methanol in colorless prisms; yield, 18.3–18.7 g. (86–88%); m. p. 149–150°. After two more recrystallizations of a sample, the m. p. was 152.5–153.5°.

*Anal.* Calcd. for $C_{17}H_{19}ON$: N, 5.53. Found: N, 5.35.

A chilled solution of 2 g. of the oxime in 40 ml. of benzene was treated with 2 g. of phosphorus pentachloride (added all at once), and the mixture was refluxed on a steam-bath for fifteen minutes. The precipitate obtained by hydrolysis with water and evaporation of the benzene weighed 1.31 g.; m. p. 156.5–157.5°. The product darkened slowly on standing in air and more rapidly on warming in a solvent in contact with air. After three recrystallizations from acetone (by cooling in an alcohol-Dry Ice-bath a solution saturated at room temperature) a sample of **4-cyclopentyl-1-acetylaminonaphthalene** formed a colorless prisms; m. p. 162–163°.

*Anal.* Calcd. for $C_{17}H_{19}ON$: N, 5.53. Found: N, 5.30.

The moist crude acetylamino compound prepared from ten times the quantities of materials used in the preceding directions was refluxed with a mixture of 700 ml. of ethanol and 45 ml. of concentrated hydrochloric acid on a steam cone under an atmosphere of carbon dioxide for twenty-four hours. The solvent was removed by distillation and the crystalline residue was recrystallized from 1.5 l. of water (Norit); yield, 9.4 g. Additional solid (1 g.) was obtained from the filtrate by making it basic with sodium hydroxide, extracting with ether and passing hydrogen chloride into the dried ethereal solution. The combined **4-cyclopentyl-1-naphthylamine hydrochloride** sublimed at 135–140° at 0.2 mm. as colorless crystals; m. p. above 260° dec.

*Anal.* Calcd. for $C_{16}H_{18}NCl$: N, 5.65. Found: N, 5.85.

## Summary

1-Cyclopentylnaphthalene was prepared from 1-bromonaphthalene. The hydrocarbon was acetylated, succinoylated, and sulfonated in the 4-position. The three primary substitution products were converted to other 4-derivatives of the parent hydrocarbon.

9-Cyclopentylphenanthrene, 9-cyclopentyl-1,2,-3,4-tetrahydrophenanthrene, and some 1-ethyl-4-substituted-naphthalenes were synthesized.

ANN ARBOR, MICHIGAN RECEIVED MAY 10, 1950

---

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

# Decomposition of Lauroyl Peroxide in Benzene and Diethyl Ether

BY W. E. CASS

A variation in the rate of decomposition of benzoyl peroxide in different solvents has been observed by a number of investigators.[1-4] The increased rate in certain solvents has been ascribed to an "induced decomposition," in which radicals from the solvent (or peroxide) attack the undissociated peroxide. Inhibition of the induced decomposition by known inhibitors for free radical reactions (*e. g.*, oxygen) has been considered evidence for a free radical chain mechanism. Isolation of the products of reaction of benzoyl peroxide with certain aliphatic ethers[5] indicated the possibility of a simple two-step chain for the induced decomposition in these cases

$$C_6H_5COO\cdot + RH \xrightarrow{k_b} C_6H_5COOH + R\cdot \quad (b)$$

$$R\cdot + (C_6H_5COO)_2 \xrightarrow{k_c} C_6H_5COOR + C_6H_5COO\cdot \quad (c)$$

The present work was undertaken to find out if lauroyl peroxide, an aliphatic diacyl peroxide, also exhibited induced decomposition.[6]

Kinetic experiments at 30° indicated that lauroyl peroxide decomposed about eight times more rapidly in diethyl ether $k_1 \sim 0.007$ hr.$^{-1}$ than in benzene $k_1 \sim 0.0009$ hr.$^{-1}$. In both solvents the reactions appeared to be first order. Data from the kinetic experiments are listed in Table I. In each case the first order rate constant and the inhibition period were obtained from the plot of the data shown in Fig. 1.

