parameters. Difference maps were used to locate the hydrogen atoms which were then refined isotropically.

Because of the size of the structure and limitations in computer core space, the least-squares refinements were carried out by a blocked full-matrix method using the computer program SHELX. The scattering factors were taken from the "International Tables for X-ray Crystallography", Vol. 4, pages 99 and 149. The weighting scheme used was $W_F = K/[(\sigma_F)^2 + gF_o^2]$ where $\sigma_F = {}^1/_2[\{\sigma^2 + (0.04P)^2\}/P(Lp)]^{1/2}$, $\sigma = T^{1/2}V$, V = scan speed, T = Pk + 4(R + L), P = [Pk - 2(R + L)]V, Pk = peak height, R = right background, L = left backgound, and Lp = Lorentz and polarization factors. The factors K and g were redetermined after each structure factor calculation and were 0.205 and 0.00161, respectively, after the final cycle of refinement.

The variance was calculated as $V = [M\sum[W_f(|F_o| - |F_c|)^2]/N\sum W_f]^{1/2}$, where N is the number of reflections in a group, M is the total number of reflections, the sum in the numerator is over all reflections in a group, and the sum in the denominator is over all the reflections. An analysis of the variance in terms of the parity of the reflection indices, sin θ, and $[F_o/F_{max}]^{1/2}$ showed no significant variation in V for various ranges of the functions tested. Refinement was terminated when all parameter shifts were less than 0.15 of their corresponding standard deviations. The final value of R for all 3880 reflections was 0.039 and for R_w where $R_w = \sum W_f^{1/2}[|F_o| - |F_c|]/\sum W_f^{1/2}|F_o|$ was 0.051.

Acknowledgment. We gratefully acknowledge partial support of this work by the U.S.P.H.S. National Institutes of Health and the National Cancer Institute, Grants CA 22770 (K.D.B.) and CA 17562 (D.v.d.H.).

Supplementary Material Available: A listing of hydrogen parameters, thermal parameters, and final fractional coordinates for the nonhydrogen atoms and structural factors (16 pages). Ordering information is given on any current masthead page.

Reactions of (Alkylperoxy)cobaloximes in Acidic Aqueous Solutions

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Abstract: Bis(dimethylglyoximato)cobalt(III) complexes containing coordinated alkylperoxy groups have been studied. The compounds examined are (1) $ROOCo(dmgH)_2$(pyridine) complexes with R = isopropyl, 2-butyl, cyclopentyl, benzyl, and isopropyl-d_7 and (2) $(CH_3)_2CHOOCo(dmgH)_2L$ complexes with L = pyridine, piperidine, water, and ammonia. The complexes react with aqueous perchloric acid to form the cobalt(III) product $(H_2O)Co(dmgH)_2L^+$ and a mixture of ketone and hydroperoxide. The organic products are formed in parallel pathways, each by a kinetic equation having the same algebraic form, and are the products of respective oxygen–oxygen and cobalt–oxygen bond cleavage reactions. Kinetic data were determined as a function of $[H^+]$ and, in the case of the 2-butyl complex, temperature. The rate constants for reactant disappearance and of product formation were determined, as was the ratio of ketone to hydroperoxide in the products. An important preequilibrium is the protonation of the oxime oxygens; the equilibrium constant varies in a way which reflects the basicity of the axial ligand L. The kinetic data and other results can be used to formulate a *separate* pathway leading to each product. Hydroperoxide formation is best accounted for by a pathway in which internal proton transfer from H^+ bound to oxime oxygen occurs. Ketone production, on the other hand, shows an appreciable kinetic isotope effect: $k^H/k^D = 8.9 \pm 1.5$, suggesting C–H bond breaking is a major part of the activation process.

Introduction

The title compounds[1] are formed photochemically, either by insertion of oxygen into the cobalt–carbon bond of alkylcobaloximes,[2-7] as in eq 1 (which, for some R groups, also occurs thermally), or by the substitution process[8] of eq 2 (with R = *tert*-butyl or cumyl):

$$RCo(dmgH)_2L + O_2 \xrightarrow{h\nu} ROOCo(dmgH)_2L \quad (1)$$

$$R'Co(dmgH)_2L + 2ROOH \xrightarrow{h\nu} ROOCo(dmgH)_2L + ROOR' \quad (2)$$

The alkylperoxy compounds are isolated—with R representing a wide range of alkyl and aralkyl groups and L a conventional Lewis base such as pyridine (usually)—as stable, red-brown crystals. The formulation given has been thoroughly verified by spectroscopic methods (^1H NMR, UV[7], and IR[2]), as well as by elemental analysis.[2-8] Crystal structures have been determined for the L = pyridine derivatives of compounds with R = 2-phenylethyl[9] and 2-phenyl-2-propyl[8] (or cumyl), verifying that ROO and L occupy trans positions on either side of the planar $Co(dmgH)_2$ unit.

