ml. of this there was obtained 0.13 g. of the 2,4-dinitrophenylhydrazone, m.p. 153.5–154.5°. From 0.5 ml. of the liquid residue was obtained 0.33 g. of semicarbazone, m.p. 188–192° (total immersion thermometer). Literature values are 156° and 198°. The yield of phenylacetone from the olefin, based upon the 2,4-dinitrophenylhydrazone, was 41%.

Reaction of IV_a *with potassium permanganate.* There was added to an alkaline solution of 0.7 g. (0.0034 mole) of IV_a, m.p. 136°, a solution of 5.4 g. (0.034 mole) of potassium permanganate in 300 ml. of water. The resulting mixture was stirred for 24 hr., being heated to boiling four times during this period. After the mixture was heated to boiling a final time, decolorized with a few drops of formic acid and filtered, it was extracted four times with ether which was discarded. The water layer was evaporated to a volume of 50 ml., acidified, and extracted continuously with ether for 24 hr. The solid material remaining after removal of the ether (0.16 g.) was recrystallized from water several times. The final material melted at 208–211° (block). A mixture melting point with phthalic acid was not depressed. Acid IV_b was converted to phthalic acid similarly.

Reaction of IV_a *with N-bromosuccinimide.* In a 100 ml. round-bottomed flask were placed 1.0 g. (0.005 mole) of acid IV_a, m.p. 136°, 1.78 g. (0.01 mole) of N-bromosuccinimide, 50 ml. of carbon tetrachloride and about 0.01 g. of benzoyl peroxide. The contents were heated slowly to boiling and then refluxed 2.5 hr. As the contents reached the boil, there was a sharp increase in boiling rate and the solution became red, and then again colorless, rapidly. The cooled mixture was washed twice with sodium bicarbonate, twice with 5% sodium hydroxide, once with water and dried. A pale orange oil remained after removal of the solvent. The oil was heated to boiling momentarily with one gram of pyridine, diluted to 50 ml. with benzene, washed with 5% hydrochloric acid and water, and again freed from solvent. At this point, the crude oil was collected with 20 ml. of methanol which was then reduced, after the addition of 1.0 g. of picric acid, to 5 ml. by boiling. The first crop of crystals, yellow plates, identified as picric acid, was discarded. Later crops consisted of yellow-orange needles. After two recrystallizations from methanol these melted at 115–116°, a value which did not change on further recrystallization.[12] A confirmatory analysis was desired.

Anal. Calcd. for $C_{18}H_{15}N_3O_7$: C, 56.10; H, 3.92. Found: C, 56.03; H, 4.51.

Acid IV_b, when treated similarly, gave the same picrate (a mixture melting point was not depressed) and also the styphnate, m.p. 114-115°.[12]

Use of one molar equivalent of *N*-bromosuccinimide did not produce a bromoacid intermediate but a mixture of starting material and naphthalenic hydrocarbon.

Acknowledgment. The authors wish to thank the Office of Ordnance Research, U.S. Army for generous support for the program of which this work is a part.

KINGSTON, R. I.

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[12] M. C. Kloetzel, *J. Am. Chem. Soc.*, **62**, 1708 (1940), reported 117–118° as the melting point of the picrate of 1,3-dimethylnaphthalene and 116–118° as the melting point of the styphnate.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Effect of Cobaltous 2-Ethylhexanoate and Other Salts on the Decomposition of Tetralin Hydroperoxide

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The decomposition of tetralin hydroperoxide, when catalyzed by cobaltous 2-ethylhexanoate in xylene was of apparent first order in hydroperoxide and second order in catalyst. However, the rate constants varied with the initial concentration of hydroperoxide and decreased with time under some conditions. The decomposition was retarded by acetic acid, chloroform, carbon tetrachloride, water, α-tetralone, and hydroquinone. The amount of α-tetralone produced at 100% decomposition was not markedly affected by changes in temperature, catalyst concentration, and solvents.

Manganous 3-cyclohexane propionate, suspended in benzene at 25°, was four times as active a catalyst as cobaltous 2-ethylhexanoate. Lead cyclohexane carboxylate, in tetralin solution at 80°, was much less active than the cobalt catalyst at 25°.

