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Low Temperature Autoxidation of Hydrocarbons. The Kinetics of Tetralin Oxidation[1,2]

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The kinetics of the liquid phase oxidation of tetralin have been studied for reactions initiated thermally, by free radical producing compounds (benzoyl peroxide and azobisisobutyronitrile) and by a heavy metal activator, cobaltous acetate. It is demonstrated that the oxidation reactions initiated by the latter two agencies are uniquely related. A steady, maximum rate of oxidation is obtained in the cobaltous acetate activated oxidation which can also be calculated from the rates of the benzoyl peroxide and azobisisobutyronitrile initiated oxidations knowing the rates of spontaneous decomposition of these two initiators. The cobaltous acetate activated oxidation leads to the formation of steady concentrations of tetralin hydroperoxide which have been determined by an initial rate technique. The dependence of the steady concentration of hydroperoxide on temperature and concentration of reactants has been measured and the results interpreted in terms of an earlier theory.

The liquid phase oxidation of tetralin (1,2,3,4-tetrahydronaphthalene) has been studied by several investigators.[3-6] The recent work of Bamford and Dewar[6] clearly demonstrated that this oxidation is a radical chain process following the general scheme of Bolland and Gee[7] for autoxidation reactions. The initial reaction product is α-tetralyl hydroperoxide, whereas a number of oxygenated products are formed after extensive oxidation.[5] Heavy metal ions have been shown to greatly accelerate the oxidation of tetralin as well as the decomposition of the hydroperoxide.[3-5,8] The mechanism of these reactions, however, is quite complicated and there does not appear to be any unified concept of the role that metal activators play in the oxidation reaction.

In an earlier article,[9] a general discussion of the kinetics of autoxidation reactions was presented. By a straight-forward mathematical extension of the mechanism presented by Bolland and Gee[7] for ethyl linoleate oxidation, certain features regarding the *extensive* autoxidation of hydrocarbons were predicted. Those features predicted, that are pertinent to the work presented in this article, may be summarized as follows: (1) the occurrence of a steady, maximum rate of hydrocarbon oxidation for reactions carried out in the presence or absence of activators such as light or heavy metal ions which promote the decomposition of hydroperoxides, (2) the occurrence of steady concentrations of hydroperoxide accompanying the maximum rate of oxidation, and (3) specific dependencies of the maximum rate of oxidation and steady concentration of hydroperoxide on concentration of reactants. The present studies of tetralin oxidation were undertaken in an attempt to experimentally explore these items and to demonstrate any unique relationship that may exist in oxidations initiated thermally, by free radical producing compounds (benzoyl peroxide and azobisisobutyronitrile), and by a heavy metal activator, cobaltous acetate.

Experimental

Reagents.—Tetralin (Fisher Scientific, purified grade), was washed with concd. sulfuric acid until the washings were colorless and then washed repeatedly with distilled water and stored over anhydrous magnesium sulfate. Prior to use it was distilled under purified nitrogen and the fraction distilling at 46° (1 mm.) collected. The purified product gave no response to iodometric peroxide tests.

Tetralin hydroperoxide was prepared by air oxidation of tetralin. Purified tetralin (700 ml.) was placed in a 1-liter round-bottomed flask fitted with a reflux condenser. Dry air was blown through the solution for 48 hours at 70°. The oxidized mixture was then concentrated to 150 ml. by vacuum distillation at 60° bath temperature. The concentrated solution was cooled to −5° for 12 hours and the material that crystallized collected on a sintered glass filter. The product was further crystallized three times from petroleum ether (40–60°) and dried *in vacuo* at room temperature, m.p. 55.7–56°; conversion 7–10%. The peroxide content agreed with the theoretical value within the limits of error of iodometric determinations.

Benzene (Mallinckrodt, analytical reagent) was stored over sodium. Chlorobenzene (Eastman Kodak Co., b.p. 130–132°) was used as received. Biphenyl (City Chemical, technical grade) was crystallized three times from petroleum ether (40–60°) and dried *in vacuo*.

Acetic acid (J. T. Baker, glacial, analyzed reagent) was used as received from freshly opened bottles; 1% by volume acetic anhydride was added 24 hours before use.

Anhydrous cobaltous acetate was prepared from cobaltous acetate tetrahydrate (Fisher Scientific, tested purity) by the procedure of Bawn and Williamson.[10]

Benzoyl peroxide (Fisher Scientific C.P. grade) was used as received.