The (alkylperoxy)cobaloximes are subject to decomposition in solution upon prolonged UV irradiation or thermolysis.[10] In addition,[11] solutions in chloroform or carbon tetrachloride react with acids ($HClO_4$ or CF_3COOH), forming hydroperoxide ROOH (eq 3) and (in parallel or perhaps by decomposition[12] of a primary or secondary hydroperoxide) the corresponding ketone or aldehyde.

$$ROOCo(dmgH)_2L + H^+ = ROOH + [Co^{III}(dmgH)_2L]^+ \quad (3)$$

We have found that the (alkylperoxy)cobaloximes also react with acid in aqueous solution. This medium, where the species

(1) Cobaloxime is the trivial name given to bis(dimethylglyoximato)cobalt complexes: Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97.
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and their activities are better defined, has been chosen for this study of the mechanism of the reactions of the peroxycobalt complexes with acid. Product ratios were evaluated to determine whether the reactions of eq 4 and 5 occur concurrently, or whether eq 4 is followed by eq 6.

$$(CH_3)_2CHOOCo(dmgH)_2L + H_3O^+ = (CH_3)_2CHOOH + H_2OCo(dmgH)_2L^+ \quad (4)$$

$$(CH_3)_2CHOOCo(dmgH)_2L + H^+ = (CH_3)_2CO + H_2OCo(dmgH)_2L^+ \quad (5)$$

$$(CH_3)_2CHOOH = (CH_3)_2CO + H_2O \quad (6)$$

Various techniques were used to determine the product yields and their relative rates of formation. Supporting data in the form of deuterium kinetic isotope effects were obtained by using $(CD_3)_2CDOOCo(dmgH)_2py$.

The results may also have a bearing upon reactions of a chromium(III) analogue, $(H_2O)_5CrOOCH(CH_3)_2^{2+}$, which has been proposed[13] as an intermediate in the thermal reaction of O_2 with $(H_2O)_5CrCH(CH_3)_2^{2+}$.

Results and Interpretation

Reaction Products. The inorganic product of the decomposition reaction was exclusively the cobalt(III) cobaloxime $(H_2O)Co(dmgH)_2L^+$. This result was established from the ^1H NMR spectra of the reaction products in comparison with those for the known and independently synthesized complexes having both water[14] and pyridine[15] as the axial base. The product from reaction of i-$C_3H_7OOCo(dmgH)_2py$ with aqueous $HClO_4$ retains the axial pyridine; i-$C_3H_7OOCo(dmgH)_2OH_2$ yields $(H_2O)_2Co(dmgH)_2^+$. Since these reactions require a considerable length of time to reach completion, a typical half-time being 23 min at 0.2 M H^+, this provides definitive proof that the axial base of the parent (alkylperoxy)cobalt complexes is *not* equilibrated with solvent water on this time scale:

$$ROOCo(dmgH)_2py + H_3O^+ \not\rightarrow ROOCo(dmgH)_2OH_2 + Hpy^+ \quad (7)$$

This contrasts with the very rapid equilibration noted[16,17] between organocobaloximes $RCo(dmgH)_2L$ with various axial bases, including pyridine and water. In addition, it accounts for a finding detailed in a subsequent section: The complexes i-$C_3H_7OOCo(dmgH)_2L$, with L = H_2O and py, react with H^+ at notably different rates, consistent with the ligand-substitution process shown in eq 7 not being an important preequilibrium by which the two species would be interconverted prior to the decomposition.

The organic products obtained from reactions in aqueous perchloric acid consist of mixtures of ketone and hydroperoxide. The product ratios obtained from $ROOCo(dmgH)_2py$, expressed as [ketone]/[hydroperoxide], are as follows: R = i-C_3H_7, 35/65 (by ^1H NMR) and 42/58 (by peroxide titration), with the latter probably the more accurate; R = 2-C_4H_9, 35/65 (by ^1H NMR); R = i-C_3D_7, 8/92 (by peroxide titration). On the other hand, the more rapidly reacting aquo complex i-$C_3H_7OOCo(dmgH)_2OH_2$ yielded ≥95% isopropyl hydroperoxide. It should be noted that the secondary alkyl hydroperoxides so produced are perfectly stable for long periods of time in aqueous perchloric acid at room temperature.

Kinetics of Disappearance of $ROOCo(dmgH)_2py$. The rate constants for the reactions of the (alkylperoxy)cobalt complexes in acidic solutions were determined spectrophotometrically, usually at 300–340 nm. The spectral changes accompanying the reaction are shown in Figure 1.

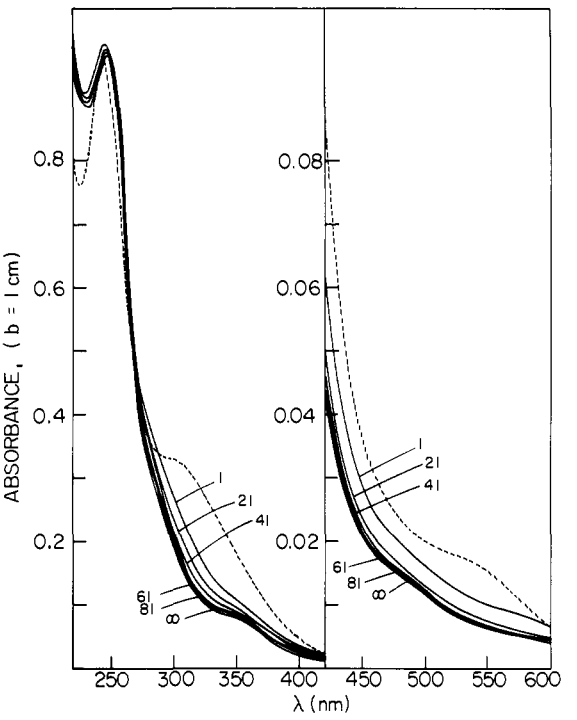

Figure 1. UV–vis spectral scans during reactions of $(CH_3)_2CHOOCo(dmgH)_2py$ with H^+. Conditions: $[H^+]$ = 0.500 M, μ = 1.00 M, T = 25 °C, $t_{1/2}$ = 18 min (k_{obsd} = 6.42 × 10^{-4} s^{-1}), 10^4[complex]$_0$ = 1.5 M (right), 0.40 M (left). The number shown for each spectrum is the time (minutes) at which the scan was begun. The dotted line shows the spectrum of an unacidified solution of the same complex at μ = 1.0 M, the difference between it and the first spectrum recorded in 0.500 M H^+ solution arising from the rapidly established protonation equilibrium of eq 10.