Relatively few detailed kinetic studies have been made on the metal-catalyzed decomposition of hydroperoxides, a reaction of importance in the polymerization of drying oils. The rate of decomposition of tetralin hydroperoxide with cobaltous naphthenate in tetralin was studied by Robertson and Waters,[2] and the decomposition with cobaltous acetate in glacial acetic acid–benzene solution was studied by Woodward and Mesrobian.[3] The cleavage of hydroperoxides in the presence of various metal salts was studied by Williams and coworkers[4] and by Kharasch and coworkers.[5]

The present report deals chiefly with the effect of cobaltous 2-ethylhexanoate on the rate of breakdown of tetralin hydroperoxide in xylene and other solvents. Some data are also given on the decomposition of this hydroperoxide in the presence of lead cyclohexane-carboxylate and manganous 3-

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[1] From the Ph.D. theses of Kenneth R. Carle (1955) and Donald E. Weiman (1953); Armstrong Cork Company Research Fellows.

[2] A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1578 (1948); *Trans. Faraday Soc.*, **42**, 201 (1946).

[3] A. E. Woodward and R. B. Mesrobian, *J. Am. Chem. Soc.*, **75**, 6189 (1953).

[4] J. W. L. Fordham and H. L. Williams, *Can. J. Research*, B, **28**, 551 (1950); *J. Am. Chem. Soc.*, **72**, 4465 (1950) and **73**, 1634 (1951). R. J. Orr and H. L. Williams, *Can. J. Chem.*, **30**, 985 (1952).

[5] M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950); M. S. Kharasch, P. Pauson, and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953).

cyclohexanepropionate. Since the use of commercial "drier" solutions might lead to errors due to uncertainties of composition, pure samples of the metal salts were prepared. The cobaltous 2-ethylhexanoate is a well-known "drier"; the manganous and lead salts may be considered to be simple models of metal naphthenates. The cobaltous and lead salts were soluble in hydrocarbon and halogenated solvents, but the manganese salt was not. Hence, homogeneous reaction media were involved in the first two cases and heterogeneous systems in the third. Kinetic data were obtained by analysis for peroxide content.

The cobaltous 2-ethylhexanoate and the manganous 3-cyclohexanepropionate are very active catalysts which must be used in low concentration or at 25° to give reactions slow enough to measure. With the less active lead salt it was necessary to work at 80°. Control experiments showed the absence of appreciable thermal decomposition of the hydroperoxide under the conditions used.

Typical first-order graphs of the cobalt-catalyzed decomposition of tetralin hydroperoxide at 25° in xylene are given in Figs. 1 and 2, and rate constants are shown in Table I. First order dependence on hydroperoxide concentration was observed by Robertson and Waters[2], using tetralin as solvent and cobalt naphthenate as catalyst, and by Woodward and Mesrobian[3], using benzene–glacial acetic acid as solvent with cobaltous acetate. In the current work with xylene and cobaltous 2-ethylhexanoate, straight lines were obtained at temperatures above 25° (Fig. 2) and at 25° when the ratio [hydroperoxide]/[catalyst] was greater than 300 or less than 100 (Fig. 1, lowest line). At intermediate ratios the values of the rate constants decreased with time. At all temperatures the rate "constants" varied with initial hydroperoxide concentration.

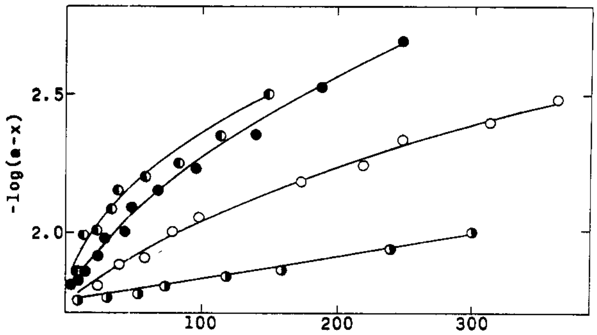

Fig. 1. Decomposition of tetralin hydroperoxide catalyzed by cobaltous 2-ethylhexanoate in xylene at 25.5°. (a) Conc. of THP, $M \times 10^2$; (b) Conc. of Co^{+2} salt, $M \times 10^5$. ◐ (a) 1.77, (b) 17.2. ● (a) 1.99, (b) 13.3. ○ (a) 1.84, (b) 10.8. ◑ (a) 1.84, (b) 5.74

