Kinetics and Mechanism of the Formation of Alkylcobalt(chelate) Complexes from Organic Peroxides and Cobalt(II)[1]

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Abstract: The reactions of some cobalt(II) macrocyclic complexes with some *tert*-alkyl hydroperoxides occur with a 2:1 (cobalt:peroxide) stoichiometry and lead to the formation of alkyl-cobalt products. Kinetic studies carried out at $\mu = 0.10$ M ($HClO_4$-$LiClO_4$) in 1:1 (v/v) *tert*-butyl alcohol-water media showed the reaction to be first order in both cobalt(II) complex and hydroperoxide. The bimolecular rate constants varied over the range 6.4-409 $M^{-1}\ s^{-1}$ with the reactivity order being $Co(dmgH)_2 > Co(dpnH)^+ > B_{12r} \approx Co(tim)^{2+} > Co(Me_6[14]4,11\text{-}dieneN_4) > Co(Me_6[14]aneN_4)$. The reactions of $Co(tim)^{2+}$ with a variety of peroxides showed little effect on varying the alkyl group of the hydroperoxide, but were substantially inhibited by substituting groups OR for the hydroxyl group of the hydroperoxides. Comparisons of these reactions with the analogous chromium(II) reactions will be made.

Reactions useful for formation of cobalt-carbon σ bonds in macrocyclic chelate complexes such as vitamin B_{12} and related model complexes have recently been reviewed.[2,3] One general method consists of the coupling reaction of an appropriately generated carbon-centered radical R· with a Co(II) chelate, thereby forming an organocobalt(III) complex:

$$R\cdot + (Co^{II}) \rightarrow R\text{-}(Co^{III}) \qquad (1)$$

As far as we are aware, no reports have appeared in which organic hydroperoxides (and related functions) have been used as sources of organic radicals for preparation of organocobalt complexes, despite the known utility of this method for organochromium complexes of the family $(H_2O)_5CrR^{2+}$.[4-8]

The idealized reaction scheme consists of reactions 2 and 3

$$RC(CH_3)_2OOH + (Co^{II}) \xrightarrow{k_1} RC(CH_3)_2O\cdot + (Co^{III})OH \qquad (2)$$

$$RC(CH_3)_2O\cdot \xrightarrow{\text{fast}} (CH_3)_2CO + R\cdot \qquad (3)$$

followed by 1; in practice, however, certain other reactions must be considered as well. This work utilizes a selected group of cobalt(II) complexes[9] of tetradentate N_4 macrocyclic (and pseudomacrocyclic) ligands, including vitamin B_{12r}, as shown in Figure 1. For most of the complexes studied the simple alkyl derivatives have been prepared by alternative routes, most commonly the nucleophilic displacement reaction of $(Co^I)^-$ and RX (eq 4).[10]

$$(Co^I)^- + RX \rightarrow R(Co) + X^- \qquad (4)$$

The latter method, while preferable, is widely but not universally applicable. Failures result from at least two circumstances, however: (a) inability to form the cobalt(I) complex in cases such as $Co(Me_6[14]dieneN_4)^+$ and $Co(Me_6[14]aneN_4)^+$, even with powerful reductants such as BH_4^- or Na/Hg, and (b) reaction rates of the alkyl halide and a cobalt(I) nucleophile such as $Co(tim)^+$ which reacts with most RX's more slowly than it undergoes internal reductive decomposition. The use of reaction 1 promises to alleviate both problems, although its success requires rapid and convenient synthetic quantities of R· under solvent conditions in which R· reacts sufficiently selectively to give good yields of the desired RCo(III) product. A previous approach to the problem for the case of R = CH_3 has been realized by Roche and Endicott,[11] who generated $CH_3\cdot$ by photolysis of the acetate complex $(NH_3)_5CoO_2CCH_3^{2+}$, and by Goedkin and co-workers[12] based on reactions of organic hydrazines.

This work emphasizes the verification of the $R(Co^{III})$ products, their isolation in some instances, and the stoichiometry, kinetics, and mechanism of the reactions leading to their formation.

Experimental Section

Materials. The following complexes (refer to Figure 1) were prepared by literature methods: $Co(dmgH)_2(H_2O)_2$,[13] $[Co(dpnH)(H_2O)_2](ClO_4)_2$,[14] $[Co(\textit{meso}\text{-}Me_6[14]4,11\text{-}dieneN_4)](ClO_4)_2$,[15] and $[Co(tim)(H_2O)_2](ClO_4)_3$.[16]

The complex $[Co(\textit{meso}\text{-}Me_6[14]aneN_4)](ClO_4)_2$ was prepared from $[Ni(Me_6[14]4,11\text{-}dieneN_4)](ClO_4)_2$[17] first by reduction of the ligand with $NaBH_4$ and separation of the reduced meso complex as described by Warner and Busch,[18] followed by liberation of the free ligand,[19] and complexation with cobalt(II).[14] Anal. Calcd for $CoC_{16}H_{36}N_4Cl_2O_8$: Co, 10.87; C, 35.44; H, 6.69: N, 10.33. Found: Co, 10.82; C, 35.26; H, 6.76: N, 10.24.

