first 5 ml. of distillate. The distillate was diluted to 10 ml. with ethanol, and further dilutions were made using 50% ethanol.

Aliquots (2 ml.) of the indole solution were treated with 1 ml. of 2.5% alcoholic dimethylaminobenzaldehyde and 1 ml. of 6 *N* hydrochloric acid. The indoles gave characteristic wine-violet colors ($\lambda_{\max}$ in the range of 570–585 mμ). Unreacted III also reacted with the periodate, and the amine formed was also steam distilled. The amine reacted with the Ehrlich reagent to give a yellow color (around 430 mμ). Therefore, it was possible to follow simultaneously the decrease in the concentration of III and the increase in the concentration of the tetrahydroquinolinol. Calibration curves were prepared by using solutions of the tetrahydroquinolinol of known concentrations in the analysis.

Cyclization Procedure.—The substituted 1-anilino-3-halo-2-propanol (III) was added to the reaction solvent together with the base (usually diethylaniline). The molar ratio of base to III was usually 6:1. When picrates were used for the cyclization, they were first treated with saturated lithium hydroxide and the addition compound was extracted with the reaction solvent. The solution was washed with water and dried with sodium sulfate before the addition of diethylaniline. Reaction mixtures were adjusted to about 0.042 *M* and then boiled under reflux. It was helpful to follow the course of the cyclization by the procedure outlined above even if calibration curves were not available in order to determine the best reaction time. Isolation was accomplished essentially by the procedure previously reported.[1] This involved extraction with 5% hydrochloric acid, neutralization with sodium hydroxide, extraction with benzene, and purification by means of alumina chromatography. The product was eluted with benzene–ether mixtures and ether. Evaporation of the eluates frequently gave very pure fractions while less pure fractions were recrystallized or converted to salts.

For kinetic experiments concentrations of addition compounds usually were adjusted to 0.0042 *M*. This gave cyclization yields of greater than 80%, but the concentrations were too low to make the procedure practical for most preparative purposes. The amount of III used at the concentration of 0.0042 *M* was only about 1 g./l. of solvent.

The effect of small amounts of water on the cyclization was negligible, but, if additional water was added, the yield was decreased. At the high temperatures used for the reaction the water tended to be carried up into the condenser. With larger amounts of water (1 ml./l.) a separate layer was present in the reaction mixture. This may have led to hydrolysis of the addition compound or to hydrolysis of an intermediate epoxide.

It is important to point out that tertiary bases, such as triethylamine, pyridine, γ-picoline, could be used in the cyclization. Pyridine salts of III could also be used. In the absence of base yields were very low and cyclization using 1-*p*-toluidino-3-chloro-2-propanol led to the formation of 1,3-di-*p*-toluidino-2-propanol, m.p. 113–115° (lit.[7] m.p. 113.5–114°). Positive identification of this product was established by analysis.

Anal. Calcd. for $C_{17}H_{22}N_2O$: C, 75.52; H, 8.20; N, 10.36. Found: C, 75.73; H, 7.52; N, 10.42.

Pyridine Salt of 1-*p*-Toluidino-3-chloro-2-propanol.—1-*p*-Toluidino-3-chloro-2-propanol (2.00 g.) was dissolved in pyridine (5 ml.), and the mixture was boiled under reflux for 1 hr. The mixture was cooled, and the yellow crystalline salt was recovered and washed with acetone. Addition of acetone to the mother liquor gave more product, 2.13 g. (76%). The compound, after recrystallization from acetone–methanol, had m.p. 192°.

Anal. Calcd. for $C_{15}H_{19}N_2OCl$: C, 64.62; H, 6.87; N, 10.05. Found: C, 64.36; H, 7.15; N, 9.77.

Oxidation of the Tetrahydroquinolinols to Indoles.—The procedure used was essentially that previously reported.[1] When the indole crystallized in the steam distillate, it was recovered by filtration and the mother liquor was extracted with ether. If purification proved necessary, alumina chromatography was effective.

Acknowledgment.—This work was supported by a National Science Foundation Undergraduate Research Participation Grant and by a National Science Foundation Research Grant (G16783).

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[7] B. J. Ludwig, W. A. West, and D. W. Farnsworth, *J. Am. Chem. Soc.*, **76**, 2893 (1954).

