

The Cobalt(II) Decomposition of *t*-Butyl Hydroperoxide

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Cobalt(II) chelated with ethylenediaminetetraacetic acid (EDTA) is irreversibly oxidized to cobalt(III) by *t*-butyl hydroperoxide in 50% aqueous acetic acid. This allows an investigation of the reaction which may accompany the cobalt(II) to -(III) change in the catalytic decomposition of hydroperoxide. The observed rate law is: $v = k_2[\text{Co(II)}][t\text{-C}_4\text{H}_9\text{OOH}] + k_3[\text{Co(II)}]^2[t\text{-C}_4\text{H}_9\text{OOH}]$. The first term in the rate law is proposed to result from a unimolecular decomposition of a cobalt(II) hydroperoxide complex, while the second term is suggested to arise from a bimolecular reaction between the cobalt(II) hydroperoxide complex and another cobalt(II) species. Both reactions are primarily one-electron change processes. The *t*-butoxy radicals, which result from these reactions, undergo primarily fragmentation to give acetone and methyl radicals. To a lesser extent the *t*-butoxy radicals give *t*-butyl alcohol. The methyl radicals give solely methane by hydrogen atom abstraction. Induced decomposition of *t*-butyl hydroperoxide by these radical intermediates is ruled out. Alternative mechanisms for hydroperoxide decomposition are discussed in the light of these results.

Introduction

Hydroperoxide decomposition by cobalt salts has been the subject of several papers.¹ However, the mechanism of this reaction is still obscure. Besides the intrinsic interest of the reaction, its importance is evident in cobalt salt catalyzed autoxidation.²

The most complete study to date has been made by Dean and Skirrow^{1b} for the decomposition of *t*-butyl hydroperoxide by cobalt acetate in acetic acid. However, the marriage of their kinetic data to a mechanism was not completely satisfying. The catalytic reaction is no doubt complicated by simultaneous cobalt(II) and -(III) reaction sequences. A more definitive mechanism might be obtained by studying the cobalt(II) and -(III) reaction sequences separately. We have initiated a mechanistic study of cobalt salt decomposition of hydroperoxides with an investigation of the cobalt(II) to -(III) change effected by *t*-butyl hydroperoxide. This change can be studied without accompanying cobalt(III) to -(II) changes by employing cobalt(II) chelated with ethylenediaminetetraacetic acid

(EDTA). This paper constitutes part I of a series of three papers concerned with cobalt salt catalyzed decomposition of *t*-butyl hydroperoxide. Parts II and III will appear later.

Experimental

***t*-Butyl Hydroperoxide.** *t*-Butyl hydroperoxide (90% Wallace and Tiernan, Lucidol Division) was purified by the azeotropic distillation method of Bartlett and Hiatt.³ The purified *t*-butyl hydroperoxide was shown to be 100% pure by the iodometric titration described below.

Dipotassium Ethylenediaminetetraacetatocobaltate (II). To 50 g. (0.510 mole) of potassium acetate and 25.0 g. (0.100 mole) of cobalt acetate tetrahydrate in 240 ml. of distilled water was added 29.6 g. (0.101 mole) of EDTA (Eastman White Label). The solution was stirred for 1 hr. and then partially concentrated on a rotary evaporator to give a precipitate. A minimum amount of water was added to dissolve the solid, and ethanol was added to the hot solution until solid began to precipitate. The mixture was cooled, filtered, and the solid was washed with six 40-ml. portions of absolute ethanol and dried at 100° (30 mm.), yielding 30.8 g.

Anal. Calcd. for $\text{K}_2[\text{Co}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)] \cdot 1.5\text{H}_2\text{O}$: C, 26.6; H, 3.27; N, 6.2. Found: C, 27.0; H, 4.0; N, 6.1. The empirical formula used for the calculation is based on the disodium salt.⁴

Solvents. The solvent used was 50 vol. % aqueous acetic acid (Baker and Adamson, reagent grade), with the exception of experiments in deuterated solvent. The complex cobalt salt was insoluble in 50% aqueous acetic acid; however, solution was effected by dissolving the salt in water and then adding an equal amount of acetic acid. The deuterated solvent was prepared from equal volumes of deuterium oxide (Bio-Rad Lab., 99.9% deuterium) and acetic-*d*₁ acid.

Acetic-*d*₁ Acid. To a solution of 97.6 g. (0.957 mole) of acetic anhydride (Baker's reagent grade) and a drop of perchloric acid was added dropwise 19.13 g. (0.957 mole) of deuterium oxide. After the exothermic reaction subsided, the acetic acid was distilled over the range 117.5–118.0° (uncor.). The acetic acid was further purified by distillation from potassium dichromate and sodium acetate. The perchloric acid was partially deuterated by distilling a solution of 0.2 ml. of 70% perchloric acid and 1.0 ml. of deuterium

(1) For example, (a) J. A. Bigot, *Rec. trav. chim.*, **80**, 825 (1961); (b) M. H. Dean and G. Skirrow, *Trans. Faraday Soc.*, **54**, 849 (1958); (c) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 72 (1959); (d) M. S. Kharasch, P. Pauson, and W. Nudenberg, *ibid.*, **18**, 322 (1953); (e) M. S. Kharasch, A. Fono, W. Nudenberg, and B. Bischof, *ibid.*, **17**, 207 (1952); (f) H. Kropf, *Ann.*, **637**, 111 (1960).

(2) (a) C. E. H. Bawn, *Discussions Faraday Soc.*, **14**, 181 (1953); (b) E. T. Denisov and E. M. Emanuel, *Russ. Chem. Rev.*, **29**, 645 (1960).