Aquocobalamin was commercially available (Sigma Chemical), and was converted to the Co(II) complex vitamin B_{12r} by reduction with amalgamated zinc in 0.1 M aqueous perchloric acid. For use in reaction studies, the cobalt(II) complexes[9] $Co(dpnH)^+$ and $Co(tim)^{2+}$ were generated in solution by reduction of the corresponding diaquo-Co(III) complexes with a deficiency of Cr_{aq}^{2+}. Alternatively, solid samples of the latter complex were prepared utilizing a variant of the published method[20] for $[Co(tim)Br_2]Br$. Under a stream of nitrogen 1,3-diaminopropane (30 g, 0.20 mol) was dissolved in methanol (700 cm^3), followed by the dropwise addition of 70% $HClO_4$ (34 cm^3, 0.20 mol) over 20-30 min. Biacetyl (2,3-butanedione, 34.4 g, 0.400 mol) was added, followed ***immediately*** by $Co(OAc)_2\cdot 4H_2O$ (49.8 g, 0.200 mol), and the solution stirred under N_2 for 4 h. At this time 20 cm^3 of deoxygenated water and 50 cm^3 of 70% $HClO_4$ were added, following which methanol was partially removed by passing N_2 through the solution for an additional 5 h. The precipitated complex was filtered under N_2, washed with ether and dried under vacuum; yield ca. 20 g of $[Co(tim)(H_2O)_2](ClO_4)_2$ (40%). Anal. Calcd for $CoC_{14}H_{28}N_4Cl_2O_{10}$: Co, 10.87; C, 31.00; H, 5.21; N, 10.33. Found: Co, 10.77; C, 31.17, H, 5.19; N, 10.14.

Some organic peroxides were commercially available (*tert*-butyl hydroperoxide and *tert*-butyl peroxybenzoate); others were prepared by literature methods[6] (ethyl-*tert*-butyl peroxide,[21] *tert*-amyl hydroperoxide,[22] 2,4,4-trimethylpentyl 2-hydroperoxide,[22] 2-methyl-1-phenylpropyl 2-hydroperoxide,[22] perbenzoic acid,[23] and cumene hydroperoxide).[24] Stock solutions were prepared fresh as needed by dissolving the neat peroxide in a known volume of solvent (1:1 *tert*-butyl alcohol-H_2O), and were analyzed by standard methods.[25]

Distilled *tert*-butyl alcohol was used to make up solutions for all of the experiments, many of which were performed in a solvent mixture consisting of 1:1 (v/v) *tert*-butyl alcohol-water. Chromium(II) perchlorate solutions were prepared by reduction of $Cr(ClO_4)_3$ with

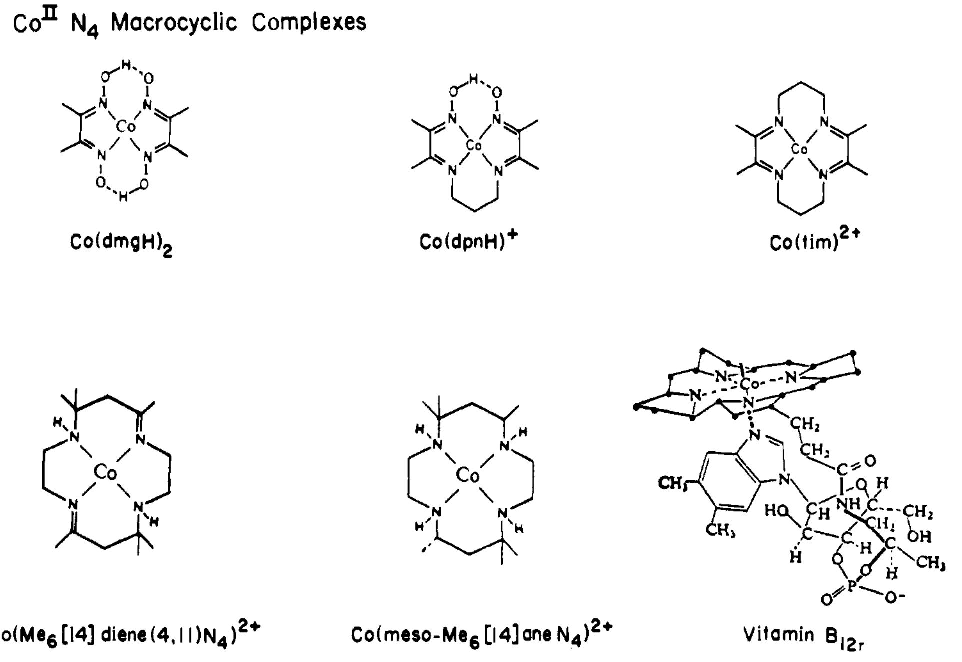


Figure 1. Structures of the macrocyclic cobalt complexes.

amalgamated zinc in the desired solvent, water or aqueous *tert*-butyl alcohol. Hydrated lithium perchlorate was recrystallized twice from water.