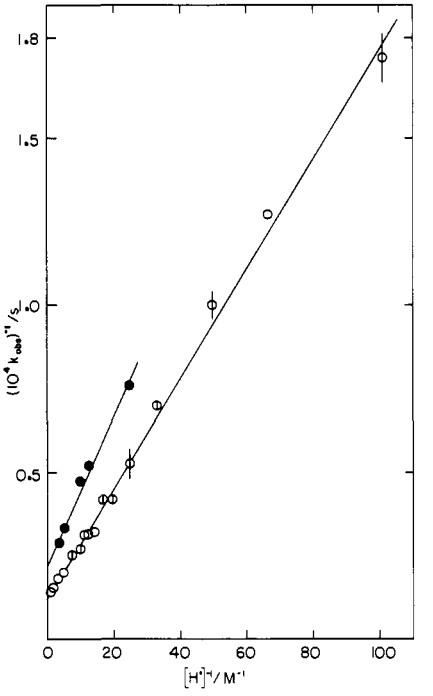

Figure 2. Kinetic data for the reaction of (isopropylperoxy)(pyridine)cobaloxime with aqueous perchloric acid. The plot depicts the linear variation of $1/k_{obsd}$ with $1/[H^+]$ according to eq 8. The points represent the experimental values and their standard deviations, and the line corresponds to a fit of the data to eq 8, using a nonlinear least-squares computation. Open circles, i-C_3H_7; filled circles, i-C_3D_7.

The studies were carried out in aqueous solution at constant temperature, usually 25 °C, and a constant ionic strength of 1.00 M maintained by lithium perchlorate in the presence of a sub-

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Table I. Observed[a] and Calculated[b] Pseudo-First-Order Rate Constants for the Overall Disappearance of (Isopropylperoxy)(pyridine)cobaloxime at Various Hydrogen Ion Concentrations

$[H^+]$/M	$10^4 k_{obsd}$[a]/s^{-1}	$10^4 k_{calcd}$[b]/s^{-1}
0.00987	0.574 (25)	0.561
0.0151	0.787	0.827
0.0201	1.00 (3)	1.06
0.0302	1.42 (2)	1.50
0.0404	1.90 (10)	1.89
0.0503	2.35 (5)	2.22
0.0602	2.38 (4)	2.52
0.0700	3.10 (5)	2.79
0.0799	3.16 (8)	3.03
0.0898	3.15 (13)	3.25
0.100	3.62 (18)	3.46
0.133	3.97 (13)	4.03
0.200	5.00 (1)	4.84
0.300	5.48	5.57
0.604	6.50	6.58
0.940	6.99 (61)	7.02

[a] Experimental conditions (1.0–3.8) × 10^{-4} M Co, 25.0 ± 0.1 °C, ionic strength 1.00 M (lithium perchlorate); the level of uncertainty in the last digit of k_{obsd}, represented by the standard deviation between duplicate or triplicate runs, is shown in parentheses. [b] Calculated according to eq 8 using the values of $k' = 8.00 \times 10^{-4}$ s^{-1} and $K_H = 7.63$ M^{-1}.

Table II. Kinetic Parameters[a] for the Overall Disappearance of (Alkylperoxy)(pyridine)cobaloximes, $ROOCo(dmgH)_2py$

R	T/°C	$10^4 k'$/s^{-1}	K_H/M^{-1}
2-propyl	25.0 ± 0.1	8.00 ± 0.20	7.63 ± 0.29
cyclopentyl	25.4 ± 0.4	12.0 ± 0.3	6.60 ± 0.23
2-butyl	15.8 ± 0.1	2.04 ± 0.15	8.1 ± 0.10
	25.4 ± 0.4	9.3 ± 0.3	7.35 ± 1.0
	31.4 ± 0.2	23.5 ± 0.1	9.9 ± 0.9
	38.6 ± 0.2	65.2 ± 0.5	11.9 ± 0.1
	44.3 ± 0.3	178 ± 22	13.1 ± 3.0
2-propyl-d_7	25.0 ± 0.05	4.7 ± 0.2	8.6 ± 0.8
benzyl	22 ± 3	~14	~2

[a] The parameters are those of eq 8; conditions: aqueous solution, 1.00 M ionic strength.

stantial excess of $[H^+]$, 0.010–0.98 M, over $[ROOCo(dmgH)_2py]_0$, (1.0–5.5) × 10^{-4} M. Values of the pseudo-first-order rate constant, k_{obsd}, increased with $[H^+]$ but the increase became less at higher $[H^+]$, with k_{obsd} tending to reach a plateau. The value of k_{obsd} at each $[H^+]$ for R = isopropyl is given in Table I, with data for other complexes also available.[18] A plot of k_{obsd}^{-1} vs. $[H^+]^{-1}$ is linear over the entire range examined as shown in Figure 2, in accord with the equation

$$k_{obsd} = k'[H^+]/(K_H^{-1} + [H^+]) \quad (8)$$

Accurate values of the two parameters k' and K_H of eq 8 were calculated by using a nonlinear least-squares program. Values of k' and K_H are summarized in Table II. Discussion of these results will be presented in a subsequent section, but it is useful to note that both parameters show a narrow range of values, rather insensitive to the variation among the various alkyl groups R.

