

yield 22.2 g. of an amber-colored oil. Gas chromatography on 20% Carbowax 20M-20% polyethylene glycol programmed from 100 to 250° at 11°/min. indicated a complex mixture with one of the peaks having the same retention temperature (150°) as biphenyl. Comparison with standard biphenyl solutions gave a value of 2.0 g. (0.0130 mole) of biphenyl.

A portion (13.5 g.) of the oil was chromatographed on acid-treated alumina with hexane and thirty-two 30-ml. fractions were collected. Fractions 3 to 7 were

combined to yield 809.5 mg. of a white solid, m.p. 68.5–69.5°, with the characteristic odor of biphenyl. Admixture did not lower the melting point (69–70°) of pure biphenyl. The remaining fractions, consisting of oils containing small amounts of biphenyl (v.p.c.), were not further examined.

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Metal Ion Decomposition of Hydroperoxides. II. Kinetics and Mechanism of Cobalt Salt Catalyzed Decomposition of *t*-Butyl Hydroperoxide¹

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*A thorough kinetic and product investigation of cobalt acetate tetrahydrate catalyzed decomposition of *t*-butyl hydroperoxide in acetic acid is reported. The order in cobalt salt varies with temperature. At 50, 60, and 70° the orders are 1.28, 1.52, and 1.39, respectively. The order in *t*-butyl hydroperoxide increases from 1.086 ± 0.007 to 1.17 ± 0.01 between 50 and 70°. Reaction products are acetone, methanol, methyl acetate, *t*-butyl alcohol, di-*t*-butyl peroxide, and oxygen. The effect of reactant concentrations on the yield of products was investigated. A mechanism, based on cobalt-hydroperoxide complexes, is proposed to explain the data. To determine the generality of this mechanism where the solvent does not complex strongly with the cobalt salt, the kinetics and products of cobalt 2-ethylhexanoate catalyzed decomposition of the *t*-butyl hydroperoxide in chlorobenzene were studied. The order in cobalt, at low concentrations, varies from 1.0 to 1.56 at 20°. With higher cobalt concentrations at 0°, the order varies from 1.5 to 0.05. First-order dependence on hydroperoxide is observed throughout. *t*-Butyl alcohol and oxygen are the major products and di-*t*-butyl peroxide and acetone are the minor products. These results are accommodated by the mechanism proposed for cobalt acetate catalysis in acetic acid.*

Introduction

Some kinetic studies of cobalt ion-catalyzed decomposition of hydroperoxides have been reported²; however, all the data are not in agreement. Although there has been a considerable interest in reactions of

hydroperoxides with metal ions, an adequate mechanism has been lacking.³

The first paper in this series reported a study of the irreversible Co(II) to Co(III) change by *t*-butyl hydroperoxide.¹ A kinetic and product study of cobalt-catalyzed hydroperoxide decomposition is now reported where both valence states are reactive. As an aid to formulating a general mechanism, we have studied the reaction in acetic acid and chlorobenzene, which differ widely in their complexing ability with cobalt. Decomposition of *t*-butyl hydroperoxide was studied primarily because complicating reactions such as hydration and rearrangement may be avoided with a tertiary alkyl hydroperoxide. Also, a direct comparison may be made with other investigations where *t*-butyl hydroperoxide was used.

Experimental

Materials. Reagent grade chemicals were used when available without further purification unless specified. Reagent grade acetic acid was further purified by distillation from chromic acid. Cobalt acetate tetrahydrate (Baker's reagent grade) was used throughout this investigation. We have found that anhydrous cobalt acetate is insoluble in glacial acetic acid in contrast to a previous report.² Also, *in situ* dehydration of the tetrahydrate by acetic anhydride caused precipitation from acetic acid solvent.⁴ Ninety per cent *t*-butyl hydroperoxide (Lucidol Division, Wallace and Tiernan, Inc.) was purified by azeotropic distillation.⁵ The purified hydroperoxide was shown to be 99.3% pure by iodometric titration.¹ Chlorobenzene was first dried over Drierite and the residual water

(1) Part I: W. H. Richardson, *J. Am. Chem. Soc.*, **87**, 247 (1965).

(2) (a) H. Tomiška, *Collection Czech. Chem. Commun.*, **27**, 1549 (1962); (b) H. Kropf, *Ann.*, **637**, 111 (1960); (c) E. Dyer, K. R. Carle, and D. E. Weiman, *J. Org. Chem.*, **23**, 1464 (1958); (d) M. H. Dean and G. Skirrow, *Trans. Faraday Soc.*, **54**, 849 (1958); (e) A. E. Woodward and R. B. Mesorbian, *J. Am. Chem. Soc.*, **75**, 6189 (1953); (f) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1578 (1948).

(3) For a review see A. G. Davies, "Organic Peroxides," Butterworth and Co. (Publishers), Ltd., London, 1961, Chapter 12.

(4) J. Z. Pasky, unpublished results.

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

was removed in the forerun as an azeotrope. The heart cut was stored over Drierite.

Cobalt(II) 2-ethylhexanoate was prepared by adding 62.30 g. (0.250 mole) of cobalt acetate tetrahydrate (Baker's reagent grade) to an aqueous solution of sodium 2-ethylhexanoate. The latter solution was prepared by adding a solution of 20.0 g. (0.500 mole) of sodium hydroxide in 250 ml. of water to 72.10 g. (0.500 mole) of 2-ethylhexanoic acid until pH 7-8 was reached. After extraction of the mixture with two 250-ml. portions of mixed hexanes, followed by washing with three 200-ml. portions of water, the hexane solution was dried over anhydrous sodium sulfate. Removal of hexane solvent on a rotary evaporator and drying the residue at 100° (20 mm.) gave the amorphous blue salt.