The possibility that the decrease in rate with time was due to a heat effect in the initial reaction was eliminated by experiments showing that the temperature rise was negligible. The change in slope could be due to the formation of a complex between a product, such as α-tetralone, and the cobalt ions. This complex might be less reactive than the one presumably formed by the tetralin

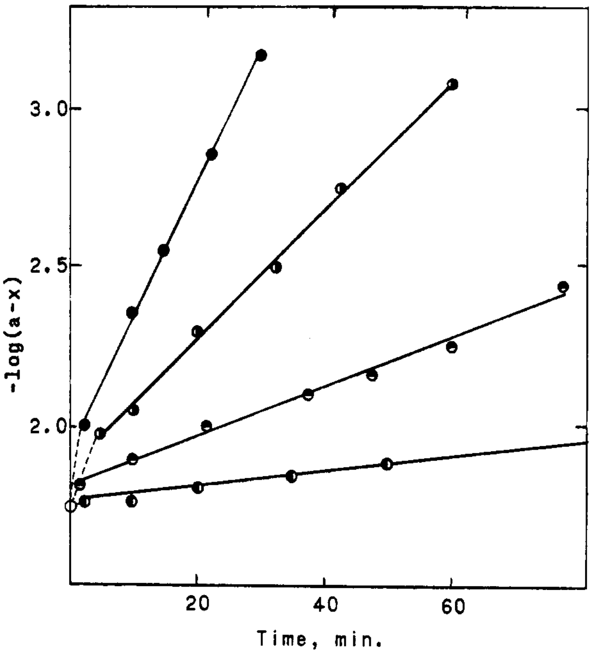

Fig. 2. Decomposition of tetralin hydroperoxide catalyzed by cobaltous 2-ethylhexanoate in xylene at various temperatures. (a) Conc. of THP, $M \times 10^2$; (b) Conc. of Co salt, $M \times 10^5$; (c) Temp., °C. ● (a) 1.81, (b) 5.69, (c) 77.0. ◑ (a) 1.83, (b) 10.7, (c) 50.5. ◒ (a) 1.74, (b) 5.25, (c) 50.5. ◐ (a) 1.83, (b) 5.35, (c) 35.0

TABLE I

FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION OF TETRALIN HYDROPEROXIDE IN XYLENE IN THE PRESENCE OF COBALTOUS 2-ETHYLHEXANOATE

Run No.	THP Conc., $M \times 10^2$	Cat. Conc., $M \times 10^4$	Temp., °C.	k_1,[a] $Sec.^{-1}$ $\times 10^5$
1	1.76	0.53	25.5	4.2
2	1.86	0.54		3.8
3	1.84	0.57		3.5
4	1.77	1.72		36^b
5	1.72	1.72		23^b
6	1.84	1.08		17^b
7	1.99	1.33		22^b
8	1.90	2.58		46
9	2.91	1.40		12^b
10	2.90	1.86		21^b
11	2.92	2.79		48^b
12	2.90^c	1.86		8.3
13	2.90^d	1.86		
14	1.83	0.54	35.0	8.1
15	1.74	0.54	50.5	27
16	1.83	1.07		77
17	1.81	0.57	77.0	150

[a] Obtained from initial slopes, beginning about 2 min. after addition of the catalyst. [b] Retardation of rate after 45–55% completion. [c] Reaction mixture contained 7.4% by volume of glacial acetic acid. [d] Reaction mixture contained equimolar amounts of glacial acetic acid and xylene; in 6 hr. only 11% THP was decomposed.

hydroperoxide and the cobalt at the outset. Supporting evidence for this idea is the marked reduction in the rate of decomposition of the hydroperoxide in the presence of α-tetralone (*vide infra*).

Upon addition of the catalyst to the reaction mixture a portion of the hydroperoxide decomposed almost instantaneously and the color quickly changed to green. In a typical run (2.9×10^{-2} *M* in hydroperoxide and 1.4×10^{-5} *M* in catalyst) about 10% of the hydroperoxide decomposed in less than two minutes, when the first sample was withdrawn. Since the amount of hydroperoxide decomposed in this time was proportional to the catalyst concentration, it is probable that this initial disappearance of hydroperoxide is related to the oxidation of cobaltous to cobaltic ions.