(3) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).
(4) D. T. Sawyer and P. J. Paulsen, *ibid.*, **81**, 816 (1959).

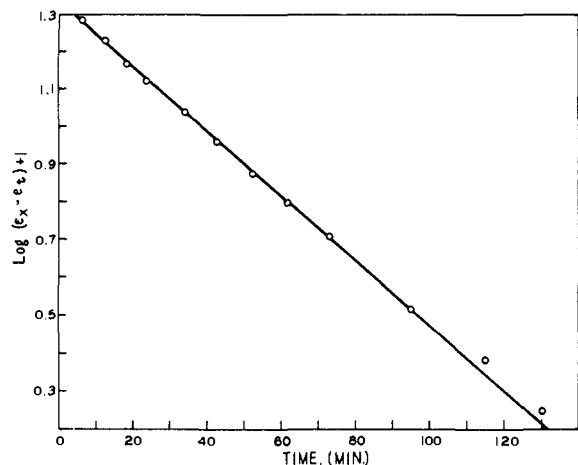


Figure 1. First-order rate plot at 45.25°; initial concentrations: $[K_2Co^{II}EDTA]_0 = 7.00 \times 10^{-3} M$, $[t-C_4H_9OOH]_0 = 1.11 M$, $[NaClO_4] = 0.112 M$; first-order rate constant is $3.33 \times 10^{-4} \text{ sec.}^{-1}$ and the half-life is 37 min.

oxide to give 0.5 ml. of partially deuterated perchloric acid as pot residue.

Thermal Decomposition of Di-*t*-butyl Peroxide in 50% Aqueous Acetic Acid. The procedure was analogous to that of Williams and co-workers.⁵ A mixture of $9.97 \times 10^{-2} \text{ g.}$ (6.83×10^{-4} mole) of di-*t*-butyl peroxide (RAM Corp.) and 2.076 g. of 50% aqueous acetic acid was heated for 7.5 hr. at 135° in a sealed tube which had been evacuated at Dry Ice-acetone temperature. The products were analyzed by vapor phase chromatography (v.p.c.) as described below. Analysis indicated a 62% yield of acetone and a maximum of 0.34% yield of *t*-butyl alcohol. Since di-*t*-butyl peroxide was found to contain 2.5% *t*-butyl alcohol by v.p.c. analysis, there may be no *t*-butyl alcohol produced.

Product Analyses. All analyses for condensable products were made by v.p.c., using a 10-ft., 0.25-in. column packed with 20 wt. % polypropylene glycol on firebrick. Column and injector temperatures were maintained no higher than 85°. For quantitative analysis, a weighed mixture of *n*-butyl alcohol and the sample was analyzed by v.p.c. Areas were corrected by reference to the v.p.c. record of a mixture containing known weights of the expected components and *n*-butyl alcohol. Retention times of known compounds were used to identify reaction products.

Gaseous products were collected in a gas buret. The system was previously evacuated and pressurized with helium. This procedure was repeated until no oxygen or nitrogen could be detected with a Fisher gas partitioner. The pressure of the system was maintained at 1 atm. by adjusting a variable mercury head. Gas samples were analyzed after completion of reaction with a Consolidated Model 101 (modified) mass spectrometer. A sensitivity correction was applied to give corrected percentages of the components.

The cobalt(III)-EDTA complex was isolated from a reaction mixture where the initial concentration of the cobalt(II) complex was $4.44 \times 10^{-2} M$ and *t*-butyl hydroperoxide was $1.92 \times 10^{-2} M$. The reaction mixture was concentrated to dryness on a rotary

evaporator at 45°. Remaining acetic acid was azeotropically distilled from the mixture with *n*-hexane. The residual solid was recrystallized from water-methanol to give 1.60 g. (93.5% yield) of the cobalt(III) complex. The infrared spectrum of the isolated salt was identical with an authentic sample of the salt, with the exception of a weak absorption at 1620 cm.^{-1} which may be due to a small amount of potassium acetate. The authentic cobalt(III)-EDTA complex was prepared by the method of Dwyer and Garvan.⁶

Kinetic and Stoichiometric Methods. The rate of appearance of cobalt(III)-EDTA, as determined by spectral means, was the primary kinetic method. Aliquots were withdrawn from the reaction flask, which was thermostated between $35 \pm 0.02^\circ$ and $65 \pm 0.05^\circ$. Spectra were measured on a Cary 10-11 spectrophotometer. If the rate was slow, the spectrum of the aliquot was measured immediately. If the rate was rapid, the aliquots were quenched by cooling in Dry Ice-acetone. After all the aliquots were taken, each aliquot was warmed until complete solution resulted (*ca.* 20°), and the spectrum was immediately measured. At high initial cobalt(II) concentration ($4.44 \times 10^{-2} M$), a band at $615 \text{ m}\mu$ was used. At this concentration, the band did not follow Beer's law, so a working curve of per cent cobalt(III) vs. the molar extinction coefficient was used. At lower cobalt concentrations (0.4 to $10 \times 10^{-3} M$), a band at $383 \text{ m}\mu$, which obeyed Beer's law, was used to determine cobalt(III) concentration. The reactions were conducted under nitrogen. Ionic strength was maintained constant with sodium perchlorate when the cobalt salt concentration was varied. Kinetics were usually measured through about three half-lives. Figure 1 shows an example of a rate plot.