Anal. Calcd. for C₁₆H₃₀CoO₄: Co, 17.1. Found: Co, 17.5.

Product Analyses. Yields of condensable and gaseous products were determined by gas liquid chromatography (g.l.c.) and by mass spectrometry, respectively.¹ The condensable products were identified by comparison of g.l.c. retention times and by infrared and mass spectrometry analysis of the product mixture, which was isolated by preparative g.l.c. Reactions were allowed to proceed for at least 10 half-lives before analysis. Di-*t*-butyl peroxide is stable under the conditions used for the cobalt acetate-*t*-butyl hydroperoxide reaction since little or no decomposition of 0.101 *M* peroxide in acetic acid with 0.104 *M* cobalt acetate tetrahydrate was observed after 7.3 hr.

Kinetic Method. The rate of hydroperoxide disappearance was determined by iodometric titration.¹ Temperature was determined by a thermometer calibrated against an NBS platinum resistance thermometer and was maintained constant within ±0.01°. The rates were followed through 2-3 half-lives, and in isolated measurements first-order rate plots for the cobalt acetate reaction were linear through 3-4 half-lives. As an example, the first-order rate constant with probable error is 4.61 ± 0.03 × 10⁻⁴ sec.⁻¹ at 49.88° with initial cobalt acetate and *t*-butyl hydroperoxide concentrations of 2.60 × 10⁻² *M* and 0.168 *M*, respectively. In some instances, the first-order plots for the cobalt 2-ethylhexanoate reaction showed an upward drift after about 2 half-lives. As an example, one of the better plots yields a first-order rate constant with probable error of 7.98 ± 0.11 × 10⁻⁴ sec.⁻¹ at 0° when cobalt 2-ethylhexanoate and *t*-butyl hydroperoxide concentrations are 1.81 × 10⁻³ *M* and 6.66 × 10⁻² *M*, respectively. It was found that the half-life for thermal decomposition of *t*-butyl hydroperoxide (0.168 *M*) in acetic acid at 70° was approximately 38 hr., which is more than adequately stable for measurements with cobalt salt.

Molecular Weight Determinations. A Mechrolab osmometer Model 301 was used to determine the molecular weight of cobalt 2-ethylhexanoate in benzene at 39.0°.

Analysis of the Co(III)/Co(II) Ratio. The Co(III)/Co(II) ratio was determined polarographically, using cobalt hexammines as the standard.⁶ For cobalt 2-

(6) See G. W. C. Milner, "Principles and Applications of Polarography and Other Electroanalytical Processes," Longmans, Green and Co., London, 1957, pp. 210-212.

ethylhexanoate-*t*-butyl hydroperoxide reactions, the chlorobenzene solutions were extracted with a 1 *M* ammonium hydroxide solution and measured immediately. A plot of the optical density ratio $D_{375m\mu}/D_{607.5m\mu}$ vs. the polarographic Co(III)/Co(II) ratio appeared to be linear from a three-point plot. Solutions of varying Co(II)/Co(III) content were prepared by adding cobalt(II) 2-ethylhexanoate to a Co(III)-Co(II) mixture. The latter mixture was prepared by allowing cobalt(II) 2-ethylhexanoate to react with *t*-butyl hydroperoxide followed by removal of solvent and products under vacuum. Similar methods were used for the cobalt acetate-*t*-butyl hydroperoxide reaction.

Decomposition of *t*-butyl hydroperoxide (1.03 × 10⁻³ *M*) by cobalt 2-ethylhexanoate (6.66 × 10⁻² *M*) was followed spectrally at 0 ± 1° for about 10 half-lives. The per cent cobalt(III) was found to be constant over this period with a value of roughly 45%, which was determined from the plot of $D_{375m\mu}/D_{607.5m\mu}$ vs. the polarographic Co(III)/Co(II) ratio. Polarographic analysis showed 48% cobalt(III) after more than 10 half-lives.

Electron Spin Resonance Spectra. A conventional Varian X-band spectrometer, equipped with a Varian dual sample cavity, was employed using a 100-kc. field modulation of 4 gauss.

Visible Spectra. For 0° measurements, a Cary 14 spectrophotometer was fitted with a polystyrene foam cell compartment, which was cooled by a steam of nitrogen which had been passed through liquid nitrogen.

Kinetic Derivations. For eq. 1-13 addition of the steady-state equations for [Co(III)Co(II)], [RO·] followed by subtraction of the steady-state equation for [CH₃·] gives (i). At steady-state conditions, the ratio of [Co(II)₂] to [Co(III)Co(II)] will be constant (ii).⁷

$$2k_4[\text{Co(III)}_2][\text{ROOH}] + 2k_5K_1[\text{ROO}\cdot][\text{Co(III)Co(II)}] \times [\text{ROOH}] - 2k_8K_6[\text{Co(II)}][\text{ROOH}] - 2k_{10}K_9K_6[\text{Co(II)}_2][\text{ROOH}] + 2k_{12}[\text{RO}\cdot] = 0 \quad (\text{i})$$

$$K[\text{Co(III)Co(II)}] = [\text{Co(II)}_2] \quad (\text{ii})$$

$$[\text{Co(III)Co(II)}] = \frac{k_4}{k_3K_1}[\text{Co(III)}_2] \quad (\text{iii})$$