Metal Ion Decomposition of Hydroperoxides. III. Intermediates in Cobalt Salt Catalyzed Decomposition of *t*-Butyl Hydroperoxide[1a]

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Evidence for peroxy radical intermediates during the cobalt salt catalyzed decomposition of *t*-butyl hydroperoxide is given by electron spin resonance (e.s.r.) spectra and the effect of hydrogen atom donors on rate. Reactions of the peroxy radicals support a mechanism previously proposed. No evidence for peroxy radical–π-aromatic complexes was observed from kinetic or e.s.r. data. A deuterium isotope effect (k_H/k_D) of 1.93 was found for cobalt 2-ethylhexanoate catalyzed decomposition of *t*-butyl deuterioperoxide in chlorobenzene. In contrast, no isotope effect was observed with cobalt acetate catalysis in acetic acid-*d*. The isotope effects were rationalized in terms of the relative oxidation state of cobalt in the two systems. The effect of added 2-ethylhexanoic acid could not be solely explained on the basis of competition between the acid and hydroperoxide for cobalt ligand sites. It is suggested that the acid may not only compete for ligand sites, but that it may be hydrogen bonding the hydroperoxide and/or peroxy radicals.

Previously, a kinetic and product study of the catalytic decomposition of *t*-butyl hydroperoxide by cobalt acetate in acetic acid and by cobalt 2-ethylhexanoate in chlorobenzene was reported.[1a] The principal products, *t*-butyl alcohol and oxygen, were proposed to originate from the reactions between peroxy radicals and cobalt–hydroperoxide complexes.[1a,2] Further evidence for these intermediates is given. In addition, the question of peroxy radical–π-aromatic complexes, the mode of di-*t*-butyl peroxide formation, and the significance of a deuterium isotope effect with *t*-butyl deuterioperoxide is considered.

Experimental

Materials.—Hydrocarbon solvents were distilled from calcium hydride and stored over the hydride. Cumene (Phillips, 99 mole %) was first purified by repeated extractions with concentrated sulfuric acid, concentrated sodium hydroxide, and water. The dried product was fractionated through a 30-in. glass helices

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[1] (a) Part II: W. H. Richardson, *J. Am. Chem. Soc.*, **87**, 1096 (1965); (b) Department of Chemistry, San Diego State College.

[2] M. H. Dean and G. Skirrow, *Trans. Faraday Soc.*, **54**, 849 (1958).

packed column and the heart cut was retained, b.p. 85.4–86.0 (95.5 mm.). Gas–liquid chromatography (g.l.c.) analysis showed the presence of only cumene. 2-Ethylhexanoic acid was purified by fractionation through a 30-in. column packed with glass helices, b.p. 111.8–112.0 (8.0 mm.).

t-Butyl deuterioperoxide was prepared by exchange with 99.9% deuterium oxide (Bio-Rad Laboratories, Richmond, Calif.), followed by removal of water by azeotropic distillation.[3] Starting with 5 g. (5.5×10^{-2} mole) of *t*-butyl hydroperoxide, three exchanges were made each with 1.18 g. (5.85×10^{-2} mole) of deuterium oxide. N.m.r. analysis indicated the exchanged deuterioperoxide contained at least 99% deuterium in the O–D bond by comparison with known weights of methanol in benzene.

Preparation, purification, or purity of the other materials was given previously.[1a]

Kinetic Method.—The rate of hydroperoxide decay was measured iodometrically.[1a]

Product Analyses.—The reactions were conducted under a nitrogen or helium atmosphere. Condensable and gaseous products were analyzed by gas–liquid chromatography (g.l.c.) and by mass spectrometry, respectively.[1a]

Electron Spin Resonance Spectra.—A Varian X-band spectrometer, equipped with a dual-sample cavity, was employed using a 100-kc. field modulation of 4 gauss. The reference cavity contained potassium nitrosyl disulfonate, which shows three hyperfine lines with a splitting of 13 ± 0.1 gauss.[4] The line widths of the radicals produced from hydroperoxide and cobalt salt are based on this standard. Solutions containing the hydroperoxide and cobalt salt were mixed and immediately introduced into a Pyrex tube which was placed in the e.s.r. spectrometer cavity.