Reaction rates were also measured by the rate of *t*-butyl hydroperoxide disappearance and by the rate of gas evolution. The former method was used to determine stoichiometry with regard to cobalt(II) *t*-butyl hydroperoxide. The rate of *t*-butyl hydroperoxide disappearance was measured iodometrically. An aliquot was added to 2 ml. of an aqueous 4.8 *M* potassium iodide solution and then 20 ml. of acetic acid was added. The flask was swept with nitrogen and stoppered. After standing for 10 min., 100 ml. of water was added, and the solution was titrated with standard sodium thiosulfate solution. Blanks were determined containing varying amounts of cobalt(III)-EDTA. The rate of gas evolution was determined in a thermostated flask which was agitated by a wrist-action shaker at about 200 cycles per minute.

The stability of cobalt(II)-EDTA in 50% aqueous acetic acid, in the absence of *t*-butyl hydroperoxide, is more than adequate. After 670 min. at 60° and an additional 740 min. at 35°, a maximum of 1.2% cobalt(III) was produced when the cobalt concentration was $4.51 \times 10^{-2} M$. With cobalt(II) acetate ($4.70 \times 10^{-2} M$) and *t*-butyl hydroperoxide ($5.83 \times 10^{-2} M$) at 60°, the iodometric titer was constant over 700 min. This demonstrates that EDTA-complexed cobalt(II) is responsible for reaction with *t*-butyl hydroperoxide and not cobalt acetate which may be formed by ligand exchange. It was also found that *t*-butyl hydroperoxide ($5.76 \times 10^{-2} M$) in 50% aqueous acetic acid

(5) A. L. Williams, E. A. Oberright, and J. W. Brooks, *J. Am. Chem. Soc.*, **78**, 1190 (1956).

(6) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 2955 (1959).

was stable for 375 min. at 60° plus an additional 900 min. at 35°.

*Calculation of the Amount of *t*-Butyl Hydroperoxide (ROOH) Consumed by the Second- and Third-Order Reactions.* Considering $d[\text{Co(II)}]/dt = -d[\text{ROOH}]/dt = k_2[\text{Co(II)}][\text{ROOH}] + k_3[\text{Co(II)}]^2[\text{ROOH}]$, let x = amount of ROOH consumed in time t , then $2x$ = amount of Co(II) consumed in time t . Also, let x and x_2 equal the amount of ROOH consumed in time t by the second- and third-order reactions. Initial concentrations of Co(II) and ROOH are given by a and b . With $a = 2b$, eq. i results and, since $dx/dt = (x_1 + x_2)/dt$, eq. ii follows. Dividing ii by i gives eq. iii.

$$\frac{dx}{dt} = 2k_2(b - x)^2 + 4k_3(b - x)^3 \quad (\text{i})$$

$$\frac{dx_1}{dt} = 2k_2(b - x)^2 \quad (\text{ii})$$

$$\frac{dx_1}{dt} = \frac{k_2}{k_2 + 2k_3(b - x)} \quad (\text{iii})$$

Integrating iii and recognizing that $x_1 = 0$ when $x = 0$, gives eq. iv

$$x_1 = \frac{k_2}{2k_3} \ln \left[\frac{k_2 + 2k_3b}{k_2 + 2k_3(b - x)} \right] \quad (\text{iv})$$

At 100% conversion, if x and $b = 1.82 \times 10^{-2} M$ (this calculation approximates entry one in Table I), then $x_1 = 7.60 \times 10^{-3}$ mole and $x_2 = 10.6 \times 10^{-3}$ mole. Thus the per cents of ROOH consumed at 100% reaction by second- and third-order reactions are 41.8 and 58.2%, respectively.

Results

Stoichiometry. Figure 2 shows the results of a stoichiometric determination at 60°. The per cent decay of *t*-butyl hydroperoxide is based on the stoichiometric ratio of one *t*-butyl hydroperoxide/two cobalt(II)-EDTA and is expressed in eq. 1. The subscript mole % decay of $t\text{-C}_4\text{H}_9\text{OOH} =$

$$2 \left[\frac{[t\text{-C}_4\text{H}_9\text{OOH}]_0 - [t\text{-C}_4\text{H}_9\text{OOH}]_t}{[\text{K}_2\text{Co}^{\text{II}}\text{EDTA}]_0} \right] \times 10^3 \quad (1)$$

zero refers to initial concentrations while the subscript t refers to the concentration at a given time. A duplicate set of measurements resulted in the same stoichiometry. As seen from Figure 2, the stoichiometric ratio of 1:2 for *t*-butyl hydroperoxide, $\text{K}_2\text{Co}^{\text{II}}\text{EDTA}$, holds to about 70% reaction. With further reaction, the apparent per cent of cobalt(III) rapidly drops and appears to level off at 44.5% cobalt(III); however, 94% $\text{KCo}^{\text{III}}\text{EDTA}$ was isolated after completion of reaction. In contrast, the decay of *t*-butyl hydroperoxide proceeds uniformly to 86.5%. With the exception of the molar extinction coefficient, the spectrum of the reaction mixture when near completion is that of cobalt(III)-EDTA. Anomalous spectral behavior of cobalt(III)-EDTA with *t*-butyl hydroperoxide was noted when a solution of these two components in 50% aqueous acetic acid was allowed to stand at 60°. The concentrations were 5.18×10^{-2} and $5.82 \times 10^{-2} M$, respectively. The optical density of the solution decreased to a value corresponding to 35–38%