From the steady-state equation for [Co(III)₂], eq. iii results. Substituting (ii), (iii), and the value of [RO·] from the steady-state equation for [RO·] into (i) gives

$$[\text{ROO}\cdot] = \frac{(k_3^2k_4k_{11}KK_2^2 + k_3k_4k_8k_{11}K^2K_1K_6)[\text{Co(III)}_2]}{k_3k_4k_5k_{11}KK_1^2[\text{Co(III)}_2] + k_3^2k_5k_{12}K_1^3} + \frac{k_4^2k_{10}k_{11}K^3K_6K_9[\text{Co(III)}_2]^2}{k_3k_4k_5k_{11}KK_1^2[\text{Co(III)}_2] + k_3^2k_5k_{12}K_1^3} \quad (\text{iv})$$

(iv). Assuming the concentration of cobalt complexed with hydroperoxide is small compared to uncomplexed cobalt salt, eq. v results, where [Co]_{st} is the total

$$[\text{Co(III)}_2] = \frac{[\text{Co}]_{\text{st}}}{1 + \frac{k_4K}{k_3K_1} + \frac{k^4}{k_3K_1}} \quad (\text{v})$$

(7) It was verified spectrally that the Co(II)/Co(III) ratio is constant through at least 10 half-lives.

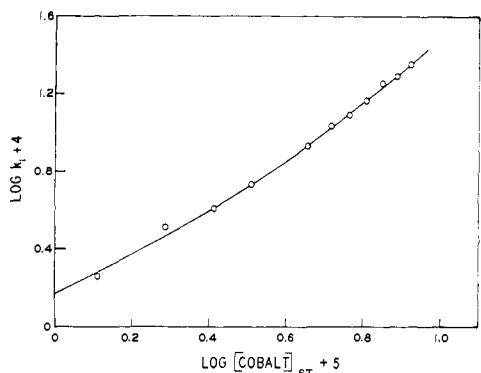


Figure 1. Order in cobalt 2-ethylhexanoate at 20°. Slope corresponds to order and varies from 1.0 to 1.56 over a concentration range of 1.29×10^{-6} to 8.40×10^{-6} M.

amount of cobalt. Substitution of eq. iv and v into the expression for rate of hydroperoxide disappearance gives the general eq. 15 (cf. Discussion). Replacement of eq. 13 by 14 in the proposed mechanism yields eq. 16 (cf. Discussion) by a similar solution.

Addition of reactions 19a-c to the mechanism using (13) results in the general expression for $[\text{ROO}\cdot]$ shown in (vi); where $a = (k + k^{\text{II}}[\text{Co}(\text{III})_2])$, $b = (k^{\text{III}}[\text{Co}(\text{III})_2] + k^{\text{IV}}[\text{Co}(\text{III})]_2^2[\text{ROOH}])$, and $c = (k^{\text{V}}[\text{Co}(\text{III})_2] + k^{\text{VI}}[\text{Co}(\text{III})_2]^2 + k^{\text{VII}}[\text{Co}(\text{III})]_3^3[\text{ROOH}])$. Substitution of (vi) into the expression for rate of hydroperoxide disappearance will give terms greater than first order in hydroperoxide, since the latter expression contains the terms $k_7 K_6 [\text{ROO}\cdot][\text{Co}(\text{II})_2][\text{ROOH}]$ and $k_5 k_1 [\text{ROO}\cdot][\text{Co}(\text{III})\text{Co}(\text{II})][\text{ROOH}]$.

$$[\text{ROO}\cdot] = -\frac{b \pm (b^2 - 4ac)^{1/2}}{2a} \quad (\text{vi})$$

(III)₂ + $k^{\text{IV}}[\text{Co}(\text{III})]_2^2[\text{ROOH}]$, and $c = (k^{\text{V}}[\text{Co}(\text{III})_2] + k^{\text{VI}}[\text{Co}(\text{III})_2]^2 + k^{\text{VII}}[\text{Co}(\text{III})]_3^3[\text{ROOH}])$. Substitution of (vi) into the expression for rate of hydroperoxide disappearance will give terms greater than first order in hydroperoxide, since the latter expression contains the terms $k_7 K_6 [\text{ROO}\cdot][\text{Co}(\text{II})_2][\text{ROOH}]$ and $k_5 k_1 [\text{ROO}\cdot][\text{Co}(\text{III})\text{Co}(\text{II})][\text{ROOH}]$.

Results

Kinetics. A. Cobalt Acetate in Acetic Acid. The order in *t*-butyl hydroperoxide, which was determined from a log $t_{1/2}$ vs. log $[t\text{-C}_4\text{H}_9\text{OOH}]$ plot,⁸ increases

Table I. Effect of Temperature on the Order in *t*-Butyl Hydroperoxide

$[t\text{-C}_4\text{H}_9\text{OOH}]_0 \times 10^2$ M	$[\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}] \times 10^2$ M	Temp., °C.	k_1, sec^{-1}	Order in <i>t</i> -C ₄ H ₉ OOH
3.33	1.56	49.88	2.01 ^a	
6.76	1.56	49.88	2.17 ^a	
16.8	1.56	49.88	2.25	
33.4	1.56	49.88	2.41 ^a	
50.1	1.56	49.88	2.52 ^a	
66.6	1.56	49.88	2.64 ^b	1.086 ± 0.007
3.34	1.04	70.20	7.17	
6.82	1.04	70.20	7.86	
16.8	1.04	70.20	8.86	
33.4	1.04	70.20	10.7	
50.1	1.04	70.20	11.0	
66.6	1.04	70.20	11.6	1.17 ± 0.01

^a Average of two runs. ^b Average of three runs.

slightly with increasing temperature (Table I). Previously, the order in *t*-butyl hydroperoxide with an-

(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 43.