Results

Effect of Hydrogen Atom Donors on Rate.—The rate of cobalt 2-ethylhexanoate catalyzed decomposition of *t*-butyl hydroperoxide in the presence of hydrogen atom donors is given in Table I. A smaller rate retardation was observed for cobalt acetate (2.60×10^{-2} *M*) decomposition of *t*-butyl hydroperoxide (0.168 *M*) in acetic acid with 2.50 *M* cumene at 60°. In acetic acid solvent, the rate is retarded by a factor of 3.27 with 2.50 *M* cumene compared with 12.2 in the chlorobenzene solvent (Table I). A plot of k_{obsd} *vs.* cumene concentration (Figure 1) shows that the rate is significantly changed by cumene concentration up to about 1.5 *M*. Higher cumene concentrations have little effect on k_{obsd}.

TABLE I

EFFECT OF HYDROGEN ATOM DONATING AGENTS ON REACTION RATE[a]

RH	$k_{obsd} \times 10^4$, sec.$^{-1}$	Expected/obsd. retardation[b]
(Chlorobenzene)	10.1	...
Cumene	0.829	100
Ethylbenzene	0.912	45.5[c] 18.0[d]
Toluene	1.82	15.2
Mesitylene	0.820	11.2
t-Butylbenzene	6.73	1.37
Cyclohexane	5.40	1.28
n-Heptane	8.51	0.970[e] 0.610[f]

[a] [Co(2-ethylhexanoate)$_2$] = 2.58×10^{-3} *M*, [*t*-C_4H_9OOH] = 6.66×10^{-2} *M*, [RH] = 2.50 *M*, in chlorobenzene, $t = 0°$. [b] Expected retardation assumes each hydrogen is as easily abstracted as the tertiary cumene hydrogen. [c] Corrected to 2 hydrogens. [d] Corrected to 5 hydrogens. [e] Corrected to 10 hydrogens. [f] Corrected to 16 hydrogens.

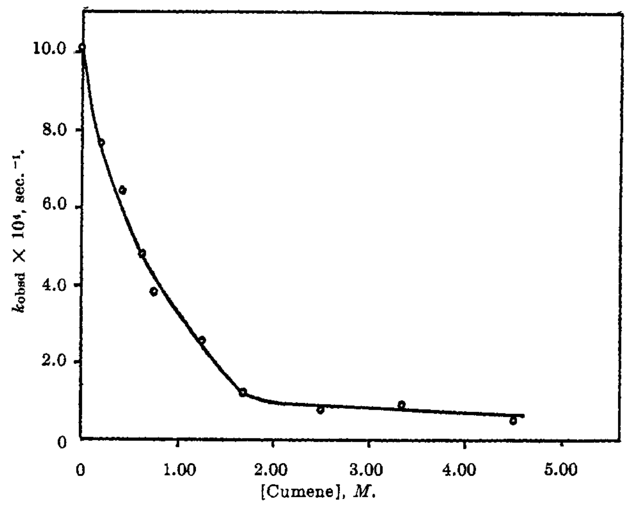

Figure 1.—Variation in rate of *t*-butyl hydroperoxide (6.66×10^{-2} *M*) decomposition by cobalt 2-ethylhexanoate (2.58×10^{-3} *M*) with added cumene at 0°.

Deuterium Isotope Effect.—A deuterium isotope effect (k_H/k_D) of 1.93 was observed at 0° with 6.77×10^{-2} *M* *t*-butyl deuterioperoxide and 5.20×10^{-3} *M* cobalt 2-ethylhexanoate. The calculated[5] normal maximum isotope effect at 0° is 12.3 using the hydroperoxide free O–H and O–D stretching frequencies of 3590 and 2650 cm.$^{-1}$, respectively. A kinetic isotope effect was not observed for the cobalt acetate catalyzed decomposition at 50° using acetic acid-*d* solvent. Under these conditions the per cent *t*-butyl deuterioperoxide is about 98%.[6] A normal maximum isotope effect at 50° is calculated[5] to be 7.95.

Electron Spin Resonance Spectra.—Hydrogen atom donors caused noticeable line-width changes in the electron spin resonance (e.s.r.) absorption resulting from cobalt salt catalyzed decomposition of *t*-butyl hydroperoxide. Poorer donors (*cf.* Table I) caused the greatest line broadening. In contrast, cumyl hydroperoxide decomposition does not show line broadening in cyclohexane. These results, obtained in chlorobenzene solvent, are given in Table II. Hyperfine structure was not observed in any spectrum. In comparison, the cobalt acetate catalyzed decomposition of *t*-butyl hydroperoxide in acetic acid showed a line width of 16 ± 2 gauss. No e.s.r. absorption was