TABLE I

DECOMPOSITION OF LAUROYL PEROXIDE IN SOLVENTS AT 30 ± 0.2°

| Solvent | Total time, hr. | $a$ | $a - x$ | Inhib., hr. | $k_1$, hr.$^{-1}$ |
|---|---|---|---|---|---|
| Ether | 218 | 0.0515 | 0.0121 | 14 | 0.0072 |
| Ether | 217.5 | .1020 | .0238 | 12 | .0072 |
| Ether | 211.7 | .2010 | .0515 | 11 | .0068 |
| Benzene | 362 | .2020 | .1462 | 20 | .00092 |

TABLE II

PRODUCTS OF REACTION OF LAUROYL PEROXIDE WITH DIETHYL ETHER AT ~37°

| Product | Approx. yield, mole per mole peroxide dec. |
|---|---|
| Carbon dioxide | 0.92[a,b], 0.8[c] |
| Hendecane | .84[d] |
| 1-Ethoxyethyl laurate | .88,[e] 0.84[d] |
| Acid (lauric ?) | .037[b] |
| Ester (unknown) | .16[a,b,e] |

[a] Calcd. from (alkaline) sapon. equiv. of ether-free residue. [b] Calcd. from neut. equiv. of residue. [c] Detd. by absorption in Ascarite. [d] Yield of crude product isolated, [e] Calcd. from (acid) sapon. equiv. of residue.

---

(1) Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(2) Bartlett and Nozaki, *ibid.*, **69**, 2299 (1947).

(3) Cass, *ibid.*, **68**, 1976 (1946).

(4) Barnett and Vaughan, *J. Phys. & Colloid Chem.*, **51**, 926, 942 (1947).

(5) Cass, THIS JOURNAL, **69**, 500 (1947).

(6) Kharasch, Jensen and Urry, *J. Org. Chem.*, **10**, 386 (1945), postulated the following induced decomposition steps as part of their mechanism for the reaction of diacetyl peroxide with methyl chloroacetate

$$CH_3COO\cdot + (CH_3COO)_2 \longrightarrow CH_3COOCH_3 + CH_3COO\cdot + CO_2$$

$$CH_3\cdot + (CH_3COO)_2 \longrightarrow CH_3COOCH_3 + CH_3COO\cdot$$

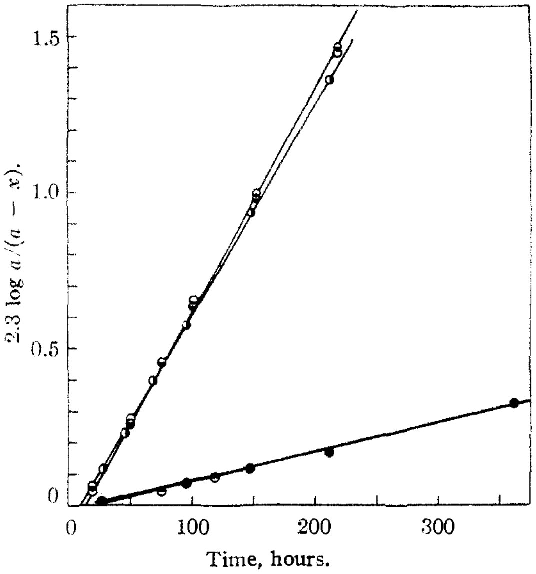

Fig. 1.—Rate of decomposition of lauroyl peroxide in solvents at 30 ± 0.2°: diethyl ether, ○, $a = 0.0515$; ◒, $a = 0.1020$; ◑, $a = 0.2010$; ◓, $a = 0.1050$, quinone concn. = 0.005 $M$; benzene, ●, $a = 0.2020$.

The more rapid decomposition in ether was found to be strongly retarded by quinone and oxygen, indicating a free radical chain mechanism. By reference to Fig. 1 it will be noted that the rate of decomposition of the peroxide in ether in the presence of quinone is comparable (for the two points determined) to the rate in benzene in the absence of quinone.

The products of reaction of lauroyl peroxide in boiling diethyl ether are listed in Table II.