The rates of the first measurable reactions (after two minutes) are dependent on the square of the initial cobaltous octoate concentration. In Fig. 3 are given plots of the logs of the initial catalyst concentrations against the logs of the k_1 values for two sets of reactions having approximately constant hydroperoxide concentrations. The slopes of the two lines are 2.0. Woodward and Mesrobian[3] found the same dependence on the catalyst concentration when cobaltous acetate was used.

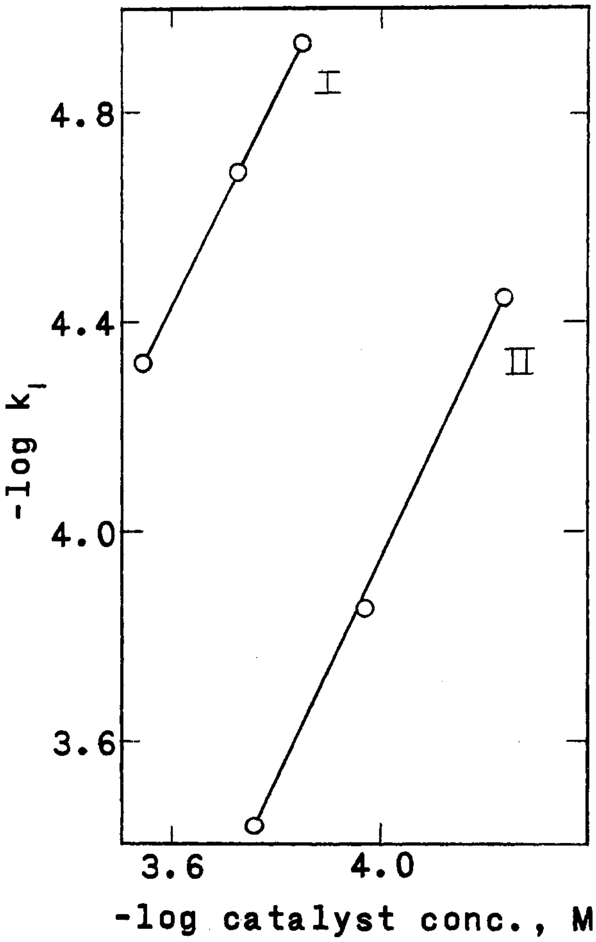

Fig. 3. Determination of dependence on catalyst concentration of decomposition of tetralin hydroperoxide in xylene at 25.5°. I, Conc. of THP, $1.8 \times 10^{-2}M$; conc. of Co salt, 1.72×10^{-4}, 1.08×10^{-4}, $5.75 \times 10^{-5}M$. II, Conc. of THP, $2.9 \times 10^{-2}M$; conc. of Co salt, 1.40×10^{-4}, 1.86×10^{-4}, $2.79 \times 10^{-4}M$

The energy of activation for the decomposition of tetralin hydroperoxide catalyzed by cobaltous 2-ethylhexanoate in xylene was determined from the k_1 values at 25.5, 35.0, 50.5, and 77° for reactions done with approximately $1.8 \times 10^{-2}M$ hydroperoxide and $0.54 \times 10^{-4}M$ catalyst solutions. From the slope of the line in Fig. 4, E was calculated to be 17.4 ± 2 kcal. Woodward and Mesrobian[3] reported a slightly higher value for the cobaltous acetate–catalyzed decomposition of tetralin hydroperoxide in acetic acid–benzene solution.