TABLE II

EFFECT OF HYDROGEN ATOM DONORS ON E.S.R. LINE WIDTH

RH[a]	Hydroperoxide	Line width, gauss
(Chlorobenzene)	*t*-C_4H_9OOH[b]	18 ± 1[c]
Cumene	*t*-C_4H_9OOH[d]	12.1 ± 0.8[e]
Tetralin	*t*-C_4H_9OOH[f]	15.5 ± 0.7[g]
Toluene	*t*-C_4H_9OOH[h]	21.9 ± 1.4[i]
Cyclohexane	*t*-C_4H_9OOH[d]	24.5 ± 1.5[i]
n-Heptane	*t*-C_4H_9OOH[j]	28.9 ± 2.2[i]
(Chlorobenzene)	$C_6H_5C(CH_3)_2OOH$[d]	12.2 ± 0.6[i]
Cyclohexane	$C_6H_5C(CH_3)_2OOH$[k]	10.1 ± 0.8[i]

[a] 2.50 *M* in chlorobenzene. [b] 3.50×10^{-2} *M*. [c] [$Co(C_7H_{15}CO_2)_2$] = 3.23×10^{-5} *M*. [d] 5.56×10^{-2} *M*. [e] [$Co(C_7H_{15}CO_2)_2$] = 8.07×10^{-5} *M*. [f] 3.48×10^{-1} *M*. [g] [$Co(C_7H_{15}CO_2)_2$] = 1.29×10^{-3} *M*; at lower concentration, no signal was observed. [h] 5.51×10^{-2} *M*. [i] [$Co(C_7H_{15}CO_2)_2$] = 1.63×10^{-4} *M*. [j] 5.62×10^{-2} *M*. [k] 5.67×10^{-2} *M*.

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(3) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

(4) G. E. Pake, J. Townsend, and S. J. Weisman, *Phys. Rev.*, **85**, 682 (1952).

(5) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(6) For a discussion of *t*-butyl hydroperoxide exchange rate with acetic acid-*d*, see part I: W. H. Richardson, *J. Am. Chem. Soc.*, **87**, 247 (1965).

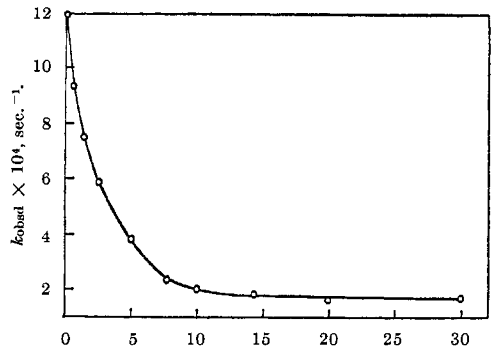

Figure 2.—Effect of 2-ethylhexanoic acid on the decomposition rate of *t*-butyl hydroperoxide (6.66×10^{-2} *M*) by cobalt 2-ethylhexanoate (5.18×10^{-3} *M*) in chlorobenzene with 2-ethylhexanoic acid at 0°.

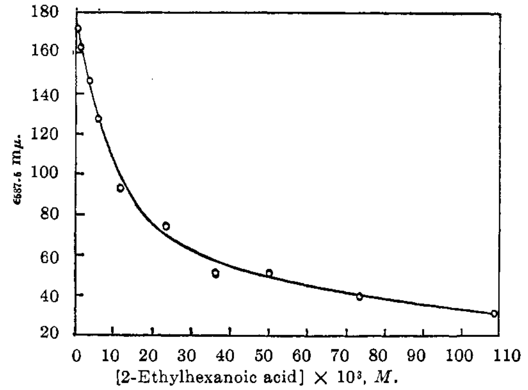

Figure 3.—Effect of 2-ethylhexanoic acid on the molar extinction coefficient of cobalt(II) 2-ethylhexanoate. The molar extinction coefficient is calculated on the basis of the formula weight.

noted for cobalt acetate (0.104 *M*) in acetic acid or for cobalt(II) 2-ethylhexanoate in chlorobenzene (9.70×10^{-6} to 1.5 *M*).

Variation in π Basicity of Aromatic Solvents.—The data of Tables I and II indicate the presence of radical intermediates; however, no evidence for radical–π-aromatic complexes[7] was detected when π basicity of aromatic solvents was varied (Table III). A change in e.s.r. absorption line width might also be expected from radical–π-aromatic complexes with varying aromatic solvents. The line width was the same in benzene, chlorobenzene, benzotrifluoride, and anisole. Rate retardation ($k_{obsd} = 0.555 \times 10^{-4}$ sec.$^{-1}$, [t-C_4H_9OOH] $= 5.12 \times 10^{-2}$ *M*) was observed with anisole, but this is most likely due to cobalt salt–anisole–oxygen complexation similar to that observed with carboxylic acids (below).