Kinetic Studies. Spectrophotometric methods, conventional or stopped-flow as appropriate, were used for rate determinations, with Cary 14, Durrum D-110, and Canterbury SF-3A instruments. These studies were carried out at 0.10 M ionic strength ($\mathrm{HClO_4}$-$\mathrm{LiClO_4}$) in 1:1 v/v *tert*-butyl alcohol-water, at 25.0 °C except as noted. This solvent mixture provides a good solubility range for the peroxides, yet apparently does not readily react with radical intermediates (other than OH·). The reactions for kinetic purposes employed a pseudo-first-order excess of peroxide over Co(II), and were followed by recording the decrease in absorbance of the Co(II) complexes[26] with occasional determinations at other wavelengths. Slight modification of the conditions was necessary for Co(dmgH)$_2$ and Co(dpnH)$^+$, whose decompositions to $\mathrm{Co_{aq}}^{2+}$ in aquecus perchloric acid proceed too rapidly under the acidic reaction conditions otherwise employed. In these cases the electrolytes are 0.1 M NaOAc and 0.1 M $\mathrm{LiClO_4}$, respectively; independent determinations with the reaction of Co(tim)$^{2+}$ and *tert*-butyl hydroperoxide showed identical rate constants in 0.1 M solutions of $\mathrm{HClO_4}$, $\mathrm{LiClO_4}$, and NaOAc ($1 < \mathrm{pH} < 9$), suggesting the validity of this change for the other complexes as well.

Product Isolation and Identification. Efforts were made to identify, and in some cases to isolate in solid form, the organocobalt complexes which we anticipated as products. In many cases the absorption spectrum of the reaction solution itself afforded such evidence; to cite one such example, reaction of *tert*-butyl hydroperoxide and Co$^{\mathrm{II}}$(tim)$^{2+}$ in an aqueous medium produced a solution showing the characteristic absorption bands of $\mathrm{CH_3Co(tim)H_2O^{2+}}$ at λ 485 nm (ϵ 2.4 × 10^3) and 420 (1.70 × 10^3). Exposure of such solutions to sunlight for a few minutes resulted in complete loss of these bands and conversion to the characteristic spectrum of the Co(III) complex $\mathrm{Co(tim)(H_2O)_2}^{3+}$. Similar spectral identification of other known organocobalt products was made. The yield of $\mathrm{CH_3Co(tim)}^{2+}$ was accurately determined spectrophotometrically from several reactions of Co(tim)$^{2+}$ and $\mathrm{(CH_3)_3COOH}$ in aqueous solution.

In other instances formation of alkylcobalt complexes was confirmed by thin layer chromatography on cellulose (methylcobalamin) or on silica gel (methyl cobaloxime).

Larger scale reactions of the appropriate Co(II) complex and peroxide, usually in strictly aqueous solution, were used for isolation of the alkyl cobalt products as solid samples: $\mathrm{[CH_3Co(tim)H_2O](BPh_4)_2}$, $\mathrm{[CH_3CH_2Co(tim)H_2O](BPh_4)_2}$, $\mathrm{[(CH_3)_3CCH_2Co(tim)H_2O](BPh_4)_2}$, $\mathrm{[C_6H_5CH_2Co(tim)H_2O](BPh_4)_2}$, $\mathrm{[CH_3Co(Me_6[14]dieneN_4)H_2O](BPh_4)_2}$, $\mathrm{[CH_3Co(Me_6[14]aneN_4)H_2O](BPh_4)_2}$. These compounds and others, especially the higher alkyls, are rather less stable thermally and photochemically than their cobaloxime counterparts. The general preparative method consists of treating the aqueous reaction solution with an acetone solution of $\mathrm{NaBPh_4}$, which precipitates the alkylcobalt complex leaving the other reaction product, $\mathrm{Co^{III}(chel)(H_2O)_2}^{3+}$, in solution. One specific procedure is as follows. A sample of $\mathrm{[Co(Me_6[14]4,11\text{-}dieneN_4)](ClO_4)_2}$ (0.5 g, 1.1 mmol) was dissolved in 100 cm^3 of water and treated with an aqueous solution of *tert*-butyl hydroperoxide (20 cm^3 of 0.05 M). After 30 min an acetone solution of $\mathrm{NaBPh_4}$ (0.3 g, 0.9 mmol) was added, and the solution stirred for an additional 5 min. The solid product was filtered, washed with methanol and with ether, and air dried. The product was recrystallized from acetone by addition of water. The initial reaction was conducted under N$_2$, and all reactions and operations were carried out in the dark owing to the very photosensitive nature of the complex. Anal. Calcd for $\mathrm{[CH_3Co(Me_6[14]4,11\text{-}dieneN_4)H_2O](BPh_4)_2}$: Co, 5.83; C, 77.38, H, 7.47, N, 5.55. Found: Co, 5.72; C, 76.85; H, 7.81; N, 5.88.