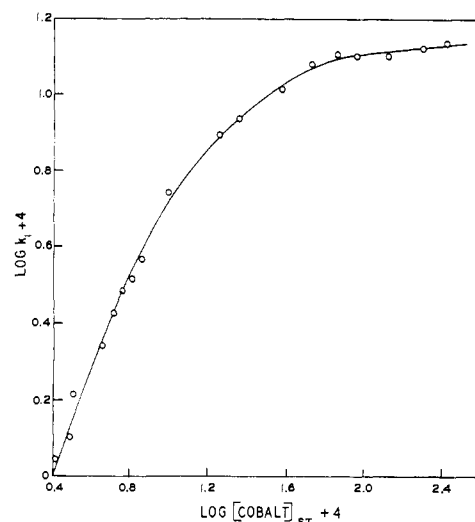


Figure 2. Order in cobalt 2-ethylhexanoate at 0°. Slope corresponds to order and varies from 1.5 to 0.05 over a concentration range of 2.60×10^{-4} to 260×10^{-4} M.

hydrous cobalt acetate at one temperature (55°) was reported to be 1.1.²

The order in cobalt acetate was determined at 50, 60, and 70° with at least a tenfold change in cobalt concentration. The data are tabulated in Table II. From

Table II. Data for Order in Cobalt Acetate as a Function of Temperature^a

$[\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}] \times 10^3$ M	$k_1 \times 10^4 \text{ sec}^{-1}$		
	49.88°	59.88°	70.20°
1.30	0.586
2.60	1.35
3.12	...	0.416	...
5.20	0.499	0.803	3.44
7.80	6.17
8.32	...	1.84	...
10.4	1.44	...	8.86
13.0	...	3.50	13.2
15.6	2.25	5.09	16.2
18.2	23.0
20.8	3.36	7.24	...
26.0	4.61	10.4	...
31.2	5.33
36.4	6.74
41.0	7.32
41.6	...	19.7	...
52.0	10.2

^a $[t\text{-C}_4\text{H}_9\text{OOH}]_0 = 0.168$ M.

the slope of a log-log plot of cobalt acetate concentration vs. k_1 the order in cobalt acetate was obtained. The order in cobalt acetate, determined by least squares, and the correlation coefficients at the following temperatures are: 50°, 1.28 ± 0.03 , $r^2 = 0.995$; 60°, 1.52 ± 0.03 , $r^2 = 0.998$; and 70°, 1.39 ± 0.02 , $r^2 = 0.997$. In comparison, Dean and Skirrow^{2d} report 1.4 order in cobalt acetate at 55° for *t*-butyl hydroperoxide decomposition in acetic acid. Data at 50, 60, and 70° with 1.56×10^{-2} M cobalt acetate give an activation energy E_a of 21.5 kcal./mole.

B. Cobalt 2-Ethylhexanoate in Chlorobenzene. The order in *t*-butyl hydroperoxide was determined at three different cobalt concentrations (Table III). First-

Table III. First-Order Dependence on *t*-Butyl Hydroperoxide at 0°

$[t\text{-C}_4\text{H}_9\text{OOH}]_0^a$ $\times 10^2 M$	$k_1 \times 10^4$ sec. ⁻¹	$[t\text{-C}_4\text{H}_9\text{OOH}]_0^b$ $\times 10^2 M$	$k_1 \times 10^4$ sec. ⁻¹	$[t\text{-C}_4\text{H}_9\text{OOH}]_0^c$ $\times 10^2 M$	$k_1 \times 10^4$ sec. ⁻¹
1.32	1.06	1.30	3.36	1.40	10.2
6.66	1.25	2.55	3.74	4.01	10.2
10.0	1.14	2.56	3.77	6.79	9.68
13.3	1.09	5.12	3.48	10.0	10.0
13.4	1.14	5.36	3.83	13.4	10.1, 10.5
20.4	1.08	13.0	3.70		
$k_1^{av} = 1.13 \pm 0.05$		$k_1^{av} = 3.65 \pm 0.15$		$k_1^{av} = 10.1 \pm 0.20$	

^a The concentration of $\text{Co}(\text{II})(2\text{-ethylhexanoate})_2$ is: ^a $2.58 \times 10^{-4} M$, ^b $5.16 \times 10^{-4} M$, and ^c $38.7 \times 10^{-4} M$ in chlorobenzene.

Table IV. First-order Dependence on *t*-Butyl Hydroperoxide at 0° with $1.50 \times 10^{-2} M$ 2-Ethylhexanoic Acid^a

$[t\text{-C}_4\text{H}_9\text{OOH}]_0 \times 10^2 M$	$k_1 \times 10^4 \text{ sec.}^{-1}$
6.66	1.80
16.7	1.88
39.7	1.83
66.6	1.93
$k_1^{av} = 1.86 \pm 0.05$	

^a $[\text{Co}(\text{II})(2\text{-ethylhexanoate})_2] = 5.20 \times 10^{-3} M$ in chlorobenzene.