TABLE III

VARIATION OF π-BASICITY OF AROMATIC SOLVENT[a]

Solvent	$k_{obsd} \times 10^4$, sec.$^{-1}$
C_6H_6-C_6H_5Cl[b]	3.46
C_6H_5Cl[c]	3.65
$C_6H_5CF_3$[c]	3.69

[a] [Co(2-ethylhexanoate)$_2$] $= 5.20 \times 10^{-4}$ *M*, t = 0°. [b] 98:2 (v./v.) to prevent freezing, [t-C_4H_9OOH] $= 2.54 \times 10^{-2}$ *M*. [c] [t-C_4H_9OOH] $= 6.66 \times 10^{-2}$ *M*.

Effect of 2-Ethylhexanoic Acid on Rate.—Addition of a carboxylic acid reduces the rate of cobalt 2-ethylhexanoate catalyzed decomposition of *t*-butyl hydroperoxide in chlorobenzene.[1a] The effect of 2-ethylhexanoic acid concentration on rate is shown in Figure 2. The rate ($k_{obsd} = 0.330 \times 10^{-4}$ sec.$^{-1}$) is further decreased only slightly at 348×10^{-3} *M* acid. Acetic acid causes a greater rate retardation. Under the same conditions as for Figure 2, but with 2.52×10^{-3} *M* acetic acid, k_{obsd} was 1.66×10^{-4} sec.$^{-1}$ compared to 5.85×10^{-4} sec.$^{-1}$ with the same concentration of 2-ethylhexanoic acid. Carboxylic acids also affect the spectrum of cobalt 2-ethylhexanoate, causing a decrease in the blue absorption and appearance of absorption at 525 mμ (pink) which is characteristic of octahedral cobalt(II). The decrease in absorption at 587.5 mμ (blue) with added 2-ethylhexanoic acid is shown in Figure 3. Acetic acid is considerably more effective in causing a decrease in blue absorption. With 11.5×10^{-3} *M* acetic acid and the same cobalt 2-ethylhexanoate concentration as Figure 3, the molar extinction coefficient was 29.4, compared to about 99 (from plot) with the same 2-ethylhexanoic acid concentration. Assuming there is an equilibrium (1) between uncomplexed (C) and acid-complexed (C·A) cobalt 2-ethylhexanoate, eq. 2 and 3 can be written

$$C + A \rightleftharpoons C{\cdot}A \qquad (1)$$

where A is acid, y is the fraction of uncomplexed salt C, $\epsilon_{587.5}$ is the observed molar extinction coefficient,

$$\epsilon_{587.5} = y\epsilon_C + (1 - y)\epsilon_{C \cdot A} \qquad (2)$$

ϵ_C and $\epsilon_{C \cdot A}$ are the coefficients for A and C·A. Fitting the data of Figure 3 to eq. 2 and 3b give $K = 91$ ($r^2 =$

$$K = \frac{[C{\cdot}A]}{[C][A]} \qquad (3a)$$

$$K = \frac{(1 - y)}{y[A]} \qquad (3b)$$

0.993), where r is the correlation coefficient. Similar procedures have been described previously.[8] Unfortunately, as the observed molar extinction coefficients decrease slowly with time, this is only an approximate value. An attempt to fit the data to equilibrium 4 gave an extremely poor correlation ($r^2 = 0.409$).

$$C + 2A \rightleftharpoons C{\cdot}2A \qquad (4)$$

Products.—Previously,[1a] it was found that *t*-butyl alcohol and oxygen were the major reaction products of cobalt 2-ethylhexanoate catalyzed decomposition of *t*-butyl hydroperoxide in chlorobenzene. The minor products were di-*t*-butyl peroxide and acetone. Product distribution is relatively unaffected by the presence of cumene (Table IV). Prior results indicate that product yields do not vary appreciably with changing cobalt or hydroperoxide concentrations.[1a]

Discussion

Peroxy Radical Intermediates. A. Effect of Hydrogen Atom Donors.—A mechanism was presented[1a,2] for cobalt salt catalyzed decomposition of *t*-butyl hydroperoxide where the major products resulted from eq. 5.