2,2′-Azobisisobutyronitrile (m.p. 103–104°) was prepared and purified according to the method of Overberger, *et al.*,[11] adapted from the procedure of Thiele and Heuser.[12]

Reagent grade materials were employed in the analytical procedure for estimation of hydroperoxides.

Procedure. Measurements of Oxygen Absorption.—The rates of oxygen absorption were measured at constant pressure. A silicon oil (Dow Corning Number 200) manometer was used to detect small changes in internal pressure. Two reaction flasks were used (50- and 125-ml.) depending upon the volume of the oxidizing solution. The entire

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(2) Taken in part from the dissertation of Arthur E. Woodward, submitted in March, 1953, in partial fulfillment of the requirements for the Ph.D. degree. This paper was presented before the Division of Polymer Chemistry at the 124th meeting of the American Chemical Society in Chicago, Illinois, September, 1953.

(3) (a) P. George, *Proc. Roy. Soc.* (*London*), **A186**, 337 (1946); (b) *Trans. Faraday Soc.*, **42**, 210 (1946).

(4) (a) P. George and A. Robertson, *Proc. Roy. Soc.* (*London*), **A185**, 309 (1946); (b) *Trans. Faraday Soc.*, **42**, **217** (1946).

(5) (a) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1574, 1578, 1585 (1948); (b) *Trans. Faraday Soc.*, **42**, 201 (1946).

(6) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (*London*), **A198**, 252 (1949).

(7) (a) J. L. Bolland, *ibid.*, **A186**, 218 (1949); (b) *Trans. Faraday Soc.*, **44**, 669 (1948); (c) *Quart. Revs.*, **3**, 1 (1949); (d) J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, 236, 244 (1946).

(8) M. S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, *J. Org. Chem.*, **17**, 207 (1952).

(9) A. V. Tobolsky, D. J. Metz and R. B. Mesrobian, THIS JOURNAL, **72**, 1942 (1950).

(10) C. E. H. Bawn and J. B. Williamson, *Trans. Faraday Soc.*, **47**, 721, 735 (1950).

(11) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, **71**, 2661 (1949).

(12) J. Thiele and C. Heuser, *Ann.*, **290**, 1 (1896).

apparatus was maintained at constant temperature (±0.05°) in a paraffin oil-bath. The reaction vessel was attached to the arm of an eccentric and could be shaken up to 250 strokes per minute.

The procedure employed for measurements of oxygen absorption in the thermal and benzoyl peroxide or azobisisobutyronitrile catalyzed runs was as follows: The reaction flask was cooled to Dry Ice temperature prior to addition of reactants. Each reagent was then added separately, allowing sufficient time for the reagent to turn solid. The system was evacuated and flushed with oxygen three times. The reaction flask was then warmed to room temperature and immediately inserted in the oil-bath. Excess oxygen pressure formed during the warming period was released from the system. The reactants were maintained at bath temperature for four minutes before taking the first reading. All measurements were carried out under oxygen at atmospheric pressure. An alternate procedure, used in studies of metal-catalyzed oxidation, differed from the above in the following manner. The liquid reactants were separately heated to the temperature of the run and then rapidly added to the reaction vessel maintained in the oil-bath. The uptake of oxygen was recorded beginning one minute after addition of reactants. This procedure was required for metal-catalyzed runs wherein the induction period was to be specified.

In order to determine the proper shaking speed of the reaction vessel, studies were made on the dependence of oxidation rate on shaking speed. It was found that for all runs herein encountered a shaking rate of 150 strokes per minute was sufficiently rapid to ensure oxidation rates independent of shaking speed.

Hydroperoxide Determinations.—The analytical procedure used for all tetralin hydroperoxide estimations was essentially the method described by Wagner, Smith and Peters.[13] This iodometric procedure appears to be very satisfactory for tetralin hydroperoxide. Although it might be expected that the end-point for iodometric titrations in the presence of cobalt ion would be difficult to determine, it was noted that the green color due to the addition of an aliquot of cobalt ion in acetic acid to an isopropyl alcohol solution of sodium iodide could be completely discharged by addition of a small amount of water. Accordingly, iodine liberated from samples containing hydroperoxide and cobalt ion could be titrated with aqueous thiosulfate to a colorless end-point.