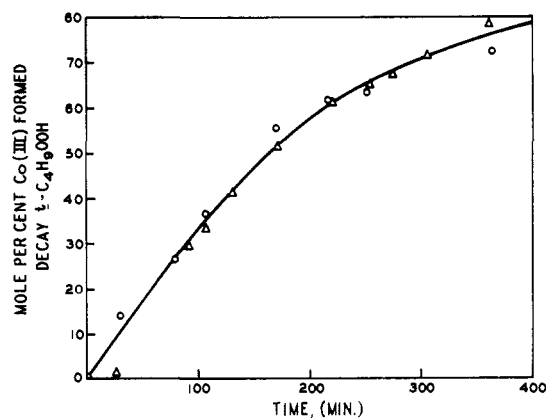


Figure 2. Stoichiometry of *t*-butyl hydroperoxide- $\text{K}_2\text{Co}^{\text{II}}$ -EDTA reaction: initial concentrations, $[t\text{-C}_4\text{H}_9\text{OOH}]_0 = 5.78 \times 10^{-2} M$ and $[\text{K}_2\text{Co}^{\text{II}}\text{EDTA}]_0 = 4.44 \times 10^{-2} M$; O, mole % Co(III) formation; Δ , mole % decay of *t*-butyl hydroperoxide; temperature 60.0°.

cobalt(III) while the iodometric titer for *t*-butyl hydroperoxide remained constant over the same period of time (1350 min.). Neither EDTA-complexed cobalt(II) or -(III) are reactive in the iodometric procedure.

Products. Table I lists the condensable products, yields, and reaction conditions. Neither methanol nor formaldehyde could be detected by v.p.c.

Table I. Condensable Products from the Reaction of *t*-Butyl Hydroperoxide with $\text{K}_2\text{Co}^{\text{II}}\text{EDTA}$ in 50% Aqueous Acetic Acid

$[\text{K}_2\text{Co}^{\text{II}}\text{EDTA}]_0$ $\times 10^2 M$	$[t\text{-C}_4\text{H}_9\text{OOH}]_0$ $\times 10^2 M$	Temp., °C.	Yield, % Acetone	<i>t</i> - C ₄ H ₉ OH	Acetone/ <i>t</i> - C ₄ H ₉ OH
4.44	1.815	60.0	73.3	16.5	4.4
4.44	1.915	35.1	85.2	19.6	4.4
8.36	4.18 ^a	60.0	8.9	74.8	0.12

^a With 1.75 *M* benzaldehyde added.

The yields of gaseous products are given in Table II.

Table II. Gaseous Products from the Reaction of *t*-Butyl Hydroperoxide with $\text{K}_2\text{Co}^{\text{II}}\text{EDTA}$ at 60° in 50% Aqueous Acetic Acid

$[\text{K}_2\text{Co}^{\text{II}}\text{EDTA}]_0$ $\times 10^2 M$	$[t\text{-C}_4\text{H}_9\text{OOH}]_0$ $\times 10^2 M$	Yield, %	
		Methane	Carbon dioxide ^a
4.44	5.64	68.5	7.2
0.700	20.0	58	...

^a Calculated with an assumed stoichiometry of 1 $\text{CO}_2/1 t\text{-C}_4\text{H}_9\text{OOH}$.

A significant feature is that no oxygen is produced. The maximum yield of ethane was 0.2%; however, this is within the background error of the mass spectrometer. No other gaseous products were observed. To determine the possible sources of hydrogen for the methyl radical, the reaction was carried out in 50% deuterium oxide-acetic- d_1 acid at 60°. The minimum ratio of methane/methane- d_1 was 21 when cobalt(II)-EDTA and *t*-butyl hydroperoxide concentrations were 4.53×10^{-2} and $6.87 \times 10^{-2} M$.

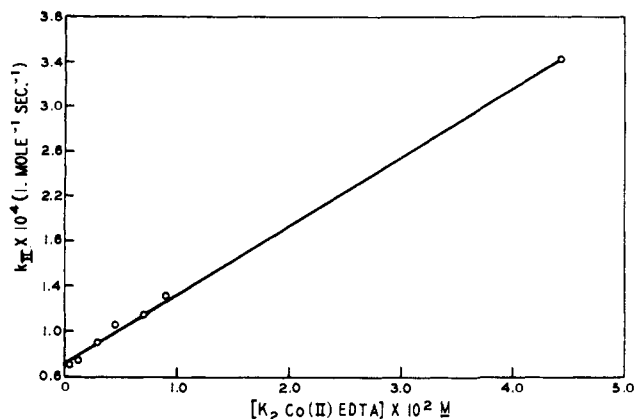


Figure 3. Order of EDTA-complexed cobalt(II) at 35.10°; initial *t*-butyl hydroperoxide concentration, 1.11 *M*.

The hydrogen atom donating ability of 50% aqueous acetic acid was determined at 135° for *t*-butoxy radicals using di-*t*-butyl peroxide as the source. The minimum ratio of acetone/*t*-butyl alcohol was 182 with an initial di-*t*-butyl peroxide concentration of 0.338 *M*. This shows the low tendency to donate hydrogen atoms by the solvent.

Kinetics. The second-order rate constants for gas evolution and hydroperoxide disappearance were 1.67×10^{-3} and 1.85×10^{-3} l. mole⁻¹ sec.⁻¹ at 70.0° with a cobalt(II)-EDTA²⁻ concentration of 4.44×10^{-2} *M*. The hydroperoxide concentrations were 5.58×10^{-2} and 5.78×10^{-2} *M*, respectively. The rate of hydroperoxide disappearance was shown to equal the rate of cobalt(III) appearance. Agreement among the three kinetic methods proves that the spectral method alone can be used to determine reaction rates.