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[7] (a) G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959); *J. Am. Chem. Soc.*, **80**, 4987 (1958); (b) C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959); (c) C. Walling and A. Padwa, *ibid.*, **85**, 1597 (1963); (d) W. V. Sherman and G. H. Williams, *J. Chem. Soc.*, 1442 (1963).

[8] J. Y-P. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953) K. B. Wiberg and T. Mill, *ibid.*, **80**, 3022 (1958).

TABLE IV

EFFECT OF CUMENE IN CHLOROBENZENE ON PRODUCT YIELDS

		% yield				
Cumene concn., *M*	Temp., °C.	*t*-C_4H_9OH	(*t*-$C_4H_9O)_2$[a]	CH_3COCH_3	Dicumyl	O_2
0[b]	35	63	13	3.4	...	(74)[c]
0.835[d]	23	76	9.3	2.2	...	(83)[e]
5.93[f]	35	71	14	0	8.3[g]	...

[a] Based on 2.0 *t*-C_4H_9OOH required for 1.0 (*t*-$C_4H_9O)_2$. [b] $[Co(C_7H_{15}CO_2)_2] = 1.29 \times 10^{-4}$ *M*, $[t\text{-}C_4H_9OOH]_0 = 6.72 \times 10^{-2}$ *M*. [c] $[Co(C_7H_{15}CO_2)_2] = 6.45 \times 10^{-2}$ *M*, $[t\text{-}C_4H_9OOH]_0 = 33.4 \times 10^{-2}$ *M*. [d] $[Co(C_7H_{15}CO_2)_2] = 25.8 \times 10^{-4}$ *M*, $[t\text{-}C_4H_9OOH]_0 = 6.94 \times 10^{-2}$ *M*. [e] $[t\text{-}C_4H_9OOH]_0 = 67.0 \times 10^{-2}$ *M*. [f] $[Co(C_7H_{15}CO_2)_2] = 31.0 \times 10^{-4}$ *M*, $[t\text{-}C_4H_9OOH]_0 = 6.66 \times 10^{-2}$ *M*. [g] Based on 2.0 *t*-C_4H_9OOH required for 1.0 dicumyl.

Cobalt 2-ethylhexanoate was dimeric and cobalt–hydroperoxide complexes were suggested as shown in eq. 5.[1a] Peroxy radicals can be regenerated by cobalt(III)–hydroperoxide reactions. Evidence for peroxy radicals is required to substantiate the proposed mechanism.

$$ROOH + Co^{II}_2 \rightleftharpoons Co^{II}_2(ROOH) \tag{5a}$$

$$ROO\cdot + Co^{II}_2(ROOH) \longrightarrow RO^- + ROH + Co^{III}Co^{II} + O_2 \tag{5b}$$

Inhibition of hydroperoxide decomposition by hydrogen atom donors, such as cumene, unmistakably points to peroxy radical intermediates. Donors which undergo hydrogen atom abstraction by peroxy radicals most readily cause the greatest inhibition in hydroperoxide decomposition. The order of inhibition is consistent, in large part, with autoxidation of these donors.[9] Rate retardation of *t*-butyl hydroperoxide decomposition with cobalt 2-ethylhexanoate decreases in the order cumene > ethylbenzene > toluene > *t*-butylbenzene > *n*-heptane.

Rate retardation is also observed with cobalt acetate decomposition of *t*-butyl hydroperoxide in acetic acid with 2.50 *M* cumene. The magnitude is considerably less ($k_0/k_{\text{cumene}} = 3.27$) than for decomposition with cobalt 2-ethylhexanoate in chlorobenzene ($k_0/k_{\text{cumene}} = 12.2$). This suggests peroxy radical reactions are more important in the latter system. In support of this is the finding that *t*-butyl alcohol yields are higher with cobalt 2-ethylhexanoate than cobalt acetate (*cf.* eq. 5b).[1a]

The effect of hydrogen atom donors (R'H) on the rate of hydroperoxide decomposition can be explained by two mechanisms, (a) eq. 5–9 and (b) eq. 6, 7, and 10.