Products. A. Cobalt Acetate in Acetic Acid. The product analyses were conducted at kinetic concentrations. The effect of cobalt acetate tetrahydrate and *t*-butyl hydroperoxide concentration on yields of condensable products is presented in Tables V and VI. No dramatic change in product distribution is observed with variation in either *t*-butyl hydroperoxide or cobalt acetate tetrahydrate concentration. There may be a small trend toward higher *t*-butyl alcohol and

Table V. Effect of Variation in Cobalt Acetate Tetrahydrate Concentration on Yield of Condensable Products at 60°^a

$[\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}]$ $\times 10^3 M$	Yield, %					
	Acetone	Methyl acetate	Methanol	Methanol + methyl acetate	<i>t</i> -Butyl alcohol	Di- <i>t</i> -butyl peroxide
5.20	37.7	17.1	3.69	20.8	43.5	4.38
26.0	35.1	5.08	10.7	15.8	49.0	4.24
41.6	26.4	7.60	10.2	17.8	46.2	4.37
52.0	29.1	3.52	12.1	15.6	49.8	4.67

^a $[t\text{-C}_4\text{H}_9\text{OOH}]_0 = 0.167 M$, and analyses are averages of two measurements.

Table VI. Effect of Variation in *t*-Butyl Hydroperoxide Concentration on Yield of Condensable Products at 60°^a

$[t\text{-C}_4\text{H}_9\text{OOH}]_0, M$	Yield, %					
	Acetone	Methyl acetate	Methanol	Methanol + methyl acetate	<i>t</i> -Butyl alcohol	Di- <i>t</i> -butyl peroxide
0.0835	34.2	6.80	12.6	19.4	49.2	2.13
0.167	35.1	5.08	10.7	15.8	49.0	4.24 ^b
0.167	11.9	2.35	13.0	15.4	43.5	3.63 ^c
0.334	27.0	4.51	9.34	13.9	47.9	5.20 ^d
0.337						
0.835	19.0	2.33	7.24	9.57	55.0	7.49 ^d
0.838						

^a $[\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}] = 2.60 \times 10^{-2} M$. ^b Average of three experiments. ^c Nitrogen bubbled through solution during reaction. ^d Average of two measurements.

order dependence was observed over approximately a tenfold change in initial hydroperoxide concentration. In the presence of $1.50 \times 10^{-2} M$ 2-ethylhexanoic acid and $5.20 \times 10^{-3} M$ cobalt 2-ethylhexanoate, first-order kinetics in *t*-butyl hydroperoxide were still observed (Table IV). In the absence of added acid, the rate constant was $11.9 \times 10^{-4} \text{ sec.}^{-1}$.

The order in cobalt 2-ethylhexanoate was dependent on cobalt concentration. At 20°, the order varies from 1.0 to 1.56 when the cobalt salt concentration is varied from $1.29 \times 10^{-5} M$ to $8.40 \times 10^{-5} M$ (Figure 1). With increased cobalt concentrations, the order begins to decrease. At 0°, the order varies from 1.5 to 0.05 when cobalt concentration is varied from $2.58 \times 10^{-4} M$ to $260 \times 10^{-4} M$ (Figure 2), which is presumably due to cobalt salt association.

di-*t*-butyl peroxide yields accompanied by lower acetone yields with either increasing *t*-butyl hydroperoxide concentration (Table VI) or increasing cobalt salt concentration (Table V). Methyl acetate is formed from methanol and acetic acid under the reaction conditions. For example, heating methanol (8.35 *M*) with cobalt acetate ($4.16 \times 10^{-2} M$) in acetic acid for 5.0 hr. at 60° gave a mixture of methyl acetate (20.7% yield) and methanol (83.1% recovery). For this reason, it is best to consider the yields of these products as a sum. Significantly, when nitrogen is bubbled through the reaction mixture to remove oxygen as it is formed, the combined yield of methanol and methyl acetate is not altered.

The yields of gaseous products at 60° with *t*-butyl hydroperoxide and cobalt acetate tetrahydrate concen-

Table VII. Product Yields with Varying Concentration of *t*-Butyl Hydroperoxide with Cobalt 2-Ethylhexanoate Concentration in Chlorobenzene

Run	[<i>t</i> -C ₄ H ₉ OOH] ₀ × 10 ² M	[Co(C ₇ H ₁₅ CO ₂) ₂] × 10 ⁴ M	Temp., °C.	Yield, %			
				<i>t</i> -C ₄ H ₉ OH	(<i>t</i> -C ₄ H ₉ O) ₂	CH ₃ COCH ₃	O ₂
1	6.70	10.3	0	58	20	2	..
2	67.0	10.3	0	63	16	0.6	..
Average of 1, 2		10.3	0	61	18	1.3	..
3	6.72	1.29	35	54.3	11.4	4.4	..
4	66.6	1.29	35	71.6	14	2.4	..
Average of 3, 4		1.29	35	63.0	12.7	3.4	..
5	33.4	6.45	0	74

trations of 0.168 M and 2.60 × 10⁻² M are: oxygen (38.6%), carbon dioxide (1.8%), and ethane (0.6%). Yields of oxygen and ethane are based on 2 moles of hydroperoxide per 1 mole of product. A 1:1 relationship was used to calculate the yield of carbon dioxide.

Our product analyses differ significantly from those of Dean and Skirrow.^{2d} At 55° they report the following products and yields: *t*-butyl alcohol (80%), di-*t*-butyl peroxide (7%), acetone (5.5%), formaldehyde (3.8%), and oxygen (54%). No methanol or methyl acetate was reported.

Both ultraviolet and polarographic methods indicate that cobalt was present as 95–98% cobalt(II) after completion of reaction.