Results and Interpretation

Stoichiometry and Products. An idealized reaction stoichiometry can be represented by the summation of reactions 1–3 (eq 5).

$$2(\mathrm{Co^{II}}) + \mathrm{R(CH_3)_2COOH} = \mathrm{R(Co)} + (\mathrm{Co^{III}})\mathrm{OH} + (\mathrm{CH_3})_2\mathrm{CO} \quad (5)$$

The indicated 2:1 stoichiometry of reactants was confirmed directly by spectrophotometric titrations for several of the reactions between Co(II) complexes and hydroperoxides. Data for two typical titrations are shown in Figure 2. In each of these cases the anticipated 2:1 stoichiometry was found.

The reactant ratio does not require the products shown: alternative or competing reactions of radical intermediates can produce different materials yet maintain the 2:1 ratio. Examples of such behavior were found for Cr^{2+} reactions with organic peroxides.[6] The limit of such a process is a reaction lacking any organometallic product, such as eq 6.

$$2(\mathrm{Co}) + \mathrm{R(CH_3)_2COOH} + \mathrm{H_2O} = 2(\mathrm{Co^{III}})\mathrm{OH} + \mathrm{R(CH_3)_2COH} \quad (6a)$$

$$2(\mathrm{Co}) + \mathrm{R(CH_3)_2COOH} + \mathrm{H_2O} = 2(\mathrm{Co^{III}})\mathrm{OH} + (\mathrm{CH_3})_2\mathrm{COH} + \mathrm{RH} \quad (6b)$$

One important mode of reaction to be considered in this

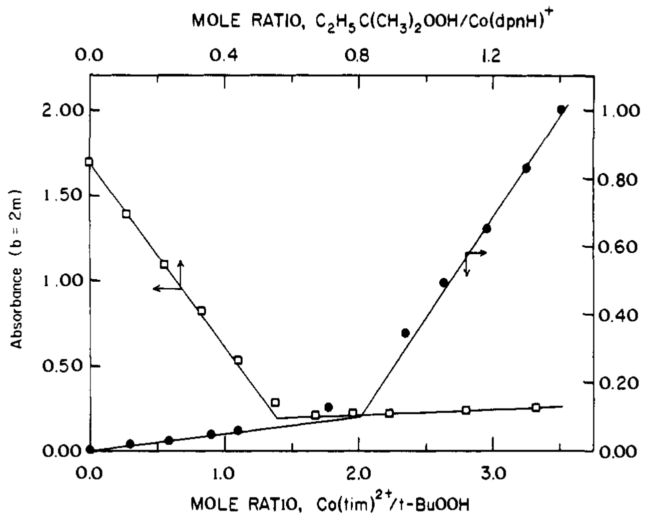
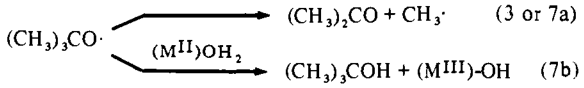


Figure 2. Spectrophotometric titration of typical Co(II)-hydroperoxide reactions: (1) open squares, *tert*-butyl hydroperoxide titrated with $Co(tim)^{2+}$ at 545 nm; (2) filled circles, $Co(dpnH)^+$ titrated with *tert*-amyl hydroperoxide at 505 nm.

respect consists of an alternative hydrogen abstraction reaction of the alkoxy intermediate, which would compete with the unimolecular β-scission process. Such competition is illustrated for the *tert*-butoxy radical in eq 7.



$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot \qquad (3 \text{ or } 7a)$$

$$(CH_3)_3CO\cdot \xrightarrow{(M^{II})OH_2} (CH_3)_3COH + (M^{III})\text{-}OH \qquad (7b)$$

If a reduction process such as 7b competes effectively with β-scission, a diminished yield of organometallic product will result. In contrast to the reaction of Cr^{2+}, reduction is apparently unimportant relative to β-scission for the cobalt(II)-hydroperoxide reactions studied here. This conclusion is based on determined yields of $CH_3Co(tim)^{2+}$ from the reaction of 5×10^{-3} M $Co(tim)^{2+}$ and 0.02 M $(CH_3)_3COOH$ in 0.1 M aqueous perchloric acid. Little variation in yield with the order of addition of reactants was found, being 46 ± 3% when the peroxide was added slowly to a well-stirred solution of $Co(tim)^{2+}$, and 43 ± 2% when the order of addition was reversed. The near identity of these two yields indicates that reaction 7b is of little importance, and the comparison with the theoretical 50% of reaction 5 supports the occurrence of steps 1-3. The small discrepancy between theoretical and experimental yield is thought to arise from two factors: inaccuracies in the molar absorptivities used in the determination and accidental leakage of O_2, which reacts very rapidly with $CH_3\cdot$.