The reaction for R = 2-butyl was studied as a function of temperature. These data, which are also summarized in Table II, indicate that k' is strongly temperature dependent, whereas K_H appears nearly invariant with temperatures within experimental error. The activated complex theory relation applied to k' is shown in Figure 3 as a plot of ln (k'/T) vs. $1/T$. A least-squares fit of the data affords the values $\Delta H^{\ddagger} = 118.4 \pm 5.9$ kJ mol^{-1} and $\Delta S^{\ddagger} = 93.3 \pm 19.2$ J mol^{-1} K^{-1}.

Kinetics of Product Formation from $ROOCo(dmgH)_2py$. A series of experiments was done for the compounds having R = isopropyl and cyclopentyl, using GLC techniques to follow the formation of ketone. Figure 4 depicts such results in comparison

(18) See supplementary material paragraph at end of paper.

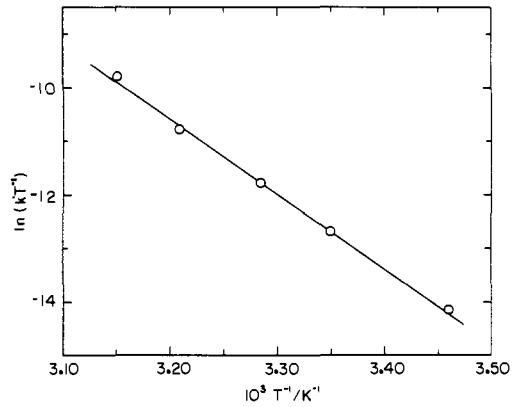


Figure 3. Plot of ln (k'/T) vs. $1/T$ illustrating the temperature dependence of k' for the reaction of $(CH_3)(C_2H_5)CHOOCo(dmgH)_2py$ with H^+. The rate constant k' represents the sum of the rate constants for independent reactions and as such the slight upward curvature may be a real effect (see text).

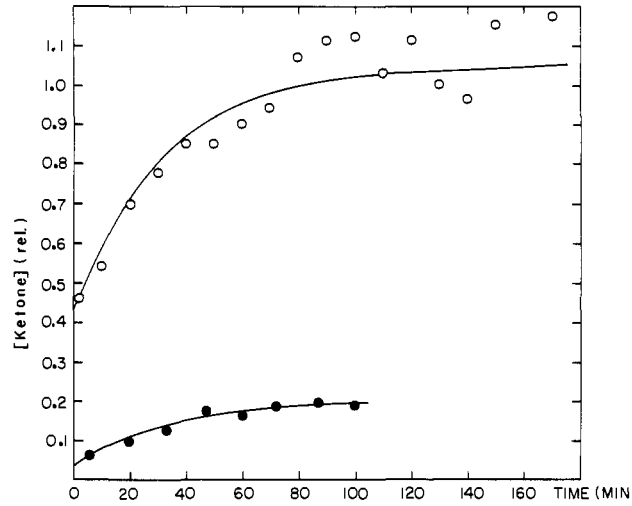


Figure 4. GC analysis of ketone product formed in the reaction of $ROOCo(dmgH)_2py$ plotted as (peak height of ketone)/(peak height of internal standard) vs. time. (○) R = isopropyl, 0.200 M H^+, ketone = acetone, internal standard, 2-propanol; (●) R = cyclopentyl, 0.100 M H^+, ketone = cyclopentanone, internal standard, acetone. The solid lines are those calculated from the rate constants as determined spectrophotometrically for reaction of the (alkylperoxy)cobalt complexes.

with those obtained spectrophotometrically. The agreement between the calculated curve and the experimental points is quite satisfactory. Ketone is thus established to be a *primary* reaction product under these conditions; it does *not* arise from a secondary reaction of the hydroperoxides such as in eq 6.

Effect of the Axial Base. Reactions of $(CH_3)_2CHOOCo(dmgH)_2L$. Rate constants and product ratios were determined for the complexes with L = piperidine, ammonia, and water. The first two react quite comparably to the pyridine complex. The values of the parameters at 25.0 °C and ionic strength 1.00 M for L = piperidine are $k' = 10.6 \times 10^{-4}$ s^{-1} and $K_H = 29$ M^{-1}, and for L = NH_3, $k' = 2.6 \times 10^{-4}$ s^{-1}, $K_H = 41$ M^{-1}. Compare, for L = py, $k' = 8.0 \times 10^{-4}$ s^{-1} and $K_H = 7.63$ M^{-1}. The ratio of acetone to isopropyl hydroperoxide is 29/71 for the piperidine complex.

The complex $(CH_3)_2CHOOCo(dmgH)_2OH_2$ was obtained only with greater difficulty, owing to its tendency to decompose. The value of k_{obsd} is some 50–190 times higher than that for the pyridine complex at a given $[H^+]$ over the region 0.01–1.0 M H^+. Values of k_{obsd} for the aquo complex also varied with $[H^+]$ according to eq 8. The parameters at 25.0 °C and $\mu = 1.00$ M are $k' = 0.25$ s^{-1} and $K_H = 1.01$ M^{-1}. The only product detected was the hydroperoxide.