B. Cobalt 2-Ethylhexanoate in Chlorobenzene. The major product was *t*-butyl alcohol and the minor products were di-*t*-butyl peroxide and acetone. In contrast to a previous report,⁹ di-*t*-butyl peroxide is produced by cobalt salt catalysis in a neutral medium. The products are essentially independent of initial hydroperoxide and cobalt salt concentration (Table VII). In addition, yields are unaffected by changing the temperature from 0 to 35°. The sole gaseous product was oxygen. No methane, ethane, or formaldehyde could be detected by means of spectral analysis. Product distribution is also relatively unaffected by the presence of 0.348 M 2-ethylhexanoic acid. With *t*-butyl hydroperoxide and cobalt 2-ethylhexanoate concentrations of 0.666 M and 5.18 × 10⁻³ M, respectively, the yields of products were: *t*-butyl alcohol (66%), di-*t*-butyl peroxide (10%), and acetone (0.99%).

Structure of Cobalt 2-Ethylhexanoate. A plot of molecular complexity (number of cobalt ions per molecule) vs. cobalt(II) 2-ethylhexanoate concentration indicates a dimeric structure at infinite dilution in benzene solution. The least-squares intercept is 2.13 ± 0.16. Somewhat similar results were obtained for zinc and copper carboxylates.¹⁰

Discussion

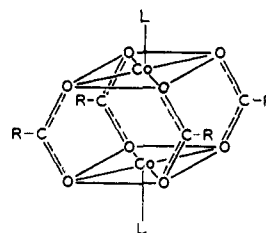
Structure of Cobalt Carboxylates. Before considering a reaction mechanism, the structure of cobalt carboxylates should be considered. To our surprise, neither cobalt acetate nor 2-ethylhexanoate shows an e.s.r. signal as would be expected since cobalt(II) has a 3d⁷ orbital with at least one unpaired electron.¹¹

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

(10) A. K. Rai and R. C. Mehrota, *J. Inorg. Nucl. Chem.*, **21**, 311 (1961); A. Gilmour, S. M. Nelson, and R. C. Pink, *Nature*, **171**, 1075 (1953).

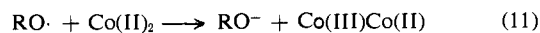
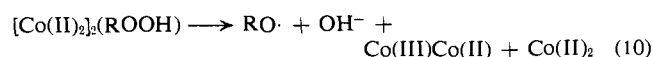
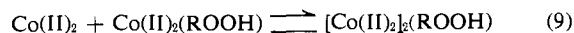
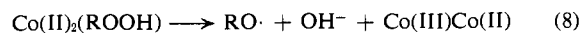
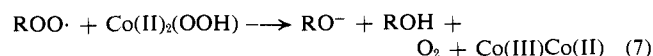
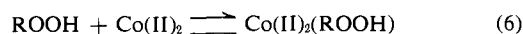
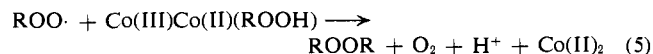
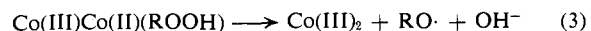
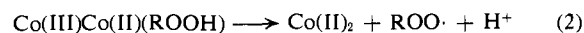
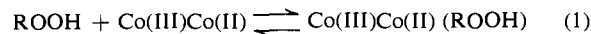
(11) In a low-spin state one unpaired electron is expected while in a high-spin state three unpaired electrons are expected. See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 40.

Dimeric cobalt carboxylate, where the odd electron on each cobalt(II) is placed in a common orbital, would solve this dilemma. Indeed, the effect of cobalt 2-ethylhexanoate concentration on molecular weight indicates a dimeric species at infinite dilution. By analogy to cupric acetate,¹² we suggest the structure shown below for the pink cobalt acetate salt, where L

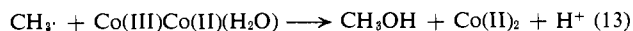
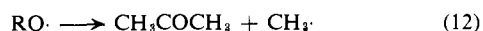


is a ligand such as water or acetic acid. The blue cobalt(II) 2-ethylhexanoate is probably void of the ligands L at infinite dilution in chlorobenzene. However, added acetic or 2-ethylhexanoic acid changes the salt from the blue to pink, where L corresponds to the added acids. The molecular changes found with varying cobalt(II) 2-ethylhexanoate concentration show that the dimer is further associated, most likely through oxygen atoms of the carboxyl groups.

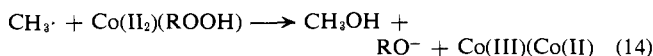
Mechanism. A. Cobalt Acetate in Acetic Acid. Incorporating the concept of dimeric cobalt species, the mechanism, shown in eq. 1–14, is proposed, consistent with the observed products, kinetics, and the catalytic nature of the cobalt salt. The path to alcohol and oxygen (eq. 7) is similar to that proposed by Dean and Skirrow.^{2d} If methanol is formed by reaction 13,



(12) R. E. Robertson, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., London, 1962, p. 647.