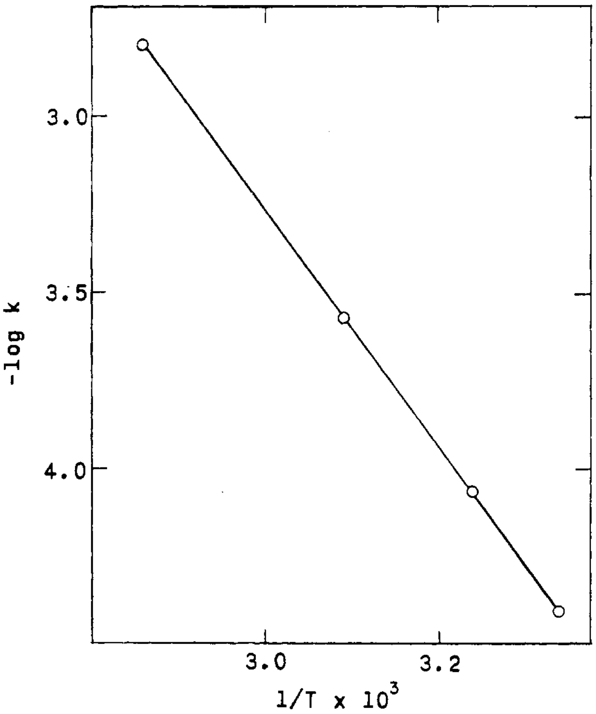

Fig. 4. Determination of energy of activation for decomposition of tetralin hydroperoxide in xylene with cobaltous 2-ethylhexanoate

It was of interest to see what effect acetic acid would have on the reactions studied in this investigation. In a medium consisting of 92.6% xylene and 7.4% glacial acetic acid the decomposition of tetralin hydroperoxide ($2.9 \times 10^{-2}M$) in the presence of the cobalt catalyst ($1.86 \times 10^{-4}M$) was first order throughout, with no decrease in slope up to 85% completion. The rate constant was smaller than for a comparable reaction without the acetic acid; (compare Runs 12 and 10 in Table I).

When equimolar quantities of glacial acetic acid and xylene were used, the decomposition of the peroxide proceeded very slowly; in six hours 11% was decomposed as compared to 90% for the reaction not containing the acetic acid. It appears that the acetic acid decreases the catalytic activity of the cobalt salt in promoting hydroperoxide decomposition. Perhaps the acetic acid competes with the hydroperoxide for complex formation with the cobalt ion (or ions).

The decomposition of tetralin hydroperoxide in cyclohexane in the presence of cobaltous 2-ethylhexanoate fitted the graph of a reaction second order in hydroperoxide, with no decrease in slope to at least 90% completion. (First order plots in cyclohexane gave curves.) The second order rate constants are shown in Table II.

TABLE II

SECOND ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF TETRALIN HYDROPEROXIDE IN CYCLOHEXANE AT 25.5° WITH COBALTOUS 2-ETHYLHEXANOATE

THP Conc., M × 10^2	Cat. Conc., M × 10^4	$k \times 10^4$ l. Mole^{-1} Sec.$^{-1}$	Completion,[a] %
1.81	1.08	9	91
1.84	1.24	11	90
1.83	1.33	15	89

[a] Minimum % following second order kinetics.

The apparent kinetics of second order dependence on hydroperoxide concentration in cyclohexane might indicate the occurrence of chain transfer to the solvent with subsequent attack of solvent-derived free radicals on the hydroperoxide. However, products containing cyclohexyl groups have not been isolated and there is only a small difference in the percents of ketonic and hydroxyl compounds formed by complete decomposition of the hydroperoxide in cyclohexane and in xylene, as shown in Table III. Another possible cause of second order kinetics could be the formation of a hydrogen-bonded dimer, as has been suggested[6] for the thermal decomposition of hydroperoxide at moderate concentrations: $\mathrm{ROOH{-}}\underset{\mathrm{H}}{\mathrm{OOR}}$. Such hydrogen bonding could occur to a greater extent in cyclohexane than in the more polar xylene.[7]

TABLE III

KETONE AND HYDROXYL CONTENT OF PRODUCTS FROM COMPLETE DECOMPOSITION OF TETRALIN HYDROPEROXIDE WITH COBALT CATALYST AT 25.5°

Solvent[a]	Ketone,[b] Mole %	Hydroxyl,[c] Mole %
Xylene	47	56
Cyclohexane	54	58

[a] With 1.96 × $10^{-2}M$ THP and 1.33 × $10^{-4}M$ cobaltous octoate. [b] By spectrophotometric method[8] for α-tetralone. [c] By acetylation in pyridine.[9]

Attempts to carry on the cobalt-catalyzed decomposition of the peroxide in chloroform showed that chloroform was a powerful inhibitor. For example, in a solution that was 1.8 × $10^{-2}M$ in hydroperoxide and 0.98 × $10^{-4}M$ in cobaltous 2-ethylhexanoate at 25.5° (comparable to Run 6, Table I), the decomposition stopped completely after 8% conversion. Subsequent additions of catalyst produced further increments of decomposition which were proportional to the amounts of catalyst added; the ratio of moles hydroperoxide decomposed per mole of catalyst added was approximately 18.