Kinetic Isotope Effect: $(CD_3)_2CDOOCo(dmgH)_2py$. This derivative reacts noticeably more slowly than the protio analogue

Table III. Kinetic Paramaters[a] for the Overall Disappearance of (Isopropylperoxy)cobaloximes with Different Axial Ligands L

L	kinetic parameters at 25.0 °C	
	k'/s^{-1}	K_H/M^{-1}
pyridine	$(8.00 \pm 0.20) \times 10^{-4}$	7.63 ± 0.29
pyridine[b]	$(4.7 \pm 0.2) \times 10^{-4}$	8.6 ± 0.8
piperidine	$(10.6 \pm 0.2) \times 10^{-4}$	28.8 ± 1.0
ammonia	$(2.59 \pm 0.06) \times 10^{-4}$	41.4 ± 2.4
water	0.254 ± 0.010	1.01 ± 0.05

[a] The parameters are those of eq 8; conditions: aqueous solution, 1.00 M ionic strength. [b] For $(CD_3)_2CDOOCo(dmgH)_2py$.

(Figure 2 and Table III). Although K_H is not different between the two beyond the limits of experimental error, the rate constants are, $10^4k'$ being 4.7 ± 0.2 and 8.0 ± 0.2 s^{-1}. The yield of this hydroperoxide was $92 \pm 5\%$. Compared with its protio analogue, the isopropylperoxy-d_7 complex shows a much lower ratio of acetone to hydroperoxide, 8/92 (D) compared to 42/58 (H).

Interpretation and Discussion

Protonation Constant K_H. Alkylcobaloximes are known to undergo a rapid and reversible equilibrium reaction with H^+.[19-23] In this process one of the two pairs of hydrogen-bonded O–H···O units is converted to two separate OH units. The principal equilibrium is

$$RCo(dmgH)_2OH_2 + H^+ \overset{K_H^R}{\rightleftharpoons} RCo(dmg_2H_3)OH_2^+ \quad (9)$$

Values of K_H^R typically lie in the range 1–4 M^{-1} for various alkyl and aryl groups R. The lability[17] of the groups trans to the cobalt–carbon bond precludes analogous measurements for the complexes $RCo(dmgH)_2L$ for L other than H_2O.

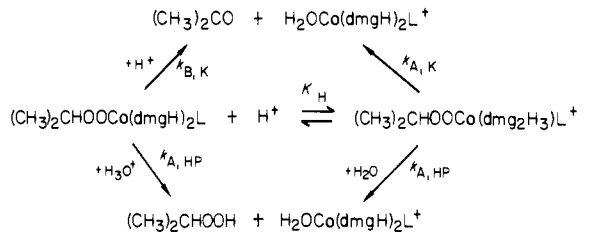
The analogous equilibria for the (alkylperoxy)cobaloximes were demonstrated in two ways: (1) the instantaneous spectral change which occurs upon acidification, a change which is very characteristic of those accompanying the reaction in eq 9; (2) the form of the kinetic data correlated by eq 8, in which the denominator term has the algebraic form of a rapid preequilibrium. The reaction is thus formulated analogously:

$$ROOCo(dmgH)_2L + H^+ \overset{K_H^{ROO}}{\rightleftharpoons} ROOCo(dmg_2H_3)L^+ \quad (10)$$

The substitution inertness with regard to solvolysis of the axial base L now permits evaluation of K_H^{ROO} for a series of axial bases, unlike K_H^R, which is accessibly only for $L = H_2O$. The value of $K_H^{i\text{-Pr}} = 4.2 \pm 0.3$ M^{-1} compared to $K_H^{i\text{-PrOO}} = 1.01$ M^{-1} in the case where $L = H_2O$, reflecting a difference in $\Delta G°_{298}$ of 3.6 kJ mol^{-1}. The difference suggests that the carbanion, a more basic center than an alkyl peroxide anion, is able to inductively transmit but a small part of its basicity to the oxime oxygens (most of it is almost certainly expended, in both cases, by formation of the covalent bond between Co(III) and R^- or ROO^-).

More substantial effects are noted, however, in comparing values of K_H^{ROO} for different axial ligands L. Now the values rise appreciably in going from water ($K_H = 1.01$ M^{-1}) to pyridine (7.6) and to the saturated amines piperidine (29) and ammonia (41). Along this same series the base strength of the free ligand increases regularly from H_2O ($pK_b = 14$) to pyridine (8.6), piperidine (2.8), and ammonia (4.7). Again, however, only a fraction of the effect can be transmitted beyond coordination to cobalt, and so values of K_H^{ROOH}, although reflecting this trend in basicity, do so much less severely than do the pK_b values.

Scheme I



It appears that such inductive effects alone account adequately for the variation in values of K_H^{ROO}, although a reversal between piperidine and ammonia is noted. That is, the replacement of small bases (H_2O, NH_3) by bulky ones (py, pip) apparently causes inappreciable conformational change in the (approximately) planar ring of the $(dmgH)_2$ pseudomacrocycle, because if it did, the values of K_H would surely be altered. In addition, π back-bonding to pyridine is probably not an appreciable factor, considering that the stronger protonic base piperidine forms a complex with $ROOCo(dmgH)_2$, which is correspondingly more basic than its pyridine complex.

Reaction Mechanism. Several mechanisms are consistent with the kinetic equations. These mechanisms all have in common the rapid preequilibrium step of eq 10. Moreover, the results obtained clearly indicate that the products, ketone and hydroperoxide, are formed by parallel and independent pathways. Both products, however, are formed with the rate law showing the same concentration dependences. This means that the pathway leading to each product may be written as either the unimolecular reaction of the protonated species, which is suggested by the reaction rate expressed as $k[ROOCo(dmg_2H_3)L^+]$ or the bimolecular reaction of H_3O^+ with the unprotonated compound, as implied by the kinetically equivalent formulation of the reaction rate as $k[ROOCo(dmgH)_2L][H_3O^+]$.

