 = 5.5 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$.[22]

Reactions of Br_2^- and R· with CrR^{2+}. The decomposition rate of $CrCH(CH_3)OC_2H_5^{2+}$ in the presence of Br^- (0.01–0.40 M) and H_2O_2 is much faster than with H_2O_2 alone. For example, $k_{obsd} = 62.4 \times 10^{-3}\ \mathrm{s^{-1}}$ at 0.40 M Br^- and 2.9×10^{-3} M H_2O_2, compared to $k_H = 2.0 \times 10^{-3}\ \mathrm{s^{-1}}$ and to $k_{obsd} \approx 7 \times 10^{-3}$–$3 \times 10^{-3}\ \mathrm{s^{-1}}$ with H_2O_2 alone (the latter, of course, refers to conditions where pseudo-first-order kinetics are not observed). The accelerated decomposition of CrR^{2+} is due to reaction with Br_2^-. The latter species is formed by reaction of HO· and Br^- (eq 20, $k_{20A} \approx 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$).[4] The reaction of CrR^{2+} with Br_2^- may, like that with HO·, take either of the paths

$$Br^- + HO\cdot \rightarrow Br\cdot + OH^- \quad (20A)$$

$$Br^- + Br\cdot \rightleftharpoons Br_2^- \quad (20B)$$



(21A)

(21B)

but the issue cannot be resolved without further study. Addition of 1 M *tert*-butyl alcohol returns the rate to the value found without Br^- present.

Other observations suggested that CrR^{2+} reacts with aliphatic free radicals R′·, the likely reaction being that represented by eq 22. Addition of *either* Cu^{2+} or *tert*-butyl alcohol reduces the rate of reaction of $CrCH(CH_3)_2^{2+}$ with H_2O_2 but does not return it to the value expected for homolysis and acidolysis alone (eq 15, $k_A + k_H = (2.9 \pm 0.1) \times 10^{-4}\ \mathrm{s^{-1}}$). On the other hand, the two reagents together (0.011 M Cu^{2+} and 1.0 M *tert*-butyl alcohol) do, giving $k_{obsd} = (3.5 \pm 0.3) \times 10^{-4}\ \mathrm{s^{-1}}$. The combined effects of *tert*-butyl alcohol (a HO· scavenger) and Cu^{2+} (a scavenger for alkyl radicals, $k_{23} \approx 4 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$),[17] but the insufficiency of either by itself, implicate both reaction 1 and reaction 22 in the decay scheme under these circumstances.

$$CrR^{2+} + R'\cdot \rightarrow RR' + Cr^{2+} \quad (22)$$

$$Cu^{2+} + \cdot CH(CH_3)_2 \xrightarrow{H_2O} Cu^+ + (CH_3)_2CHOH + H^+ \quad (23)$$

Conclusions

Several lines of experimental evidence have been used to demonstrate that hydroxyl radicals react bimolecularly with organopentaaquochromium(2+) ions. The character of these reactions is such that they lead to cleavage of the chromium–carbon bond. In addition, they generate reactive intermediates that are able to sustain the chain decomposition of the CrR^{2+} complexes, albeit in processes of relatively short chain length.

Various qualitative and semiquantitative results were used to suggest that two modes of cleavage occur and that two chain-carrying intermediates (Cr^{2+} and R·) are involved, although a definitive proof of the two independent reactions (eq 1A and 1B) was not obtained. On the basis of the rate enhancement over the homolysis rate and on the known rates of the chain-terminating reactions, estimates could be made of rate constants. These calculations support the conclusion that both Cr^{2+} and R· are intermediates of comparable importance, and they also confirm that the magnitude of the effects observed require very efficient reactions between HO· and CrR^{2+}, $k_{1A} \approx k_{1B} \approx 8 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$.

It was also found that Br_2^- and aliphatic radicals R· react with CrR^{2+}, again leading to cleavage of the chromium–carbon bond.

Experimental Section

The various $(H_2O)_5CrR^{2+}$ complexes were prepared as before[5,6,17] and were purified by ion-exchange chromatography on Sephadex C-25 resin. Reactions were monitored by UV–visible spectrophotometry. Inorganic products were identified spectrophotometrically, often following ion-exchange separations. Formaldehyde was determined spectrophotometrically on the basis of its reaction with chromotropic acid.[16a,37] The excess of H_2O_2 was determined by reaction with I^- to form I_3^-, which was determined spectrophotometrically. All the experiments were done under strictly air-free conditions, with use of Cr^{2+}-scrubbed nitrogen or argon and syringe–rubber septum techniques. All reactions were conducted in strongly acidic solution; 0.05–0.1 M perchloric acid was used except for the experiments of Table II, where 0.3 M perchloric acid was used. Ionic strength was controlled in some cases at 0.1–1.0 M, not so much for the purposes of these reactions, but for a comparison with acidolysis and homolysis reactions of given CrR^{2+} complexes determined under particular conditions.

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Registry No. $(H_2O)_5CrCH_2OCH_3^{2+}$, 78402-17-2; $(H_2O)_5CrCH(CH_3)OC_2H_5^{2+}$, 32108-97-7; $(H_2O)_5CrCH(CH_3)_2^{2+}$, 60764-48-9; HO·, 3352-57-6; H_2O_2, 7722-84-1; Br_2^-, 12595-70-9; $(H_2O)_5CrC(CH_3)_2OH^{2+}$, 32108-93-3; $(H_2O)_5CrCH_2Ph^{2+}$, 34788-74-4.

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