## Discussion

The kinetic data and the products of reaction indicate that lauroyl peroxide undergoes an induced decomposition in ether similar to that for benzoyl peroxide. However, the reaction for lauroyl peroxide seems to involve shorter chains. Thus the first order rate constant for the decomposition of benzoyl peroxide in benzene[3] at 30° was 0.000173 hr.$^{-1}$ and, in diethyl ether[7] was $\sim$0.036 hr.$^{-1}$, a 200-fold increase. The corresponding increase in rate for lauroyl peroxide in these solvents is only approximately eight-fold.

It will also be noted that the rate constant for the decomposition of lauroyl peroxide in benzene is greater than that for benzoyl peroxide, in agreement with the results of Redington[8] for the decomposition of these peroxides in styrene.

The fact that the decomposition of lauroyl peroxide in diethyl ether follows first order kinetics gives support to the suggestion of Bartlett and Nozaki[2] that "crossed termination" (which leads to first order kinetics) is to be expected in induced decomposition of peroxides.[9] In the present case the crossed termination step would be

$$C_{11}H_{23}COO\cdot + CH_3\underset{\cdot}{C}HOC_2H_5 \xrightarrow{k_d} C_{11}H_{23}COOCH(CH_3)OC_2H_5 \quad (d)$$

The inhibition periods are believed to result from a suppression of the chain decomposition by oxygen dissolved in the solutions, as was previously indicated.[3] Although the free space above the peroxide solutions in the ampules was swept with nitrogen before sealing, the solutions were not degassed. Hence the presence of dissolved oxygen is probable and oxygen inhibition of the chain decomposition is to be expected. Since oxygen inhibition apparently involves a consumption of oxygen,[2,3,4] the rates of decomposition, following the period of inhibition, are believed to be not greatly affected.

The main products of reaction of lauroyl peroxide with diethyl ether are similar to those from benzoyl peroxide[5] except that essentially no lauric acid was formed, *i. e.*, decarboxylation was much more extensive.[10] As was pointed out previously,[5] decarboxylation might occur according to any of the following steps

$$C_{11}H_{23}COO\cdot \xrightarrow{k'a} C_{11}H_{23}\cdot + CO_2 \quad (a')$$

$$C_{11}H_{23}COO\cdot + RH \xrightarrow{k'b} C_{11}H_{24} + CO_2 + R\cdot \quad (b')$$

$$R\cdot + (C_{11}H_{23}COO)_2 \xrightarrow{k'c} C_{11}H_{23}COOR + C_{11}H_{23}\cdot + CO_2 \quad (c')$$

If the hendecyl radical produced in steps (a′) or (c′) subsequently captures a hydrogen from the ether as does the lauroyloxy radical, it is difficult to ascribe the decarboxylation to any single reaction step. Recent work by Edwards and Mayo[11] on the decomposition of acetyl peroxide in various solvent mixtures is considered evidence for decarboxylation according to step (b′).

The comparatively lower yield of the acylal, 1-ethoxyethyl benzoate, and of hendecane probably resulted from the shorter chain length of the induced decomposition of lauroyl peroxide. In the present work there was no evidence for the formation of hendecene, although Kharasch, Jensen and Urry[6] found evidence for the presence of this unsaturated hydrocarbon among the products of decomposition of lauroyl peroxide in acetic acid.

---

(7) The *first order* rate constant for the decomposition of benzoyl peroxide in diethyl ether was obtained by replotting the data for the first two runs listed in Table IV, ref. 3. Because the rate constants tended to decrease as reaction progressed, they were taken from the initial slopes. The constants were 0.038 hr.$^{-1}$ ($a$ = 0.1492) and 0.034 hr.$^{-1}$ ($a$ = 0.1010).

(8) Redington, *J. Polymer Sci.*, **3**, 503 (1948).

(9) The complex, higher-order kinetics, previously found for the decomposition of benzoyl peroxide in ethers (ref. 3), may well be the result of retardation by aromatic products of the reaction (refs. 1, 3). There are no aromatic products in the case of lauroyl peroxide, thus leading to simpler kinetics.