The order in *t*-butyl hydroperoxide was determined at two cobalt(II) concentrations as shown in Table III. At both concentrations the reaction was first order in *t*-butyl hydroperoxide. As seen from Table III, the

Table III. Order in *t*-Butyl Hydroperoxide at 35.10°

$[K_2CO^{II}-EDTA]_0 \times 10^3 M$	$[t-C_4H_9-OH]_0, M$	$k_1 \times 10^5, sec.^{-1}$	$k_{11} \times 10^4, l. mole^{-1} sec.^{-1}$
44.4	0.111	3.84	3.43
44.4	0.223	7.95	3.57
44.4	0.500	16.0	3.20
44.4	0.800	28.5	3.56
44.4	1.11	37.3	3.36
			Av. $k_{11} = 3.42 \pm 0.12$
7.00	0.222	0.275	1.24
7.00	1.11	1.28	1.15
7.00	2.22	2.38	1.07
			Av. $k_{11} = 1.15 \pm 0.06$

reaction is of higher than first order in cobalt(II) (see k_{11}). However, a plot of the apparent second-order rate constant, k_{11} , vs. cobalt(II) concentration is linear (Figure 3). This corresponds to the rate law given by eq. 2. The slope of the line is k_3 and the intercept is k_2 . By method of least squares, the rate

$$\frac{d[Co(III)]}{dt} = k_2[Co(II)][t-C_4H_9OOH] + k_3[Co(II)]^2[t-C_4H_9OOH] \quad (2)$$

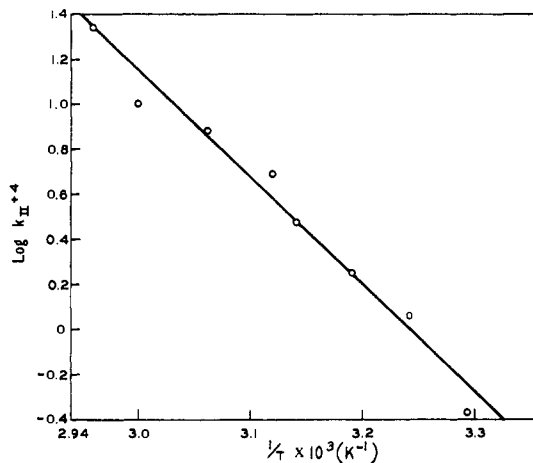


Figure 4. Effect of temperature on second-order rate constant; initial concentrations: $[K_2Co^{II}EDTA]_0 = 7.00 \times 10^{-3}$ *M*, $[t-C_4H_9OOH]_0 = 1.11$ *M*, and $[NaClO_4] = 0.112$ *M*.

constants, standard error, and correlation coefficient are calculated as $k_2 = 7.27 \pm 0.46 \times 10^{-5}$ l. mole⁻¹ sec.⁻¹, $r = 0.999$, and $k_3 = 6.10 \pm 0.12 \times 10^{-3}$ l.² mole⁻² sec.⁻¹, $r = 0.997$. The size of the error and correlation coefficient indicates that the rate law is valid over at least the range of cobalt(II) concentrations from 4.35×10^{-4} to 4.44×10^{-2} *M*.

The effect of temperature on reaction rate is shown in Figure 4. Using least squares, these data yield $E_a = 19.8 \pm 1.4$ kcal./mole for the over-all rate expression. At 50°, the heat of activation and entropy of activation are 19.2 ± 1.4 kcal./mole and -1.2 e.u.

Table IV indicates the effect of acid on reaction rate. This approach was not pursued in detail because of excessive scatter in the rate data.

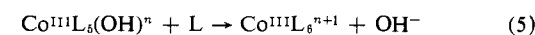
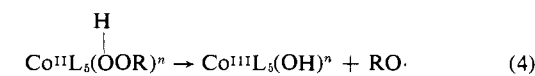
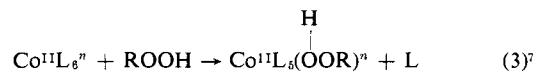
Table IV. The Effect of Perchloric Acid on the Rate of the *t*-Butyl Hydroperoxide- $K_2Co^{II}EDTA$ Reaction^a

$[HClO_4] \times 10^2 M$	$k_{11} \times 10^4, l. mole^{-1} sec.^{-1}$
0	1.15
1.39	0.864
5.73	0.535
10.0	0.311
13.3	0.166

^a $[K_2Co^{II}EDTA]_0 = 7.00 \times 10^{-3}$ *M*, $[t-C_4H_9OOH]_0 = 1.11$ *M*, 35.10°, and ionic strength constant at 0.133 *M* with sodium perchlorate.

Discussion

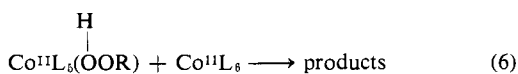
Interpretation of the Rate Law The second-order term in the rate expression (associated with k_2 of eq. 2) can be reasonably explained by the mechanism (eq. 3-5) where R is *t*-butyl. The L refers to any of the EDTA functional groups or to solvent molecules which are ligands. Thus, in this general scheme, L, if it is



part of an EDTA molecule, may not necessarily be dissociated from the complex ion. Although EDTA is a strongly bound chelating agent with a log K of 16.2 for association with cobalt(II),^{8a} ligand exchange may be rapid. Facile ligand exchange for the cobalt(II)-EDTA complex has been demonstrated by isotopic cobalt exchange. Long, Jones, and Burke^{8b} have reported the exchange to be complete in "a few minutes" at pH values of 2.44 and 5.14, where the complexed cobalt(II) and isotopic cobalt(II) concentrations were both $5 \times 10^{-3} M$. Thus, it seems reasonable that *t*-butyl hydroperoxide may enter a ligand site with some ease.

That alkoxy radicals are produced in the reaction is inferred by the effect of added benzaldehyde. Hydrogen atom abstraction from benzaldehyde by *t*-butoxy radicals has been demonstrated.⁹ The acetone/*t*-butyl alcohol ratio is shifted from 4.4 to 0.12 in the presence of 1.75 M benzaldehyde (Table I).