Carbon tetrachloride was also found to be an inhibitor for the cobalt-catalyzed decomposition of tetralin hydroperoxide, though less powerful than chloroform. The reactions stopped after moderate degrees of completion, as shown in Table IV. The kinetic data up to the stopping points gave first order rate constants of the same order of magnitude as those in xylene at comparable concentrations.

TABLE IV

FIRST ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF TETRALIN HYDROPEROXIDE IN CARBON TETRACHLORIDE AT 25.5° WITH COBALTOUS 2-ETHYLHEXANOATE

THP Conc., M × 10^2	Cat. Conc., M × 10^4	$k \times 10^5$ Sec.$^{-1}$	Completion When Reaction Stopped, %
1.82	0.51	2.0	25
1.77	0.97	12	48
1.84	1.33	15	62

The effect of various solvents on the rates of decomposition of tetralin hydroperoxide in the presence of cobaltous 2-ethylhexanoate is summarized in Table V. The successive decrease in the rates from cyclohexane to carbon tetrachloride

TABLE V

EFFECT OF SOLVENTS ON THE COBALT-CATALYZED DECOMPOSITION OF TETRALIN HYDROPEROXIDE AND ON THE THERMAL DECOMPOSITION OF BENZOYL PEROXIDE

Solvent	Decomp. in 1 Hour, %	
	THP[a]	Bz_2O_2[b]
Cyclohexane	93	51.0
Toluene	72	17.4
Benzene	69	15.5
Xylene	61	
Carbon tetrachloride	56	13.5
Chloroform	10[c]	14.5

[a] Tetralin hydroperoxide, 1.9 × $10^{-2}M$, with cobaltous 2-ethylhexanoate, 1.3 × $10^{-4}M$ at 25.5°. [b] Data of Bartlett and Nozaki[10] for benzoyl peroxide at 79.5°. [c] Reaction stopped in 4 min.

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(6) L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952); L. Bateman, H. Hughes, and A. L. Morris, *Discussions Faraday Soc.*, **14**, 190 (1953).

(7) Suggested by the referee.

(8) H. H. Willard, L. L. Merritt, and J. A. Dean, *Instrumental Methods of Analysis*, D. Van Nostrand Co., Inc., New York, 1951, p. 63.

(9) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, 2nd ed., John Wiley and Sons, Inc., New York, 1954, p. 9.

might be explained by a decrease in the activity of the free radicals formed by chain transfer. It is of interest that the rates of decomposition of benzoyl peroxide[10] in some of these solvents are in the same relative order.

However, the large decrease in rate of decomposition of tetralin hydroperoxide in chloroform solution is not parallel to the effect of this solvent on the decomposition of benzoyl peroxide. It is conceivable that the marked inhibitory effect of chloroform (and possibly also of carbon tetrachloride) on the cobalt-catalyzed decomposition is caused by the formation of stable chlorocobaltic complexes.

The effect of various other added substances on the cobalt-catalyzed decomposition of tetralin hydroperoxide in cyclohexane is shown in Table VI. The strong inhibition caused by water could be due to the formation of a complex with the cobaltous or cobaltic ions. Similarly, the retarding action of α-tetralone could be attributed to complex formation with the cobalt. An alternative explanation is that the α-methylene group of tetralone might produce inactive radicals by transfer reactions.

TABLE VI

EFFECT OF ADDITIVES ON THE DECOMPOSITION OF 0.019M TETRALIN HYDROPEROXIDE IN CYCLOHEXANE IN THE PRESENCE OF 0.00013M COBALTOUS 2-ETHYLHEXANOATE AT 25.5°

	Decomposition, %, after			
Additive	4 min.	10 min.	60 min.	180 min.
None	46	60	93	100
α-Tetralol[a]	42	68	92	100
Co^{+3} catalyst[b]	33	56	89	100
Water[c]	8	32	56	56
α-Tetralone[d]	24	37	57	63
Hydroquinone[e]	18	20	22	22

[a] Conc. was $2.64 \times 10^{-2}M$. [b] Co^{+3} was obtained by oxidation of Co^{+2} with an equivalent amount of THP, and addition of THP in cyclohexane, giving 0.00013M Co^{+3}. [c] Saturated solution in cyclohexane. [d] Conc. was $2.22 \times 10^{-2}M$.