Thus as many as four elementary reactions can be considered, given two possibilities for each independent product illustrated for the isopropylperoxy complex in Scheme I. If the four processes are incapable of further distinction, the following equations apply:

$$k_{obsd} = \frac{\{(k_{A,K} + k_{A,HP}) + K_H^{-1}(k_{B,K} + k_{B,HP})\}[H^+]}{K_H^{-1} + [H^+]} \quad (11)$$

$$\frac{[(CH_3)_2CO]}{[(CH_3)_2CHOOH]} = \frac{k_{A,K} + k_{B,K}K_H^{-1}}{k_{A,HP} + k_{B,HP}K_H^{-1}} \quad (12)$$

If this viewpoint is adopted, then only a limited resolution is possible based on the yield of ketone and hydroperoxide. Combination of eq 11 and 12 yields the following values for the isopropylperoxy complex: $(k_{A,K} + k_{B,K}K_H^{-1}) = 3.3 \times 10^{-4}$ s^{-1} and $(k_{A,HP} + k_{B,HP}K_H^{-1}) = 4.7 \times 10^{-4}$ s^{-1}.

The parameter k' is a summation of rate constants for the formation of separate products, as implied by the notation $k' = k_K + k_{HP}$. A plot of $\ln(k'/T)$ vs. $1/T$ would not be expected to be linear even if the individual rate constants obey the activated complex theory relationship. Close examination of Figure 3 reveals a very small curvature in the direction expected, although it is barely perceptible beyond experimental error. The complication does preclude an extensive consideration of the significance of the values of the activation parameters except to note that the fairly large value of $\Delta H^‡$ (118 kJ mol^{-1}) and the large positive value of $\Delta S^‡$ (93 J mol^{-1} K^{-1}) support a mechanism in which bond dissociation occurs.

There cannot be a rigorous basis from the kinetic data for further resolving the possibilities suggested by Scheme I because each of the alternatives leads to the same rate equation. We ask, however, whether any trends within the data are revealing. First, changes in the nature of the R group in the complexes $ROCo(dmgH)_2py$ give rise to a maximum rate difference of only a

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(22) Espenson, J. H.; Chao, T.-H. *Inorg. Chem.* **1977**, *16*, 2553.
(23) (a) Kornblum, N.; De La Mare, H. E. *J. Am. Chem. Soc.* **1951**, *73*, 880. (b) Bell, R. P.; McDougall, A. O. *J. Chem. Soc.* **1958**, 1697. Note, however, that the cobalt(III) complex $(H_2O)_2Co(dmgH)_2^+$ is not appreciably protonated. This is presumably the case simply because its cationic charge greatly reduces its proton affinity. Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1980**, *19*, 242.

factor of 3.0, suggesting that but a secondary influence on the reactivity. Second, the change in the nature of the axial base L causes a striking change in reactivity for the aquo complex. Furthermore, there was a substantial increase in the rate constant(s) for the pathway leading to the hydroperoxide as compared to the ketone. If the axial ligand affects the rate of bond cleavage by H^+ by means of an inductive process, then the complex having L = H_2O should have been the *least reactive* of the ones studied, since it is the *least basic* toward protonation of the oxime oxygens. Just the reverse is true, which suggests that the primary role of the axial ligand is not to act in this manner.

Mechanism of Hydroperoxide Formation. The two pathways depicted in Scheme I for hydroperoxide formation are (a) reaction of $ROOCo(dmgH)_2L$ with H_3O^+ and (b) a unimolecular protron-transfer reaction of $ROOCo(dmg_2H_3)L^+$. The first of these would presumably involve attack of H_3O^+ at the peroxide oxygen bound to cobalt, in which case one would certainly expect a higher rate for the more strongly basic group L, exactly the reverse of what was found. The second possibility might well be facilitated by a weakly basic axial ligand L since in this way the proton, being less tightly bound to an oxime oxygen, could more readily be transferred to the peroxidic group.

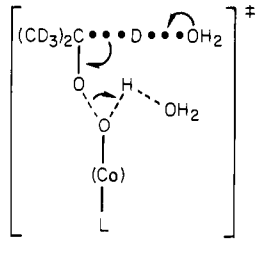
On the basis of these considerations, we suggest that $k_{A,HP}$ and not $k_{B,HP}$ provides the major pathway for hydroperoxide formation in which case the compounds having L = py are characterized by the following values of $k_{A,HP}$: isopropyl, $(4.6 \pm 0.2) \times 10^{-4}$ s^{-1}; isopropyl-d_7, $(4.3 \pm 0.3) \times 10^{-4}$ s^{-1}; 2-butyl, $(6.0 \pm 0.3) \times 10^{-4}$ s^{-1}. Virtually no difference in reactivity along this pathway is noted for the C_3H_7 and C_3D_7 compounds $k_{HP}^H/k_{HP}^D = 1.07 \pm 0.12$; this is hardly surprising since no CH bond is broken during the process in which isopropyl hydroperoxide is formed. Also, the isopropylperoxy complexes with other axial ligands have $k_{A,HP} = (7.5 \pm 0.5) \times 10^{-4}$ s^{-1} (L = piperidine) and 0.25 ± 0.01 s^{-1} (L = H_2O).