The third-order term (associated with k_3 of eq. 2) may be explained by two different schemes (eq. 6 and 7) as shown below. From the rate law one cannot differentiate between these two reaction paths. How-



ever, if there was evidence for a dimeric cobalt(II) species, there would be a basis for eq. 7. To check this, the visible spectrum of dipotassium ethylenediaminetetraacetatocobaltate(II) in 50% aqueous acetic acid was examined for adherence to Beer's law. There appears to be little or no change in the molar extinction coefficient over the concentration range 4.44×10^{-3} to $4.44 \times 10^{-2} M$. Unfortunately, the molar extinction coefficient is not large enough (14.3 at λ_{max} 506.7 $\mu\mu$) to permit an accurate determination of the optical density at lower concentrations. Providing the molar extinction coefficient of monomer and dimer is different, the visible spectrum gives no evidence for a monomer-dimer equilibrium.¹⁰ In addition, Sawyer and Paulsen⁴ have concluded that disodium ethylenediaminetetraacetatocobaltate(II) is a hexadentate complex by examining the infrared spectrum of this salt in potassium bromide pellets. A hexadentate complex implies a monomeric species. Although the dimer reaction scheme (eq. 7) cannot be ruled out, eq. 6 appears to be the more reasonable path.

Question of One- or Two-Electron Change in the Third-Order Reaction. Since two cobalt(II) ions are in the activated complex associated with the third-order term of eq. (2), either a one- or a two-electron change

(7) This mechanism assumes the concentrations of the hydroperoxide-cobalt(II) complexes are small compared to uncomplexed cobalt(II) in order to satisfy first-order dependence on hydroperoxide.

(8) (a) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, Special Publication No. 6, The Chemical Society, London, 1957, p. 76; (b) F. A. Long, S. S. Jones, and M. Burke, Brookhaven Conference Report BN-C-8, Chemical Conference No. 2, 1948, p. 106; *Chem. Abstr.*, **45**, 4166h (1951).

(9) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

(10) This method has been used to determine the equilibrium constant of the chromate-dichromate system; see J. Tong and E. King, *ibid.*, **75**, 6180 (1953).

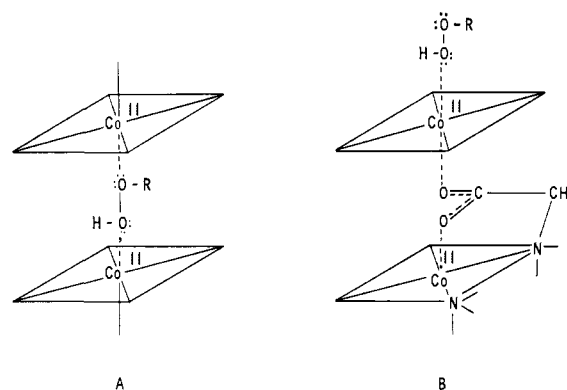


Figure 5.

could occur. In the former case, *t*-butyl hydroperoxide would give a *t*-butoxy radical and an hydroxide ion. In the latter case, a *t*-butoxide anion and an hydroxide ion would result. The second-order reaction, in contrast, can proceed only by a one-electron change. Since *t*-butoxy radicals will undergo fragmentation to give acetone and methyl radicals, it was hoped that the importance of the two-electron process could be determined, quantitatively by comparing the ratio of yields, *t*-butyl alcohol/acetone, to the per cent reaction *via* the second- and third-order reactions. At 100% reaction, it was calculated (Experimental) that 42% of the hydroperoxide was decomposed *via* the second-order reaction and 58% *via* the third-order reaction. The initial cobalt(II)/hydroperoxide ratio was assumed to be 2.0 for the calculation. In fact, the ratio was 2.44, so 58% reaction *via* the third-order reaction is a minimum value. If the third-order reaction proceeded solely by a two-electron change, giving *t*-butoxide anion, the minimum ratio of *t*-butyl alcohol/acetone would be 1.4 (= 58:42). However, a ratio of 19.6:85.2 = 0.23 was observed at 35°. This is a maximum ratio since the *t*-butoxy radical can be reduced or abstract a hydrogen atom in fast steps to give *t*-butyl alcohol. Thus, the one-electron process comprises the principal reaction course in the third-order reaction.

Additional evidence for a one-electron change is seen by the effect of changing cobalt(II) concentration on the product distribution. At lower cobalt concentrations, the third-order reaction will be less important. If the third-order reaction was a two-electron change, the yield of *t*-butyl alcohol should decrease with a simultaneous increase in yield of one-electron products (acetone and methane). Table II shows that the yield of methane is about the same, considering experimental error, over 6.3-fold change in cobalt(II) concentration. Again, the data are best interpreted by a one-electron change.

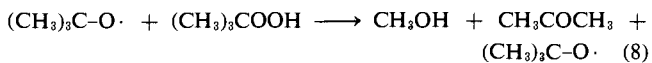
The structure of the *t*-butyl hydroperoxide-cobalt ion intermediate associated with the third-order reaction is of some interest. As in the case of the second-order reaction, we assume the hydroperoxide to enter a ligand site of cobalt(II) to form an intermediate complex. The question is whether or not each of the oxygen atoms of the hydroperoxide are bonded to two different cobalt species (Figure 5A). A structure similar to A has been proposed¹¹ to explain the kinetics of the

(11) R. G. Yalman, *J. Phys. Chem.*, **65**, 556 (1961).

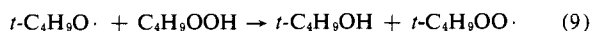
hydrogen peroxide-cobalt(II)-EDTA reaction. It seems likely that A would give *t*-butoxide and hydroxide anions. An alternative structure (Figure 5B) would seem reasonable for the major course in the third-order reaction since B would be expected to yield the *t*-butoxy radical.