$$ROOH + Co^{III}Co^{II} \longrightarrow ROO\cdot + Co^{II}_2(H^+) \tag{6}$$

$$ROO\cdot + R'H \longrightarrow ROOH + R'\cdot \tag{7}$$

$$R'\cdot + O_2 \longrightarrow R'OO\cdot \tag{8}$$

$$R'OO\cdot + R'H \longrightarrow R'OOH + R'\cdot \tag{9}$$

According to mechanism a, hydroperoxide is generated from R'H, thus decreasing the over-all rate of hydroperoxide disappearance. Rate retardation by mechanism b depends on no net change in reactants. A clear choice cannot be made between these two mechanisms, although it was found by g.l.c. analysis that dimethylphenylcarbinol was produced in the presence of cumene. The carbinol is an expected product of cobalt salt catalyzed decomposition of cumene hydroperoxide (R'OOH). The significant point is that both mechanisms require peroxy radical intermediates.

$$R'\cdot + Co^{II}_2(H^+) \longrightarrow R'H + Co^{III}Co^{II} \tag{10}$$

There is no evidence for *t*-butyl cumyl peroxide (I) formation when *t*-butyl hydroperoxide was decomposed in the presence of cumene under our conditions. Yields of *t*-butyl alcohol did not decrease and g.l.c. analysis did not indicate the presence of the mixed peroxide. When a dilute cobalt 2-ethylhexanoate solution (0.5 mole %) is slowly added to a cumene solution of *t*-butyl hydroperoxide at 60°, formation of peroxide I has been reported.[10] Under these conditions, cobalt–hydroperoxide complex concentration should be reduced and unimolecular decomposition of the complex will be favored (*e.g.*, eq. 11). Further reactions, incorporating hydrogen atom abstraction by alkoxy radicals from cumene, will give I. Bimolecular reactions between peroxy radicals and the complexes (5b), which do not lead to I are thwarted.

$$Co^{II}_2(ROOH) \longrightarrow Co^{III}Co^{II}(OH^-) + RO\cdot \tag{11}$$

B. E.s.r. Spectra.—The e.s.r. signals observed during catalytic decomposition of *t*-butyl and cumyl hydroperoxide are most consistently assigned to peroxy radicals. The presence of peroxy radicals is demonstrated above (part A). Furthermore, the line widths of the spectra (Table II) are reasonably consistent with previous reports for these peroxy radicals. Cumyl peroxy radicals, produced from autoxidation of cumene, are reported to have a line width of 11 gauss.[11] The reaction of *t*-butyl hydroperoxide with cerium(IV), which is proposed to give peroxy radicals, shows a line width of 14 gauss.[12]

It was suggested[13] that the e.s.r. signal observed in cupric phenanthroline diacetate decomposition of *t*-butyl hydroperoxide is due to the copper oxy radical Cp(O·), where Cp is cupric phenanthroline. It seems unlikely that the e.s.r. signal we observe is due to cobalt oxy radicals since cumyl and *t*-butyl hydroperoxides show different line widths with cobalt salt decomposition (12 *vs.* 18 gauss). The same line width would be expected in both reactions if the signal was due to a cobalt oxy radical.

Interestingly, preliminary results show that the line width is inversely proportional to the ease of hydrogen atom abstraction for *t*-butyl hydroperoxide decomposition. Poorer donors cause increased line widths (Table II). This was not observed with cumyl hydroperoxide in the presence of cyclohexane. From our present data, the origin of line broadening cannot be assigned. It is possible that peroxy radical–hydrocarbon complexes (ROO···H···R) are responsible.[14] These complexes have been suggested to avoid proposing dialkyl peroxide formation *via* a bimolecular reaction between peroxy and alkyl radicals.[10]

C. Question of Peroxy Radical–π-Aromatic Complexes.—There is no evidence from our data to suggest

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(9) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

(10) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 72 (1959).

(11) J. R. Thomas, *J. Am. Chem. Soc.*, **85**, 593 (1963).

(12) W. T. Dixon and R. O. C. Norman, *Nature*, **196**, 891 (1962).

(13) H. Berger and A. F. Bickel, *Trans. Faraday Soc.*, **57**, 1325 (1961).

(14) Alternatively, a referee has suggested that changes in the cobalt(II)–(III) ratio with varying hydrogen atom donors may cause line-width variation due to spin–spin relaxation. See, D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworth and Co. (Publishers) Ltd., London, 1958, p. 120.

peroxy radical–π-aromatic complexes. Variation in π-electron density of the aromatic solvent caused no change in the rate of hydroperoxide decomposition (Table III). Also, no change in e.s.r. line width was observed when the π-electron density of the solvent was varied as long as the solvent was a poor hydrogen donor. No evidence for these complexes was found in the autoxidation studies either.[15] It is possible that the energy difference between free and π-aromatic complex peroxy radicals is too small to be detected.