Mechanism of Ketone Formation. According to the complete set of reactions shown in Scheme I, the rate constant for ketone formation, k_K, is $k_{A,K} + k_{B,K}K_H^{-1}$. Alternatively, it is given by the product of the observed rate constant k' and f_K, the fraction of the product which is the ketone (eq 13). The value of k_K^H

$$k_K = k_{A,K} + k_{B,K}K_H^{-1} = k'f_K \quad (13)$$

for the protio compound $(CH_3)_2CHOOCo(dmgH)_2py$ is $(3.4 \pm 0.2) \times 10^{-4}$ s^{-1}, whereas the analogous value of k_K^D for the deuterated analog is $(3.8 \pm 0.4) \times 10^{-5}$ s^{-1}. This clearly illustrates the importance of the deuterium kinetic isotope effect for this pathway. Expressed as a ratio, $k_K^H/k_K^D = 8.9 \pm 1.5$, a very substantial effect.

The substantial kinetic isotope effect for the ketone pathway is a clear indication that C–H breaking is an important part of the rate-limiting kinetic step. Since the O–O bond is cleaved in this process, it seems likely that effects arising from the variation of L would be less severe than for the hydroperoxide pathway, considering the greater distance within the molecule over which any effect would need to be transmitted. The following activated complex is proposed for the formation of ketone:



On the basis of this formulation, the rate constants to be compared are values of $k_{B,K}$: 2.55×10^{-3} M^{-1} s^{-1} (i-$C_3H_7OOCo(dmgH)_2py$), 2.39×10^{-3} (2-$C_4H_9OOCo(dmgH)_2py$), 3.2×10^{-4} (i-$C_3D_7OOCo(dmgH)_2py$), 8.9×10^{-3} (i-$C_3H_7OOCo(dmgH)_2pip$), and $< 5 \times 10^{-3}$ (i-$C_3H_7OOCo(dmgH)_2OH_2$).

Conclusions. A free radical mechanism can definitely be discarded, since the resultant cobalt(II) cobaloximes are known to decompose rapidly under these conditions to Co^{2+}_{aq}. The results obtained clearly support the major thesis: Co–O and O–O bond-breaking reactions occur with roughly comparable rates, producing the respective alkyl hydroperoxide and ketone (or aldehyde) in parallel pathways. The rate law for both pathways has the same algebraic form; the results suggest an activated complex in which electrophilic attack of H_3O^+ occurs, most probably at the oxygen atom bonded to cobalt in the unit ROOCo. This process bears some relation to the base-catalyzed decomposition of dialkyl peroxides,[23] albeit in the acidic pH range the base attacking at the hydrogen of the isopropyl group is water rather than hydroxide ion.

It was earlier remarked that a study of the thermal reaction of $(H_2O)_5CrCH(CH_3)_2^{2+}$ with O_2 in aqueous perchloric acid suggested an isopropylperoxy intermediate was formed.[13] The reaction believed to be responsible for this consists of a homolytic displacement process:

$$(CH_3)_2CHOO\cdot + (H_2O)_5CrCH(CH_3)_2^{2+} \rightarrow (H_2O)_5CrOOCH(CH_3)_2^{2+} + (CH_3)_2CH\cdot \quad (14)$$

The presumed intermediate could not be detected, however, and its involvement was strictly a conjecture to account for the observed kinetics and products. If eq 14 occurs as written, however, it is then necessary to propose a further reaction converting it to Cr^{3+} and acetone:

$$(H_2O)_5CrOOCH(CH_3)_2^{2+} + H^+ \rightarrow Cr(H_2O)_6^{3+} + (CH_3)_2CO \quad (15)$$

This reaction would need to occur more rapidly than the overall reaction with O_2. Because the kinetic forms are different, it is not possible to place a specific limit on the rate of eq 15, but it appears the value $k_{15} \geq 5$ M^{-1} s^{-1} can be set as a conservative estimate.

Experimental Section

Materials. Various organocobalt complexes were prepared by known procedures.[24,25] Except for the complex having L = NH_3, which was not isolated, the alkylcobaloximes were isolated in pure form and characterized by elemental analysis (C, H, N, Co), ^1H NMR, and UV-vis spectrophotometry.

The alkylperoxy complexes, $ROOCo(dmgH)_2L$, were prepared[2-7] by the photochemical insertion of oxygen into the cobalt–carbon bond of the desired complex.[2-7] Typically 70–200 mg of the alkyl complex in 100 cm^3 of methylene chloride was irradiated through a Pyrex filter with an 8-W xenon lamp. Oxygen was passed into the solution through a dispersion tube and the solution cooled during the irradiation. The temperature and irradiation time varied from case to case, but typical conditions were 15 °C and a 2-h irradiation. During the latter stages the progress of the reaction was monitored by TLC. A compromise in time is necessary, as too short a time leaves starting material and too long leads to decomposition of the desired product. Generally speaking, it proved desirable to irradiate until the organocobalt was no longer detected, which gave a material more easily purified. The crude product was eluted twice from a silica gel column, using a 2:2:1 mixture of chloroform, ethyl acetate, and methanol. The decomposition products do not elute from the column during this time.

Solid $[(H_2O)_2Co(dmgH)_2]ClO_4$ was prepared by stirring $Cl_2Co(dmg_2H_3)$ with aqueous silver perchlorate overnight and precipitated with lithium perchlorate. Alternatively, a sample of $CH_3Co(dmgH)_2H_2O$ was treated with $Hg(ClO_4)_2$ in aqueous $HClO_4$.