Fate of the *t*-Butoxy Radicals. It is apparent from the preceding section that *t*-butyl alcohol must be formed mainly from the *t*-butoxy radicals. The *t*-butoxy radical may yield *t*-butyl alcohol by two possible paths, hydrogen atom abstraction from solvent and/or reduction by cobalt(II). Table I shows that the acetone/*t*-butyl alcohol ratio is temperature independent from 35 to 60°. At 135°, hydrogen atom abstraction from the solvent by *t*-butoxy radicals is of little or no consequence as seen from the thermal decomposition of di-*t*-butyl peroxide. If the acetone/*t*-butyl alcohol ratio remains temperature independent to 135°, it appears that hydrogen atom abstraction from the solvent by *t*-butoxy radicals is of little importance. Reduction by cobalt(II) is then the most likely route to *t*-butyl alcohol from the *t*-butoxy radical.

The only reactions detected in this system for the *t*-butoxy radical are reduction by cobalt(II) to *t*-butyl alcohol and fragmentation to acetone and methyl radicals, although other reactions are possible. Induced decomposition of hydroperoxides by alkoxy radicals has been suggested in the cobalt-catalyzed decomposition of hydroperoxides (eq. 8).¹² No methanol was detected and, in addition, the stoichiometry indicates this reaction to be of little importance.



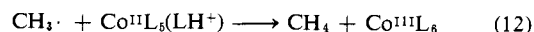
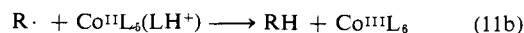
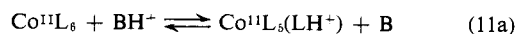
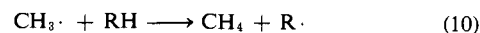
It was also been proposed that *t*-butoxy radicals abstract hydrogen atoms from *t*-butyl hydroperoxide (eq. 9).¹³ The resulting *t*-butyl peroxide radicals are suggested to give the observed products, oxygen, and di-*t*-butyl peroxide. Since neither of these products is ob-



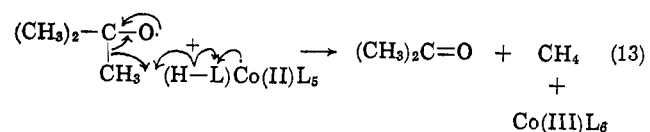
served in this study, it seems unlikely that hydrogen atom abstraction from hydroperoxide by *t*-butoxy radicals occurs in 50% aqueous acetic acid. It is surprising that reaction 9 does not occur, since activation energies of 5–8 kcal./mole have been suggested,^{13b} whereas the competing fragmentation reaction of the *t*-butoxy radical is reported to have an activation energy of 11.2 ± 2 kcal./mole.¹⁴ In the studies where eq. 9 is suggested, the reactions have been carried out in nonpolar solvents of the vapor phase. The lack of 9 in 50% aqueous acetic acid may be due to solvent hydrogen bonding of either the *t*-butoxy radical or the hydroperoxide.

Fate of the Methyl Radical. Methane was the only product detected from methyl radicals. There are two alternative sequences by which methane could be produced. The first sequence may be called indirect re-

duction (eq. 10 and 11) and the second sequence direct reduction (eq. 12). For simplicity, only hydrogen



transfer from a ligand is represented although electron transfer is equally applicable. Any other molecule that can donate a hydrogen atom is represented by RH. The stoichiometry rules out appreciable radical dimerization. Deuterated solvent experiments show the minimum ratio of methane/methane-*d*₁ is 21. This suggests that indirect reduction is the principal reaction course since direct reduction of methane (eq. 12) predicts the formation of methane-*d*₁. Also, cobalt(II)-assisted fragmentation of the *t*-butoxy radical, as shown in eq. 13, seems unlikely considering the deuterated solvent results.



The primary source of hydrogen atoms for methyl radicals is most likely the α -hydrogen atoms of acetic acid.¹⁵ Although there is no evidence for carboxyl hydrogen atom abstraction from acetic acid by alkyl radicals,¹⁵ this reaction may occur with carboxyl groups of the EDTA ligand. This would explain the small amount of carbon dioxide produced.¹⁵

Transition metal ions increased the ethane/methane ratio when *t*-butyl hydroperoxide was decomposed in water.¹⁶ It was proposed that methyl radical-transition metal ion complexes are formed which can react with methyl free radicals to give increased amounts of ethane. Complexes of transition metal ions with methyl radicals appear to be of little or no consequence in this study as seen by the lack of ethane formation and lack of direct reduction of methyl radicals by cobalt(II). The latter would be a likely alternative reaction of the methyl radical-cobalt(II) complex.

Although abstraction of oxygen-bonded hydrogen atoms from *t*-butyl hydroperoxide has been proposed in its catalytic decomposition with cobalt acetate,^{1b} no evidence could be presented here for this reaction. If methyl radicals abstracted hydrogen atoms from the hydroperoxide, methane-*d* would be produced in the deuterated solvent.¹⁷ This was not observed to any appreciable extent.

Effect of Ligands on Rate. Although a quantitative correlation between reaction rate and acidity was not made, it is apparent that increasing the acidity reduces the reaction rate (Table IV). If acid catalyzes the solvolysis of EDTA functional groups bonded to

(15) M. Szwarc and J. Smid, *J. Chem. Phys.*, **27**, 421 (1957).

(16) K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **83**, 2017 (1961).

(12) M. S. Kharasch, P. Pauson, and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953); M. S. Kharasch and A. Fono, *ibid.*, **24**, 72 (1959).