(10) Wieland and co-workers observed that alkoyloxy groups in mixed diacyl peroxides lost carbon dioxide more readily than aroyloxy groups; *cf.* Wieland and Rasuwajew, *Ann.*, **480**, 157 (1930); Wieland, Schapiro and Metzger, *ibid.*, **513**, 93 (1934).

(11) Edwards and Mayo, This Journal, **72**, 1265 (1950).

## Experimental

Reagent grade anhydrous benzene and diethyl ether were used as solvents. The ether was dried and distilled over sodium before use.

Lauroyl peroxide was a purified commercial product, assaying 97.2% and containing about 1% free fatty acid.[12]

Rate studies were conducted as previously described for benzoyl peroxide.[3]

**Peroxide Analysis.**—Because lauroyl peroxide reacted slowly with potassium iodide in acetic acid at room temperature the previous procedure[3] was modified in that the reaction mixture was heated for fifteen minutes in a 70° oven prior to dilution with water and titration. A small slit, cut in the glass stopper of the reaction flask, allowed carbon dioxide to escape, but minimized back diffusion of air.

**Inhibition Experiments.**—A 0.1050 *M* solution of lauroyl peroxide in diethyl ether was treated as follows: two samples were sealed under nitrogen in ampules; two samples were sealed under much air in large ampules; two samples were made 0.005 *M* in *p*-quinone and sealed under nitrogen. Results are given in Table III.

TABLE III

INHIBITION OF THE DECOMPOSITION OF LAUROYL PEROXIDE BY QUINONE AND OXYGEN (AIR) AT 30 ± 0.2°

| Total time, hr. | Peroxide concn., m./l. Blank ($N_2$) | Quinone (0.005 *M*) | Air |
|---|---|---|---|
| 0 | 0.1050 | 0.1050[a] | 0.1050 |
| 76.5 | .0648 | .1012[a] | .1278 |
| 119 | .0488 | .0963[a] | .1470 |

[a] Corrected for iodine liberated by quinone (*cf.* ref. 13).

The increase in peroxide content of the sample under air was probably the result of catalyzed peroxidation of the ether. Peroxide was recovered from the inhibited 76.5-hour samples by evaporation of solvent, finally under 0.5 mm. for two hours. Peroxide was recovered from the quinone-inhibited sample in 98.5% yield; assay 93%; m. p. 48–50.5°; mixed m. p. 49–51° with original peroxide (m. p. 50–51.5°). Peroxide was recovered from the oxygen-inhibited sample in 101% yield; 102% assay; m. p. 48–50; mixed m. p. 49–51°. The high assay of the peroxide recovered from the oxygen inhibited sample indicated contamination by ether peroxide.

**Reaction of Lauroyl Peroxide with Diethyl Ether.**—Reaction was carried out as previously described for benzoyl peroxide.[5] The solution of 41 g. (0.1 mole, on basis of 97.2% assay) of lauroyl peroxide in 500 ml. of anhydrous diethyl ether was kept at gentle reflux for seventeen days. Carbon dioxide was then swept from the system with a slow stream of nitrogen for four hours, a second Dry Ice-acetone cooled trap being first inserted in the line. The increase in weight of the tared Ascarite tube was 3.514 g., corresponding to 0.8 mole of carbon dioxide per mole of peroxide decomposed. (It is possible that additional carbon dioxide remained dissolved in ether in the cold traps.)

The residual solution was essentially peroxide-free. Excess ether was removed under vacuum, first at 15–20 mm., then for fifteen minutes at 0.6 mm. There was obtained 42.6 g. of oily residue plus about 0.5 g. of oily distillate. (The oily distillate gave negative tests for unsaturation with bromine and with potassium permanganate.) The residue contained 1.38 × $10^{-4}$ equiv. of acid per gram, corresponding to 0.059 equiv. of acid per mole of peroxide decomposed. Since the original peroxide contained about 0.022 equiv. of acid per mole, approximately 0.037 equiv. of acid per mole of peroxide was produced in the reaction with the ether.