Two peroxides whose reactions with Co^{II} proved different from the above, and different also from the corresponding reactions of Cr^{2+}, are perbenzoic acid and hydrogen peroxide. The former are characterized by variable and nonintegral stoichiometry.[28] Reactions of H_2O_2 with $Co(tim)^{2+}$ and $Co(Me_6[14]4,11\text{-diene}N_4)^{2+}$ were found to occur with a 1:1 stoichiometry in *tert*-butyl alcohol-water, whereas the former reaction, when carried out in a purely aqueous solution, reacted in the ratio $2Co(tim)^{2+}$:$1H_2O_2$. The solvent dependence is explained by the known very rapid scavenging of the intermediate ·OH by *tert*-butyl alcohol (eq 8).[29]

$$\cdot OH + (CH_3)_3COH \rightarrow H_2O + HOC(CH_3)_2\dot{C}H_2 \qquad (8)$$

The carbon-centered radical so produced is evidently unreactive toward Co(II). Interestingly enough, the reaction of Cr^{2+} with H_2O_2 produces $Cr(H_2O)_6{}^{3+}$ and retains its 2:1 stoichiometry in *tert*-butyl alcohol-water, as found in H_2O. This suggests that the reaction $Cr^{2+} + \cdot OH \rightarrow CrOH^{2+}$ competes effectively with eq 8 under these conditions.

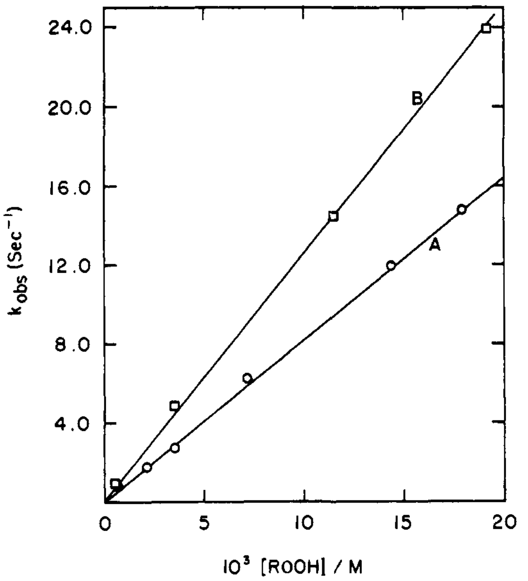
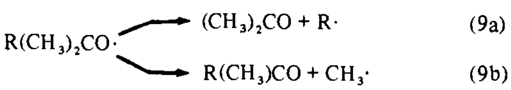


Figure 3. Typical plots of kinetic data illustrating the first-order dependence upon hydroperoxide concentration. Reactions shown are those of $Co(dmgH)_2$ with (A) *tert*-butyl hydroperoxide and (B) *tert*-amyl hydroperoxide.

The hydroperoxides $R(CH_3)_2COOH$ produce initially an alkoxy radical whose β-scission may occur in either of two ways:



$$R(CH_3)_2CO\cdot \longrightarrow (CH_3)_2CO + R\cdot \qquad (9a)$$

$$R(CH_3)_2CO\cdot \longrightarrow R(CH_3)CO + CH_3\cdot \qquad (9b)$$

For Cr^{2+} the observed[6] $Cr\text{-}R^{2+}$ product corresponds to reaction 9a for R = Et, and to 9b for R = C_6H_5; both observations are consistent with the known preferential fragmentation pattern of these radicals in organic solvents.[30] The same observations were confirmed in the present study in aqueous and aqueous butanol solutions by the production of $C_2H_5Co(tim)^{2+}$ and $CH_3Co(tim)^{2+}$, each identified spectrophotometrically in solution, from the respective reactions of *tert*-amyl hydroperoxide and cumene hydroperoxide with $Co(tim)^{2+}$. Similarly the reaction of *sec*-butyl hydroperoxide with $Co(tim)^{2+}$ in aqueous solution produced a complex with the spectrum of $C_2H_5Co(tim)^{2+}$, consistent with the known fragmentation[31] of *sec*-butoxy radical to acetaldehyde and $C_2H_5\cdot$.

Kinetic Studies. The kinetic studies were conducted in 1:1 v/v *tert*-butyl alcohol-water at 25 °C in the presence of a large excess of the hydroperoxide. The data in each run showed a pseudo-first-order dependence upon $[Co^{II}]$, and for each run a value of k_{obsd} was computed.[32] A plot of k_{obsd} vs. concentration of hydroperoxide was linear and passed through the origin; typical plots are shown in Figure 3. Inclusion of the stoichiometric factor[33] of 2 thus gives the rate expression

$$-d[Co(II)]/dt = 2k_1[Co(II)][peroxide] \qquad (10)$$

where k_1 represents the specific rate of the rate-limiting step, eq 2. Kinetic data for the various reactions are summarized in Table I.

The reactions of hydrogen peroxide were treated similarly except that the appropriate stoichiometric factor[33] in eq 10 is unity in this case. These rate constants are also given in Table I.