(13) (a) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discussions Faraday Soc.*, **10**, 242 (1951); (b) L. H. Piette and W. C. Landgraf, *J. Chem. Phys.*, **32**, 1107 (1960); (c) S. W. Benson, *ibid.*, **40**, 1007 (1964); (d) J. T. Martin and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A220**, 322 (1953).

(14) D. H. Volman and W. M. Graven, *J. Am. Chem. Soc.*, **75**, 3111 (1953).

(17) This assumes deuterium exchange with the peroxidic proton is rapid. Ethanol hydroxy protons exchange very rapidly in water ($t^{1/2} = 7.3 \times 10^{-3}$ sec. at 72°; see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 421). The fact that hydroperoxides are stronger acids than hydroxy compounds suggests the former should exchange even more rapidly [pK_a of hydrogen peroxide is 11.5 while that of water is 15.7; J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962)].

cobalt(II), the data seem reasonable since it was shown that cobalt acetate does not react with *t*-butyl hydroperoxide in 50% aqueous acetic acid. In contrast, ferrous ion complexed with EDTA shows no acid dependence in its reaction with cumene hydroperoxide.¹⁸ It was assumed that all the ferrous EDTA-solvent complexes react at the same rate with hydroperoxide.

The reactivity of cobalt(II)-EDTA and the inertness of cobalt acetate with *t*-butyl hydroperoxide in 50% aqueous acetic acid deserve comment. A previous report^{1b} indicates that the decomposition rate of *t*-butyl hydroperoxide with cobalt acetate is reduced by addition of water to acetic acid solvent. Total inactivity of cobalt acetate in 50% aqueous acetic acid is then not unexpected. On the other hand, it is known that strong anionic complexing agents stabilize the higher valence state of transition metal ions relative to the lower valence state.¹⁹ This is no doubt the reason for the observed reactivity of EDTA-complexed cobalt(II) and inert behavior of cobalt acetate and cobalt(III)-EDTA.

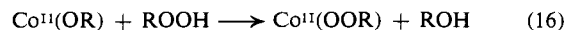
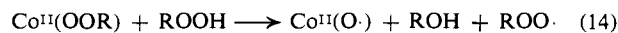
Catalyzed Decomposition. The relationship of the present results to the catalytic decomposition of *t*-butyl hydroperoxide deserves comment. Recently Berger and Bickel²⁰ proposed a mechanism for the catalytic decomposition of *t*-butyl hydroperoxide by cupric phenanthroline diacetate, which incorporated

(18) W. L. Reynolds and I. M. Kolthoff, *J. Phys. Chem.*, **60**, 996 (1956).

(19) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 61.

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

an oxide intermediate. A similar mechanism for cobalt (II) would be



where R is *t*-butyl. Obviously, this mechanism is not operative with EDTA-complexed cobalt(II) since it fits neither the products nor the stoichiometry of the reaction. For similar reasons, the mechanism does not seem likely even for the catalytic decomposition of hydroperoxides with cobalt salts.

Dean and Skirrow¹⁶ have studied the decomposition of *t*-butyl hydroperoxide in acetic acid with cobalt acetate and report orders in cobalt and hydroperoxide to be 1.4 and 1.1. The higher order term in cobalt may be, in part, due to reactions with more than one cobalt species in the activated complex. This would correspond to the third-order term observed in the present study.

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Hydrolysis of Phostonates^{1,2}

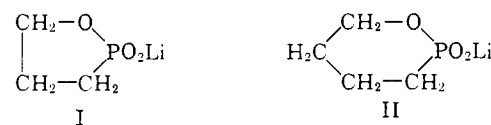
Anatol Eberhard and F. H. Westheimer

Contribution from the James Bryant Conant Laboratory of Harvard University, Cambridge, Massachusetts. Received September 29, 1964

A five-membered cyclic ester of a phosphonic acid, lithium propylphostonate (I), and a six-membered analog, lithium butylphostonate (II), have been synthesized. The rates of hydrolysis of these compounds, relative to that of sodium ethyl ethylphosphonate (sometimes compared directly, sometimes extrapolated to 75°) in acid are 5×10^4 :3:1, and in alkali are 6×10^5 :24:1. Tracer methods with ¹⁸O show that the phostonates are cleaved at the P-O bond, whereas the hydrolysis of the open-chain phosphonate occurs with about half P-O and half C-O fission. The relative rates of hydrolysis at phosphorus are then slightly more favorable to the phostonates than the figures shown above. The previously established extraordinary reactivity of cyclic five-membered esters of

phosphoric acid is thus paralleled by that of the cyclic phosphonates.

The extraordinarily large rates of hydrolysis of five-membered cyclic esters of phosphoric acid,³ as compared to those of the six-membered cyclic esters,⁴ or of



the corresponding open-chain compounds stimulated an investigation of the properties of the corresponding phosphonates. The dilithium salt of 3-bromopropylphosphonic acid was cyclized to the phostonate, by internal displacement. Similar reaction led to the

(3) J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 4858 (1956).

(4) H. G. Khorana, G. M. Tener, R. S. Wright, and J. G. Moffatt, *ibid.*, **79**, 430 (1957).

(1) Presented in part at the 140th National Meeting of the American Chemical Society, Sept. 1961, Abstracts, p. 94Q, and in part in the Abstracts of the 18th National Organic Chemistry Symposium, Columbus, Ohio, 1963, p. 53.

(2) The general name "phostonic acid" was suggested by Conant to describe cyclic phosphonic acids: J. B. Conant and A. D. Macdonald, *J. Am. Chem. Soc.*, **42**, 2337 (1920). The nomenclature here used for phostonates is patterned after the standard nomenclature for phosphonates: see *Chem. Eng. News*, **30**, 4515 (1952).