A sample of the residue was saponified with 0.5 *N* alcoholic potassium hydroxide. The solution turned brown (aldehyde gum formation) and the back titration was followed using a *p*H meter. This alkaline saponification indicated the presence of 1.10 equiv. of ester plus acid or 1.04 equiv. of ester per mole of peroxide decomposed.

That the above "ester" was mostly (but not entirely) acylal was proved by hydrolysis with dilute hydrochloric acid as previously described.[5] This hydrolysis indicated 0.935 equiv. acylal plus acid or 0.88 mole of acylal per mole of peroxide decomposed. The non-acylal ester material was not identified. A 29.5-g. portion of the oily residue was distilled under reduced pressure through a 30-cm. unpacked, heated column. Two fractions were collected: Fract. I, 9.1 g., b. p. 60–67° at 5 mm.; Fract. II, 15.8 g., b. p. 102–108° at 0.1–0.2 mm.

**Hendecane.**—Fraction I proved to be crude hendecane. It was distilled at 194–197° (63% recovery) and redistilled at 195–196°; $n^{20}\text{D}$ 1.4172; lit., b. p. 195.84°; $n^{20}\text{D}$ 1.41727.[14] The product gave negative results in tests for unsaturation using bromine in carbon tetrachloride and aqueous potassium permanganate. The crude yield of hendecane corresponded to 0.84 mole per mole of peroxide decomposed.

**1-Ethoxyethyl Laurate.**—Fraction II proved to be this acylal, the crude yield corresponding to 0.84 mole per mole of peroxide decomposed. Fraction II was redistilled at 99–103° under 0.15 mm. The redistilled product was found to contain 3 × $10^{-4}$ equiv. of acid per gram. The product was purified by dissolving in ether, adding an excess of 0.1 *N* sodium hydroxide and then adding anhydrous sodium sulfate (to break the emulsion). Redistillation at 99–100° under 0.15 mm. gave a product having 2 × $10^{-5}$ equiv. of acid per gram; $n^{25}\text{D}$ 1.4293; $d^{25}_4$ 0.8779; *MR*, 79.39 (calcd.), 80.0 (obsd.).

*Anal.* Calcd. for $C_{16}H_{32}O_3$: C, 70.56; H, 11.84. Found: C, 71.1, 71.2; H, 11.6, 11.5.

Hydrolysis of the acylal in acetone with 0.5 *N* hydrochloric acid as before[5] gave a saponification equivalent of 280 (calcd. 272), indicating some contamination with a non-acylal impurity. Lauric acid (m. p. 42°, mixed m. p. 42–43.5°, neut. equiv. 200) was recovered from hydrolyzate in 93% yield.

The product was analyzed for acetaldehyde as described previously.[5] Acetaldehyde 2,4-dinitrophenylhydrazone was obtained in 95% yield.

## Summary

1. Lauroyl peroxide has been found to decompose about eight times more rapidly in diethyl ether than in benzene at 30°. The increase in rate has been ascribed to an induced decomposition of the peroxide in the ether.

2. The chief products of reaction of lauroyl peroxide in boiling diethyl ether have been found to be carbon dioxide, hendecane and the acylal, 1-ethoxyethyl laurate. These products are believed to support the idea of an induced decomposition reaction in this solvent.

SCHENECTADY, NEW YORK RECEIVED MARCH 1, 1950

---

(12) The author wishes to thank the Lucidol Division of the Novadel-Agene Corp. which kindly furnished the purified peroxide.

(13) Quinone was found to liberate iodine quantitatively in the procedure used for peroxide analysis; *cf.* Willstätter and Dorogi, *Ber.*, **42**, 2165 (1909). In the inhibition experiment with quinone in Table III, the 0.005 *M* quinone correction applied to the 76.5 and 119 hr. samples may be somewhat in error (as was pointed out by the referee) due to conversion of part of the quinone to non-quinoid substitution products; *cf.* Cohen, THIS JOURNAL, **69**, 1057 (1947); *J. Polymer Sci.*, **2**, 511 (1947).

(14) Shepard, Henne and Midgley, THIS JOURNAL, **53**, 1948 (1931).