or



the derived rate law (eq. 15) results (*cf.* Experimental), where $[\text{Co}]_{\text{st}}$ refers to the total concentration of cobalt ions. If reaction 13 is replaced by 14, the derived law

$$\frac{-d[\text{ROOH}]}{dt} = \left(k_a[\text{Co}]_{\text{st}} + k_b[\text{Co}]_{\text{st}}^2 + \frac{k_c[\text{Co}]_{\text{st}}^2 + k_d[\text{Co}]_{\text{st}}^3}{k_e[\text{Co}]_{\text{st}} + 1} \right) [\text{ROOH}] \quad (15)$$

is modified to eq. 16. With the approximation k_{12}

$$\frac{-d[\text{ROOH}]}{dt} = \left(k_a'[\text{Co}]_{\text{st}} + k_b'[\text{Co}]_{\text{st}}^2 + \frac{k_c'[\text{Co}]_{\text{st}} + k_d'[\text{Co}]_{\text{st}}^2 + k_e'[\text{Co}]_{\text{st}}^3}{k_f'[\text{Co}]_{\text{st}} + 1} \right) [\text{ROOH}] \quad (16)$$

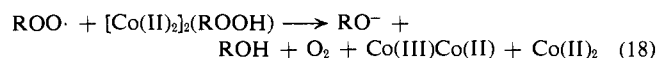
$\gg k_{11}[\text{Co(II)}_2]$, both eq. 15 and 16 simplify to 17.

$$\frac{-d[\text{ROOH}]}{dt} = (k_{sa}[\text{Co}]_{\text{st}} + k_{sb}[\text{Co}]_{\text{st}}^2)[\text{ROOH}] \quad (17)$$

This approximation seems reasonable in a polar solvent at least, since fragmentation of the *t*-butoxy radical (eq. 12) was considerably more facile than reduction (eq. 11) with cobalt(II) EDTA in 50% aqueous acetic acid.¹ The latter is a much better reducing agent than cobalt(II) acetate.¹

Between first- and second-order dependence on cobalt acetate was found as is predicted by either eq. 15, 16, or 17. Also, if the composite constants (*e.g.*, k_{sa} and k_{sb}) do not depend on temperature in the same manner, as might be expected, the order in cobalt acetate will be temperature dependent as was observed. At 60°, data for the change in observed rate constant with cobalt acetate concentration was fitted to eq. 17. Constants k_{sa} and k_{sb} with the correlation coefficient for the observed rate constants are: 2.20×10^{-2} l. mole⁻¹ sec.⁻¹, 6.20×10^{-1} l.² mole⁻² sec.⁻¹, and $r^2 = 0.997$. This indicates the order in cobalt acetate can be adequately explained by the derived rate law (eq. 17).

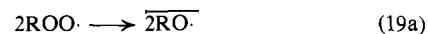
If the reaction 18 is considered where a peroxy



radical undergoes reaction with the complex shown in (9), a third-order term in cobalt acetate ($k_{sc}'[\text{Co(OAc)}_2]^3$) needs to be added to the sum of cobalt salt terms of eq. 17. Fitting the data to this equation gives: $k_{sa}' = 1.06 \times 10^{-2}$ l. mole⁻¹ sec.⁻¹, $k_{sb}' = 1.54$ l.² mole⁻² sec.⁻¹, and $k_{sc}' = -15.8$ l.³ mole⁻³ sec.⁻¹. The negative value of k_{sc}' suggests that eq. 18 must not be important for cobalt acetate catalyzed decomposition of *t*-butyl hydroperoxide in acetic acid.

According to the proposed mechanism, equal orders in the reactants are not predicted, which agrees with the data. In contrast, the rate law derived by Dean and Skirrow^{2d} predicts equal orders in the two reactants, providing the amount of cobalt complexed with hydroperoxide is small. However, slightly greater than first-order dependence on hydroperoxide was noted in

contrast to the derived rate laws. We feel this is best explained by a small contribution from eq. 19a-c, where $2\text{RO} \cdot$ represents caged radicals.



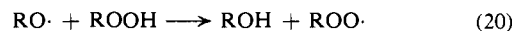
An exact solution for the law rate including eq. 19a-c results in a complex expression. However, it is apparent that greater than first-order kinetics in hydroperoxide are predicted (*cf.* Experimental). The small increase in hydroperoxide order with increasing temperature is consistent with the inclusion of eq. 19a-c. As the temperature increases, the concentration of the complex $\text{Co(II)}_2(\text{ROOH})$ available for reaction with peroxy radicals should decrease. This should favor eq. 19a-c and thereby increase the order in hydroperoxide.

B. Cobalt 2-Ethylhexanoate in Chlorobenzene. The above mechanism adequately fits the cobalt 2-ethylhexanoate data at 20°, where the order in cobalt varies from 1.0 to 1.56. Fitting the data to rate law 17 gives $k_{sa} = 10.4$ l. mole⁻¹ sec.⁻¹ and $k_{sb} = 1.92 \times 10^5$ l.² mole⁻² sec.⁻¹, with $r^2 = 0.9985$.

Only first-order dependence on *t*-butyl hydroperoxide was observed with cobalt 2-ethylhexanoate in chlorobenzene. Although the data are less precise than with cobalt acetate, 1.1 order in hydroperoxide corresponds to a 32% increase in k_1 over the concentration range 1.32×10^{-2} M to 20.4×10^{-2} M (Table III), which should be detected. Some participation by eq. 19a-c was suggested to explain greater than first-order dependence on hydroperoxide with cobalt acetate catalysis. This implies that termination between two peroxy radicals (eq. 19a) is less important in cobalt 2-ethylhexanoate catalysis. Yet, the yield of di-*t*-butyl peroxide is considerably greater with cobalt 2-ethylhexanoate catalysis than with cobalt acetate. The relative importance of eq. 5 to eq. 19a and b must then be greater with cobalt 2-ethylhexanoate catalysis.