$[H_2OCo(dmgH)_2py]ClO_4$ was prepared from 120 mg of the diaquo complex dissolved in 1 cm^3 of water at 5 °C, to which was then added 0.02 cm^3 of pyridine in 1 cm^3 of methanol. The yellow precipitate was recrystallized from methanol, giving a product which analyzed correctly.

Detailed data giving chemical analyses (C, H, N, Co), UV–vis spectra, and ^1H NMR spectra are available as supplementary material.[18]

Products. The organic products consist, in general, of a mixture of ketone and hydroperoxide. The former were identified by ^1H NMR (acetone, 2-butanone, cyclopentanone) and by GLC (acetone, cyclopentanone), using authentic samples for comparison. Hydroperoxides were also identified by ^1H NMR: isopropyl, 2-butyl, and cyclopentyl hydroperoxides were so identified. The last mentioned was confirmed

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by preparation[26,27] of the authentic compound from cyclopentyl methanesulfonate[27,28] and was identified by chemical analysis, ^{1}H NMR, and high-resolution mass spectroscopy: m/z 102.06805 (calcd m/z 102.06808). In the other instances the ^{1}H NMR spectrum of the hydroperoxide obtained by the present reactions (in D_2O) was compared with those of samples as obtained in $CDCl_3$.[11] Alkyl hydroperoxides were also determined by iodometric titration.[29,30]

Kinetics. A Cary 219 spectrophotometer was used to monitor the overall reaction rate by recording the time-dependent absorbance at a wavelength in the range 300–340 nm. Pseudo-first-order rate constants were calculated by a least-squares fit of the data to the standard equation $\ln (D_t - D_\infty) = \ln (D_0 - D_\infty) - k_{obsd}t$. In these studies the temperature was controlled by water circulating through a jacketed cell holder, and lithium perchlorate was added to maintain the ionic strength constant at 1.00 M.

In addition, the rate of production of the ketone was determined using a GC technique for two of the reactions. These runs were performed with an added internal standard on a 10% FFAP column.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division (Contract No. W-7405-ENG-82, WPAS-KC-03-02-01). We acknowledge helpful discussions with Professor W. S. Trahanovsky and are grateful to a referee for calling our attention to ref 23.

Supplementary Material Available: Tables giving analytical, NMR, and kinetic data (12 pages). Ordering information is given on any current masthead page.

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Reduction by a Model of NAD(P)H. 29. Kinetics and Isotope Effects for the Reduction of Substituted Trifluoroacetophenone

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Received March 10, 1980

Abstract: Kinetics for the reduction of substituted and unsubstituted α,α,α-trifluoroacetophenone by a model of NAD(P)H in acetonitrile in the presence and absence of a magnesium ion, a catalyst, has been studied. The catalyzed and uncatalyzed reactions show linear free-energy relationships. It is found that the magnesium ion retards the reaction of certain substituted trifluoroacetophenones. The kinetic isotope effect and the isotopic ratio in the product are also studied. These values vary depending on the substituent and on the presence or absence of the magnesium ion. The result indicates that there is at least one intermediate in the reaction and is discussed in relation to the stability of the intermediate as well as that of the transition states.

The pioneering study by Abeles et al.[1] on the mechanism of biomimetic reduction with a NAD(P)H model compound proposed that the reduction proceeds through one-step hydride transfer. Later Steffens and Chipman found that the kinetic deuterium isotope effect was much smaller than the H/D isotopic ratio in the product and proposed that there is at least one intermediate in the reduction.[2] Based on an ESR study, we claimed that the intermediate suggested by them is a charge-transfer-type complex.[3,4] Recently our claim was questioned on the basis that both the model compound and other tertiary amines behaved similarly in a spin-trapping experiment.[5] However, the model compound, a 1,4-dihydropyridine derivative, is also a tertiary amine.[6]

The rates for one-electron transfer from a photoexcited model compound to a variety of substrates were found to be much slower than those for chemical reductions.[7] However, the existence of a small but appreciable kinetic deuterium isotope effect[2,8,9] proves that the one-electron transfer involved in the chemical reaction differs completely from that in the photophysical process, where the movement of an electron is controlled by the Franck–Condon principle. Thus, it has been almost established that an electron and a hydrogen nucleus (in the form of a hydrogen atom or a proton) move separately in the reduction.

It has been found that bivalent metal ions such as magnesium and zinc catalyze the reduction of certain substrates,[10,13] whereas

Table I. Rate Constants for the Reduction of α,α,α-Trifluoroacetophenone (1a) with PNAH in Acetonitrile at 50 °C[a]

10^2[1a], M	10^2[$Mg(ClO_4)_2$], M	10^3k_{obsd}, min^{-1}	10^3k_{corr}, min^{-1}	10^2k, M^{-1} min^{-1}
0.00	2.00	0.506		
2.02	2.00	1.76	1.25	6.20
4.50	2.00	3.27	2.76	6.14
6.40	1.00	4.50	3.99	6.24
6.40	2.00	4.60	4.09	6.40
6.40	4.04	4.52	4.01	6.27
6.40	6.93	4.52	4.01	6.27
7.82	2.00	5.16	4.65	5.95
9.04	2.00	5.90	5.39	5.97
10.20	2.00	6.89	6.38	6.26
				6.18[c] ± 0.139[b]

[a] [PNAH] = 1.00×10^{-4} M. Standard deviation for each kinetic run was less than 3%. [b] Standard deviation. [c] Mean value.

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