The kinetic data for perbenzoic acid are not so easily analyzed in view of the nonintegral stoichiometry.[34,35]

The reaction between $Co(tim)^{2+}$ and ethyl-*tert*-butyl peroxide was moderately slow, and the pseudo-first-order rate plots curved badly. An estimate of k_1 from the initial rate is

Table I. Summary of Kinetic Data[a]

Co(II) complex	Peroxide	Range of initial concn, M: 10^3 [peroxide]	Range of initial concn, M: 10^5 [Co(II)]	k_1,[b,c] dm^3 mol^{-1} s^{-1}
Co(tim)$^{2+}$	$(CH_3)_3COOH$	0.41-22.3	3.2-8.8	31 ± 3 (13)
	$C_2H_5C(CH_3)_2OOH$	0.092-0.921	2.3-6.3	59 ± 3 (9)
	$PhC(CH_3)_2OOH$	0.49-3.96	4.6	117 ± 5 (8)
	$C_2H_5CH(CH_3)OOH$	2.24-11.22	6.3-6.7	30 ± 3 (4)
	H_2O_2	0.39-18.9	5.0-8.8	164 ± 13 (12)
	$C_6H_5CO_3H$	0.19-1.03	0.84-4.2	$1.24 \pm 0.05 \times 10^5$ (10)[d]
	$C_6H_5CO_3C(CH_3)_3$	7-12	3-6	~0.15
Co(dpnH)$^+$	$(CH_3)_3COOH$	1.16-22.3	3.6-7.2	239 ± 15 (7)[e]
	$C_2H_5C(CH_3)_2OOH$	1.54-30.6	7.2	303 ± 33 (8)[e]
Co(dmgH)$_2$	$(CH_3)_3COOH$	0.72-17.9	7.0	409 ± 18 (6)[f]
	$C_2H_5C(CH_3)_2OOH$	0.77-19.2	7.0	630 ± 5 (4)[f]
Co(Me$_6$[14]4,11-dieneN$_4$)$^{2+}$	$(CH_3)_3COOH$	0.29-1.17	1.9-9.1	7.8 ± 0.1 (15)
	$C_2H_5C(CH_3)_2COOH$	0.25-1.01	1.9-4.4	7.9 ± 0.2 (6)
	H_2O_2	0.39-11.3	4.5-6.8	80 ± 12 (12)
Co(Me$_6$[14]aneN$_4$)$^{2+}$	$(CH_3)_3COOH$	0.70-5.62	1.1-2.9	6.4 ± 0.4 (13)
Co^{II}(corrin)=B$_{12r}$	$(CH_3)_3COOH$	2.81-27.4	2.5	38 ± 2.0 (9)

[a] At $\mu = 0.10$, 0.10 M $HClO_4$, in 1:1 (v/v) t-BuOH-H_2O at 25.0 °C (except as noted). [b] $k_1 = k_{obsd}/\alpha[\text{peroxide}]_{av}$ where $\alpha = 1$ for H_2O_2 and $\alpha = 2$ for the hydroperoxides; see ref 33. [c] The values shown are the average, the standard deviation, and the number of determinations in parentheses. [d] Value is $k_{obsd}/[C_6H_5CO_3H]_{av}$, and is not precisely k_1 (see text). [e] In 0.1 M $LiClO_4$. [f] In 0.1 M NaOAc.

Table II. Effects of Variable Conditions[a] on the Rate of Reaction of Co(tim)$^{2+}$ and $(CH_3)_3COOH$

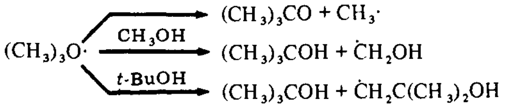
Variant	k_1, dm^3 mol^{-1} s^{-1} [b]
None[a]	31 ± 3 (13)
$0.01 < [H^+] < 0.10$ M at $\mu = 0.10$ M ($LiClO_4$)	33 ± 2 (3)
0.1 M $LiClO_4$	34 (1)
0.1 M NaOAc	34 (1)
$T = 19.0$ °C	25 ± 1 (3)
$T = 35.9$ °C	62 (2)
$T = 44.9$ °C	101 ± 2 (3)
Solvent: H_2O at 22 ± 2 °C	108 ± 10 (7)
Solvent: 1:1 CH_3OH-H_2O at 22 ± 2 °C	107 (1)

[a] "Standard" conditions are 25.0 °C, 0.10 M $HClO_4$, $\mu = 0.10$ M in 1:1 v/v t-BuOH-H_2O. [b] Table I, footnote c.

~0.05 M^{-1} s^{-1}. At the end of the reaction some Co(tim)$^{2+}$ always remained, even in a run with a 100-fold excess of the peroxide. The product spectrum indicates that some CH_3Co(tim)$^{2+}$ is formed, consistent with formation of t-BuO·. Both the nonlinear kinetic plots and the residual Co(tim)$^{2+}$ would be accounted for if the decomposition of ethyl-*tert*-butyl peroxide is catalyzed by a cobalt complex.

Effects of [H$^+$], Solvent, and Temperature. We have taken the reaction of Co^{II}(tim)$^{2+}$ with *tert*-butyl hydroperoxide as a standard of comparison, and have explored in some detail the effect of certain variables on the reaction rate. These data are summarized in Table II. Variation of [H$^+$] has negligible effect: even a change as drastic as 0.1 M $HClO_4$ to 0.1 M NaOAc does not appreciably alter k_1. The reaction rate also appears largely independent of ionic strength, as expected for a second-order reaction involving a nonelectrolyte. Solvent effects on k_1 are small but real, the rate being some three times higher in both water and 50% aqueous methanol then in the 50% aqueous *tert*-butyl alcohol solvent in which most reactions were studied.