Quantitative determinations of the α-tetralone present after 100% decomposition of tetralin hydroperoxide by the cobalt catalyst were carried on to learn whether the proportion of this product could be varied by changing conditions. After decomposing $1.9 \times 10^{-2}M$ peroxide in cyclohexane at 25.5°, 54–58 mole % of α-tetralone resulted, regardless of variations in the catalyst concentration (from 1.24 to $1.99 \times 10^{-4}M$) and in the temperature (from 25.5 to 70.0°). The use of cobaltic instead of cobaltous ions had no effect. Solvents had little effect (Table III). The presence of $2.64 \times 10^{-2}M$ α-tetralol increased the yield of ketone to 63%, probably due to oxidation of the α-tetralol.

Data on the effects of the lead and manganous catalysts are summarized in Table VII. The decomposition of the tetralin hydroperoxide in tetralin at 80° in the presence of lead cyclohexanecarboxylate was approximately first order with respect to the peroxide in the intervals from 3–19% up to 76–87% reaction. During the initial stages the rates were slower and not in accord with first order kinetics. The cause is unknown.

TABLE VII

ACTIVITY OF LEAD AND MANGANOUS SALTS AS CATALYSTS FOR THE DECOMPOSITION OF TETRALIN HYDROPEROXIDE

Salt Conc., M	THP Conc., M	THP Decomp.,[a] % in 1 Hour
Lead cyclohexanecarboxylate in tetralin at 80°		
0.0013	0.0269	14
0.0013	0.0272	14
0.0013	0.0304	11
0.0015	0.0122	15
Manganous 3-cyclohexanepropionate in benzene at 25°		
0.0000137	0.0123	69
0.0000364	0.0123	79
0.0000274	0.0246	80
0.0000364	0.0135	74
0.0000364	0.0246	81
0.0000364	0.0342	77

[a] Rates of decomposition of tetralin hydroperoxide were taken from the first order portion of the graph in the case of the lead catalyst, but from the entire curve up to 60 min. in the case of the manganous catalyst.

Manganous 3-cyclohexanepropionate was a powerful catalyst, even though insoluble in the reaction medium. In benzene at 25° the manganous catalyst produced the same amount of decomposition of tetralin hydroperoxide as cobaltous 2-ethylhexanoate used in about four times the concentration of the manganous salt. The data from these rapid heterogeneous reactions do not fit simple kinetics.

EXPERIMENTAL

Tetralin hydroperoxide.[11] Redistilled tetralin was autoxidized at 81° under ultraviolet irradiation to a peroxide content of 25%. After removal of unreacted tetralin by distillation at 0.08 to 0.05 mm. with a bath below 55°, the product was crystallized at −10°, filtered, washed with n-pentane and recrystallized from a mixture of 50 parts of n-pentane and 1 part of ethyl acetate. The white product, m.p. 55–56°, was found by iodimetric analysis to be 99.5% pure.

Purification of materials. All solvents were washed, dried, and fractionated. Nitrogen was freed from oxygen with Fieser's solution, then passed through lead acetate solution, a calcium chloride tower, a sulfuric acid trap, a bottle of mineral oil, and finally a bottle containing the solvent, to saturate the nitrogen with the solvent.

Lead cyclohexanecarboxylate. When 5.13 g. (0.04 mole) of cyclohexanecarboxylic acid was stirred with 5.18 g. (0.007 mole) of basic lead carbonate ($2PbCO_3.Pb(OH)_2$), carbon

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[10] P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

[11] M. S. Kharasch and J. G. Burt, *J. Org. Chem.*, **16**, 150 (1951).

dioxide was evolved. The mixture was slowly heated to 180°. The resulting clear melt was dissolved in 35 ml. of boiling absolute ethanol and cooled. The fine needles of the alcoholate were recrystallized again and dried to constant weight at 105°. The white salt was soluble in benzene and tetralin.

Anal. Calcd. for $C_{14}H_{22}O_4Pb$. Pb, 45.09. Found. Pb, 44.61, 44.77.