Significance of the Deuterium Isotope Effect.—A small, but detectable, isotope effect ($k_H/k_D = 1.93$ at 0°) was observed with cobalt 2-ethylhexanoate catalysis. In contrast, no isotope effect was noted with cobalt acetate catalysis in acetic acid. This may be correlated with a higher cobalt(III)–(II) ratio in the former reaction. This means the activation energy of cobalt(III) to (II) reactions are increased relative to cobalt(II) to (III) reactions in chlorobenzene. Increasing the activation energy will increase the isotope effect.[5,16] It seems most reasonable that the isotope effect is associated with the formation of peroxy radicals.

Formation of Di-*t*-butyl Peroxide.—Since the yield of di-*t*-butyl peroxide is about the same in the presence and absence of cumene (Table IV), the formation of the peroxide solely by reaction 12 is unlikely. In

$$2RO\cdot \longrightarrow ROOR \qquad (12)$$

support of this, the formation of acetone, which results from fragmentation of *t*-butoxy radicals, is reduced in the presence of cumene. This shows that *t*-butoxy radicals readily undergo hydrogen atom abstraction with cumene. This leaves reactions 13 and 14 as the major paths for di-*t*-butyl peroxide formation in the cobalt 2-ethylhexanoate catalyzed decomposition of *t*-butyl hydroperoxide. Cage alkoxy radicals are sug-

$$ROO\cdot + Co^{III}Co^{II}(ROOH) \longrightarrow ROOR + O_2 + Co^{II}{}_2 + H^+ \qquad (13)$$

$$2ROO\cdot \longrightarrow \overline{2RO}\cdot + O_2 \qquad (14a)$$

$$\overline{2RO}\cdot \longrightarrow ROOR \qquad (14b)$$

gested which may combine as in 14b or diffuse to give free alkoxy radicals. Of these two modes (13 and 14) for peroxide formation, 13 seems more likely in this system since 14b requires a bimolecular reaction between two radicals in the presence of a good hydrogen atom donor. This conclusion is also consistent with the kinetics of the cobalt 2-ethylhexanoate catalyzed decomposition.[1a]

Effect of 2-Ethylhexanoic Acid on Rate.—Changes in the spectrum of cobalt(II) 2-ethylhexanoate with added 2-ethylhexanoic acid (Figure 3) indicate cobalt coordination sites are being occupied by the acid. The effect of acid on rate of hydroperoxide decomposition (Figure 2) qualitatively agrees with this proposal.

A quantitative correlation between changes in rate and molar extinction coefficients is not found, assuming cobalt–acid complexes are catalytically inactive. The amount of uncomplexed cobalt salt can be determined from equation 3b. From this, the calculated rate constants are determined from a plot of the rate constant without added acid *vs.* cobalt concentration.[1a] A comparison of the calculated and observed rate constants are given in Table V. The observed rate constants are considerably smaller than predicted when it assumed that added acid serves only to block cobalt ligand sites. Hydrogen bonding to the hydroperoxide and/or peroxy radical by the acid may be responsible for the discrepancy between the observed and calculated rate constants in Table V.[1a,15]

TABLE V

OBSERVED AND CALCULATED RATE CONSTANTS IN THE PRESENCE OF 2-ETHYLHEXANOIC ACID

[Acid] × 10^3, *M*	$k_{obsd} \times 10^4$, sec.$^{-1}$ [a]	$k_{calcd} \times 10^4$, sec.$^{-1}$ [b]
0	11.95	11.95
0.53	9.30	11.6
1.38	7.49	11.3
2.50	5.88	10.9
5.00	3.83	10.2
7.70	2.33	9.5
10.0	2.08	9.0
20.0	1.63	7.5
30.0	1.63	6.6

[a] $[Co(C_7H_{15}Co_2)_2] = 5.18 \times 10^{-3}$ *M*, $[t\text{-}C_4H_9OOH] = 6.66 \times 10^{-2}$ *M*, $t = 0°$. [b] Based on equilibrium 3.

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[15] D. G. Hendry and G. A. Russell, *J. Am. Chem. Soc.*, **86**, 2368 (1964); C. Walling and P. J. Wagner, *ibid.*, **86**, 3368 (1964).

[16] This assumes the reaction is proceeding to a more symmetrical activated complex. See F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).