Activation parameters for Co(tim)$^{2+}$ + t-BuOOH were evaluated by means of the Eyring relation using the values of k_1 at different temperatures, and are $\Delta H_1^{\ddagger} = 40.5 \pm 3.5$ kJ mol^{-1} and $\Delta S_1^{\ddagger} = -80 \pm 11$ J mol^{-1} K^{-1}. For comparison, the reaction[36] of Cr^{2+} and t-BuOOH in the same aqueous *tert*-butyl alcohol solvent system is characterized by the parameters $\Delta H_1^{\ddagger} = 21.5 \pm 1.4$ kJ mol^{-1} and $\Delta S_1^{\ddagger} = -96.5 \pm 4.7$ J mol^{-1} K^{-1}. The product of the Cr^{2+} reaction in aqueous *tert*-butyl alcohol was identified as $CrCH_3^{2+}$ by its absorption spectrum and by its acidolysis rate in comparison with the authentic complex[5,6] prepared in water and brought to 50% t-BuOH. This result for chromium affirms production of the CH_3-Co complexes in the corresponding reactions. Thus in this mixed solvent the t-BuO· radical apparently is not scavenged by t-BuOH, in contrast to its reaction with CH_3OH (in 50% aqueous methanol solution). This lack of H-abstraction reactivity in competition with β-scission renders aqueous t-BuOH a good solvent choice; nonetheless, the synthetic reactions for alkylcobalt complexes were carried out in water.



During the course of this work a report[37] was published that reaction of Co(dmgH)$_2$py$_2$ with $(CH_3)_3COOH$ *in benzene* produces an oxygen-bonded peroxo complex, $(CH_3)_3COO$-Co(dmgH)$_2$py. Since our work demonstrated formation of CH_3Co(dmgH)$_2$ in aqueous *tert*-butyl alcohol, the course of reaction appears entirely different in the two solvents. We found that the product in benzene solution has a weak absorption maximum at 600-650 nm, a region where the aqueous products are completely transparent. Also TLC separations showed the absence of methylcobaloxime in benzene in contrast to its detection in good yield in the aqueous system.

Conclusions

Only minimal rate effects were seen for substitution at positions remote from the OH group in the hydroperoxides $RC(CH_3)_2OOH$. Thus for Co^{II}(tim)$^{2+}$, values of k_1 (M^{-1} s^{-1}) are 31 (R = CH_3), 59 (C_2H_5), and 117 (C_6H_5). Similarly, little difference in rate is noted between t-BuOOH ($k_1 = 31$) and s-BuOOH (30). These observations parallel those made in the Cr^{2+} reactions,[6] and need not be discussed in detail.

The magnitudes of the actual rates for Co(II) and Cr(II) are rather different, however. The reaction of t-BuOOH is 3 × 10^3 faster with Cr^{2+} than with Co(tim)$^{2+}$. Even correcting for the greater number of equivalent reaction positions of the former, six compared to two, a factor of 10^3 remains. The effect originates primarily in $\Delta H^{\ddagger}$, 40.5 kJ mol^{-1} for Co(tim)$^{2+}$ vs. 21.5 for Cr^{2+}. Values of $\Delta S^{\ddagger}$, even after correction for reaction sites, are much closer: -80 ± 11 J mol^{-1} K^{-1} for Co(tim)$^{2+}$ vs. -106 ± 5 for Cr^{2+} (corrected by R ln 3 to put it on the same basis as Co(tim)$^{2+}$). The reactivity difference, as seen in the increased value of k_1, undoubtedly reflects the stronger reducing strength of Cr^{2+} ($E^0 = -0.41$ V) over $Co(tim)^{2+}$ ($E^0 = +0.54$ V[16]).

A second manifestation of the relative reactivities is noted in the subsequent chemistry of *t*-BuO·. In the case of $Co(tim)^{2+}$, β-scission (eq 7a) occurs to the near exclusion of oxidation–reduction (7b), as evidenced by the nearly theoretical yield of $CH_3Co(tim)^{2+}$. In contrast, the much lower yields of $CrCH_3^{2+}$ arise largely from the competition of 7b with 7a, the former producing no organometallic product. This too seems to be another kinetic manifestation of the relative reducing strengths of $Co(tim)^{2+}$ and Cr^{2+}: the former fails to abstract a hydrogen atom from $(CH_3)_3CO\cdot$, whether for kinetic or thermodynamic reasons, and the radical reacts exclusively by β-scission (eq 3 and 7a). The ion Cr^{2+}, on the other hand, reacts sufficiently rapidly with $(CH_3)_3CO\cdot$ that a competitive situation results.

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Supplementary Material Available: tabulation of concentrations and rate constants for individual kinetic experiments, elemental analyses, and UV-visible spectra (20 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976.

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(7) One suggestion has, however, appeared[8] that the combination of RH + H_2O_2 be used in conjunction with Co^{II} to generate $R(Co^{III})$ via reaction 1, a method analogous to a peroxide-based method[5] useful for CrR^{2+}; to our knowledge this suggestion has not been implemented.

(8) Reference 2, p 12.