Attempts to prepare lead 2-ethylhexanoate by the same method gave a liquid salt of only 97% purity.

Manganous 3-cyclohexanepropionate. A mixture of 8.13 g. (0.052 mole) of 3-cyclohexanepropionic acid and 2.88 g. (0.025 mole) of manganous carbonate was heated for 12 hr. on a steam bath, then the temperature of the melt was raised to 175°. Most of the excess acid was removed by distillation at 40 mm. The residue was dissolved in boiling benzene and filtered from unreacted manganous carbonate (0.4 g.). After clarification with infusorial earth the solution was poured into three times its volume of ethyl acetate. The precipitated pink salt, now insoluble in organic solvents, was dried at 40°.

Anal. Calcd. for $C_{18}H_{30}O_4Mn$: Mn, 15.05. Found. Mn, 15.39, 14.45.

Manganous cyclohexanecarboxylate could not be obtained in pure condition by use of this method with manganous acetate.

Cobaltous 2-ethylhexanoate.[12,13] To a mixture of 8.65 g. (0.06 mole) of 2-ethylhexanoic acid, 10.3 g. of petroleum ether b.p. 90–100° and 2.4 g. of distilled water heated to 75° was added slowly with stirring 7.1 ml. of 8.4N sodium hydroxide, followed by a filtered solution of 9 g. (0.0032 mole) of cobalt sulfate, $CoSO_4.7H_2O$, dissolved in 10.3 ml. of water at 75°. After 1 hr. at 75°, the two layers were separated. The top heptane layer was washed twice with water, the solvent distilled off, the residue treated with heptane to dissolve the organic salt. After filtration, with use of filter-aid, and removal of solvent, the product was a dark purple plastic material.

Anal. Calcd. for $C_{16}H_{30}O_4Co$: Co, 17.10. Found. Co, 17.44, 17.44.

Kinetic studies. The all-glass apparatus was arranged for passage of nitrogen through the reaction mixture, which served to stir it, as well as through the introducing funnel. Care was taken to bring reactants to the temperature of the bath before mixing. The zero peroxide value was determined immediately before contact with the salt. Analyses for peroxide were done by the method of Wagner, Smith, and Peters.[14]

Free radical nature of the decompositions. Proof of the presence of free radicals was that in a mixture of 2.35×10^{-4} mole of tetralin hydroperoxide, 3×10^{-7} mole of cobaltous 2-ethylhexanoate and 1.8×10^{-3} mole of styrene, 9% of the styrene was polymerized[15] after 22 hr. at 25.5° to a polymer of limiting viscosity number 71 (in benzene), whereas a control did not polymerize.

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NEWARK, DEL.

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(12) L. Roon and W. Gotham (to Nuodex Products Co.), U. S. Patent **2,113,496**, Apr. 5, 1938.

(13) Preparative details kindly furnished by Dr. J. T. Kingsbury, Harshaw Chemical Co.

(14) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

(15) Done by Dorothy A. Delker.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Influence of Alkoxides and the Dimetalation of Some Alkylaryl Hydrocarbons[1]

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Cumene, *t*-butylbenzene, *n*-butylbenzene, toluene, and *p*-cymene were dimetalated by amylsodium in the presence and absence of various sodium alkoxides or sodium oxide. The percentage of disubstitution was higher with *n*-butylbenzene and toluene where both nuclear and lateral metalation occurred, than in cumene and *t*-butylbenzene where nuclear metalation only took place. Sodium 2-methyl-2-heptoxide accelerated metalation and favored dimetalation. A cyclic hexoxide repressed dimetalation. *p*-Cymene was dimetalated at a lateral and either of the two nuclear positions available in spite of some hindrance at the latter places. The compositions of the reacting mixtures changed slowly during storage, even over a year.

The high percentage of 1,4-polymerization of butadiene induced by the Alfin catalyst[2,3] has demonstrated the unusual and powerful influence of certain associated salts upon organosodium reagents. An effect has been realized also in common alkylation,[4] ether cleavage,[5] and metalations.[6,7] For this class of reagent, therefore, the use of associated salts to modify or alter reactions is as important as are changes in concentration, temperature, and solvent to more common chemical reagents. The present study of dimetalation and of the effect of alkoxides extends our information of this type of control and of the factors favorable to dimetalation.

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