Rate retardation by 2-ethylhexanoic acid is consistent with cobalt-hydroperoxide complexes as intermediates in the reaction. Continued first-order dependence on hydroperoxide (Table IV) and a similar product distribution in the presence of acid suggest that no change in mechanism occurs under these conditions. Less than expected rates at higher cobalt 2-ethylhexanoate concentrations (Figure 2) also can be explained on the basis of cobalt-hydroperoxide complexes. Here competition between hydroperoxide and other cobalt species for ligand sites may occur.

Reactions of the t-Butoxy Radical. A chain decomposition of hydroperoxides involving alkoxy radicals can be formulated from eq. 19a-c and 20.¹³ Cobalt



catalysis can occur by incorporating eq. 1 and 2 where peroxy radicals are produced and eq. 11 where alkoxy radicals are reduced to regenerate cobalt(III). Equa-

(13) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. F. Vaughan, *Discussions Faraday Soc.*, 10, 242 (1951); L. H. Piette and W. C. Landgraf, *J. Chem. Phys.*, 32, 1107 (1960); S. W. Benson, *ibid.*, 40, 1007 (1964).

tion 21 results by using the steady-state approximation for the following species: $\text{ROO}\cdot$, $\text{RO}\cdot$, $\overline{2\text{RO}\cdot}$, and Co(III)Co(II) . The constant K equals⁷ $[\text{Co(II)}_2]/$

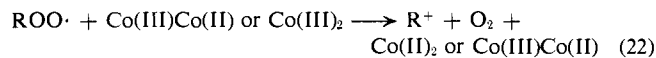
$$\frac{-d[\text{ROOH}]}{dt} = \frac{k[\text{Co}]_{\text{st}}[\text{ROOH}]}{(1 + K + K_3[\text{ROOH}])} \quad (21)$$

$[\text{Co(III)Co(II)}]$ and k is the sum of several constants. This mechanism cannot be solely responsible for the cobalt acetate reaction in acetic acid, since the order is significantly greater than first order in cobalt. However, at lower cobalt 2-ethylhexanoate concentrations in chlorobenzene, where first-order dependence in cobalt is approached, this mechanism is possible.

Previously,¹ it was shown that eq. 20 did not occur in 50% aqueous acetic acid. The suggestion was made that eq. 20 was retarded by hydrogen bonding between the hydroperoxide and the solvent. In addition, fragmentation of the alkoxy radical (eq. 16) may be facilitated by the polar solvent. The same factors may, in part, be responsible for eliminating eq. 20 as a major reaction path for cobalt acetate catalysis in acetic acid. In nonpolar solvents, such as chlorobenzene, eq. 20 may assume more importance.

The greater yield of acetone produced in the cobalt acetate reaction may be due to the valence state of cobalt as well as solvent effects. The per cent cobalt in valence state II at completion of reaction is 95–98% in acetic acid and 45–48% in chlorobenzene. With a higher ratio of $\text{Co(II)}/\text{Co(III)}$, formation of *t*-butoxy radicals (eq. 3 and 8) may become more important and thereby increase yields of acetone result by fragmentation (eq. 2).

Question of Carbonium Ion Intermediates. Oxidation of peroxy radicals by cobalt(III) to give free carbonium ions¹⁴ (eq. 22) can be excluded, since no *t*-butyl acetate (eq. 23) was detected in the cobalt acetate-

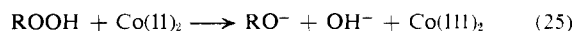
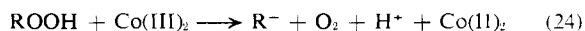


acetic acid system. Under the reaction conditions, *t*-butyl acetate does not give *t*-butyl alcohol. This is consistent with cumyl hydroperoxide decomposition by cobalt acetate in acetic acid.¹⁵

(14) M. S. Kharasch, P. Pauson, and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953).

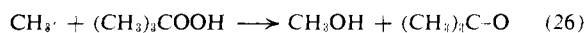
(15) M. S. Kharasch and A. Fono, *ibid.*, **24**, 72 (1959).

Since cobalt acetate is proposed to exist as a dimer, the question of a two-electron change mechanism (eq. 24 and 25) arises. Reaction 24 can be eliminated



by the previous argument against free carbonium ions. In addition, both reactions are first order in each reactant, which is contrary to the kinetic observations.

Methyl Radical Reactions. Fragmentation of *t*-butoxy radicals to acetone and methyl radicals (eq. 12) is an important reaction in the cobalt acetate-acetic acid system. The fate of the methyl radicals deserves comment. Methyl moieties appear only as methanol, methyl acetate, and traces of ethane. Methyl acetate which is stable under the reaction conditions appears to be formed, at least in part, from methanol and acetic acid. No methane was observed, and only trace amounts of ethane are formed. Previous studies,^{1,16}



have ruled out eq. 26 as a route to methanol. Since removal of oxygen during the reaction with a nitrogen stream did not alter the combined yield of methanol and methyl acetate, reaction 27 may be eliminated.



Thus, methanol cannot arise from further reactions of the methyl peroxy radical.¹⁷ Reactions similar to (13) have been suggested previously.¹⁸ At present, we cannot specify whether eq. 13 or 14 is the route of methanol.

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(16) J. Kumamoto, H. E. De La Mare, and F. F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960).

(17) With greatly increased concentrations of reactants, 27 may become detectable as indicated by production of formaldehyde.²¹ The absence of formaldehyde observed in the present study again suggests that 27 is unimportant.

(18) H. E. De La Mare, J. K. Kochi, and F. F. Rust, *J. Am. Chem. Soc.*, **85**, 1437 (1963).