(9) Systematic names for the five cobalt complexes whose structures and trivial designations are given in Figure 1 are bis(dimethylglyoximato)cobalt(II); 3,3′-(trimethylenediimino)bis(butan-2-one)oximatocobalt(II) ion; 2,3,9,11-tetramethyl-1,4,8-11 tetraazacyclotetradeca-1,3,8,10-tetraenecobalt(II) ion; 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienecobalt(II) ion; and *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanecobalt(II) ion. The formulas of the cobalt(II) complexes in solution are written without axial water molecules, to avoid specification of whether one or two water molecules are coordinated to the predominant Co(II) species in solution. The question of the major Co(II) species present, albeit under rather different solvent conditions, has been considered: J. Halpern and P. F. Phelan, *J. Am. Chem. Soc.*, **94**, 1881 (1972); J. F. Endicott, et al., *ibid.*, **99**, 429 (1977).

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(25) (a) See, for example, L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958). The exact procedure consisted of deoxygenating 30 cm^3 of acetic acid, 20 cm^3 of chloroform, and 1 cm^3 of 10^{-3} M $FeCl_3$ by a stream of N_2. Sodium iodide (2 g) was added, followed by the peroxide solution. After 30–60 min reaction under N_2, the solution was titrated with sodium thiosulfate. Solutions of H_2O_2 and of $C_6H_5CO_3H$ were analyzed in the same manner, but with omission of the $FeCl_3$ and titration after 5 min reaction; (b) Analysis of ethyl-*tert*-butyl peroxide was done on the neat compound by the method of R. M. Johnson and I. W. Siddigi, "The Determination of Organic Peroxides", Pergamon Press, Elmsford, N.Y., 1970, p 21.

(26) Wavelengths (and molar absorptivities) of the Co(II) complexes are as follows: $Co(dmgH)_2$, 460 nm (ϵ 3.84 × 10^3 M^{-1} cm^{-1}; $Co(dpnH)^+$, 505 (2.24 × 10^3); $Co(tim)^{2+}$, 545 (3.45 × 10^3); $Co(Me_6[14]dieneN_4)^{2+}$, 441 (140) and 335 (2.27 × 10^3); $Co(Me_6[14]aneN_4)$, 482 (67); and B_{12r}, 468 (8.4 × 10^3). The latter two reactions were more commonly followed at product wavelengths, 440 and 350 nm, respectively.

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(28) The reaction of $Co(tim)^{2+}$ and perbenzoic acid occurred with a 1.3:1 stoichiometry (metal:peroxide), whereas $Co(Me_6[14]dieneN_4)^{2+}$ reacted in a 1:5 ratio.

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(32) Kinetic data for individual runs are given in the supplementary material.

(33) The factor of 2 is properly included in eq 10 for all reactions following a stoichiometry $2(Co^{II})$:1 peroxide, regardless of product distribution. For hydrogen peroxide reactions following a 1:1 stoichiometry in *tert*-butyl alcohol–water, the factor of 2 should be (and was) omitted. Kinetic data for reactions of variable stoichiometry, such as those of perbenzoic acid, cannot be precisely interpreted in terms of a true rate constant for the rate-limiting step.

(34) The kinetic data with large stoichiometric excesses of perbenzoic acid over $Co(tim)^{2+}$ did follow an exact pseudo-first-order expression, affording values of k_{obsd} which proved directly proportional to $[C_6H_5CO_3H]$. The value of k_{app} (= $k_{obsd}/[C_6H_5CO_3H]$) is 1.24 ± 0.05 × 10^5 dm^3 mol^{-1} s^{-1}. Considering the stoichiometric factor, however, this second-order rate constant is not uniquely identified as k_1.

(35) The reaction of perbenzoic acid with $Co(4,11\text{-diene }N_4)^{2+}$ consumed *ca.* 5 mol of perbenzoic acid per mol of Co(II) complex. The kinetic data are complex: at peroxide:Co(II) ratios >9:1, the pseudo-first-order rate constant was 85 ± 5 s^{-1}, independent of $[C_6H_5CO_3H]$; as the ratio was lowered k_{obsd} went through a minimum value (5.3 s^{-1} at 6.5 × 10^{-4} M $C_6H_5CO_3H$, 2.7 × 10^{-4} M $Co(4,11\text{-diene}N_4)^{2+}$), then at still lower ratios (0.5:1 to 0.1:1) again approached a constant value of 30 ± 3 s^{-1}, independent of reactant concentrations. The reaction traces followed an exact pseudo-first-order expression even in experiments in which both reactants were appreciably consumed during the run.

(36) In comparison with the value of k_1 for the reaction $Cr^{2+} + (CH_3)_3COOH \rightarrow CrOH^{2+} + (CH_3)_3CO\cdot$ in 50% aqueous methanol, 1.65 × 10^4 M^{-1} s^{-1}, the value in 50% aqueous butanol is 1.03 × 10^4. Values of 10^{-4} k_1 (M^{-1} s^{-1}) at other temperatures in the latter solvent are 0.75 (18.0 °C), 1.41 (37.4 °C), and 1.85 (45.5 °C).

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