Measurement of Hydroperoxide Decomposition under Non-oxidizing Conditions.—Measured quantities of the solvents (benzene and acetic acid) containing cobaltous acetate were pipetted into a 250-ml. erlenmeyer flask and the flask closed under air with a ground-glass stopper. The contents were heated to the desired temperature in the constant temperature bath used for the oxidations. A weighed quantity of the hydroperoxide was added and the flask shaken to dissolve the peroxide. An aliquot was immediately removed for iodometric titration in order to establish the initial peroxide concentration, and subsequent samples were taken at time intervals dependent upon the rate of the reaction.

Measurement of Steady Concentrations of Hydroperoxide.—These measurements were made on multi-component systems consisting of tetralin, tetralin hydroperoxide, solvent and cobaltous acetate. An initial rate method was employed to specify the steady concentration of hydroperoxide. In this procedure, given amounts of pure hydroperoxide and cobaltous acetate were added to the other reagents previously placed in the reaction vessel of the oxygen absorption apparatus. Reaction conditions identical with oxygen absorption measurements were maintained. However, instead of recording oxygen absorption, two aliquots of the reaction mixture were taken for hydroperoxide determination. The first aliquot, removed immediately after addition of the hydroperoxide served to establish the peroxide value at zero time and the peroxide content of the second aliquot, recovered at a later fixed time interval,[14] indicated the net increase or decrease in peroxide content of the system. Through a series of successive runs, a peroxide content was established which showed a minimal change in value between the first and second readings. This peroxide content was taken as the steady concentration of hydroperoxide. The data recorded in a typical sequence of runs are summarized in Table I. In view of the fact that the amount of hydroperoxide decomposed within the time of each experiment was less than 10%, it is believed that this procedure constitutes a type of initial rate measurement. The advantage of the technique is that the change in tetralin concentration during reaction is negligibly small and also any products of peroxide decomposition or tetralin oxidation which may impart an inhibitory effect to the reaction are held to a minimal value.

TABLE I

DETERMINATION OF THE STEADY CONCENTRATION OF TETRALIN HYDROPEROXIDE IN THE OXIDATION OF TETRALIN ACTIVATED BY COBALT ACETATE AT 81°

Tetralin = 1.22 moles/l.; CoAc = 0.002 mole/l. in acetic acid.

$[\text{ROOH}]_0$, moles/l.	$[\text{ROOH}]_{3\text{ min.}}$, moles/l.	Δ ROOH[a], moles/l.
0.046_1	0.048_6	$+0.002_5$
$.051_1$	$.053_3$	$+\ .002_2$
$.0557$[b]	$.0557$	$.000_0$
$.060_0$	$.058_0$	$-\ .002_0$

[a] Change in hydroperoxide concentration of system after three minutes of reaction. [b] Best value for the steady concentration of ROOH.

Results and Discussion

(1) Oxidations Initiated by Benzoyl Peroxide and Azobisisobutyronitrile.—On the basis of the Bolland and Gee[7] scheme, the oxidation of tetralin initiated by benzoyl peroxide (BzO_2) or 2,2′-azobisisobutyronitrile (AZBN) at high oxygen pressure (greater than 50 mm. of oxygen[6]) may be written as

$$\left.\begin{array}{ll}
(1A) & \text{Initiator} \xrightarrow{k_7} 2R'\cdot \xrightarrow{2RH} 2R\cdot \\
(2A) & R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \\
(3A) & RO_2\cdot + RH \xrightarrow{k_3} ROOH + R\cdot \\
(4A) & RO_2\cdot + RO_2\cdot \xrightarrow{k_6} \text{Products} + O_2
\end{array}\right. \qquad (A)$$

The radical pair ($2R'\cdot$) formed by spontaneous decomposition of the initiator molecule start the oxidation by reaction with tetralin (RH) to form tetralyl radicals ($2R\cdot$). Kinetic analysis of mechanism (A) leads to the following rate expression for oxygen absorption

$$-d[O_2]/dt = k_3(e_ik_7/2k_6)^{1/2}[RH][\text{Initiator}]^{1/2} \qquad (1)$$

where e_i is the efficiency of initiation, *i.e.*, the ratio of the number of oxidation chains started to the number of initiator molecules decomposed.

For tetralin oxidation initiated by either BzO_2 or AZBN, Bateman and Morris[15] have shown that e_i is the same for both initiators (*viz.*, $e_{AZBN}/e_{BzO_2} = 1.01$ at 55°).

From equation 1 the rate of tetralin oxidation should be first order with respect to tetralin concentration and one-half order with respect to initiator concentration. These concentration dependencies

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

(14) The time required for the second reading was determined in the following way. In order that a steady concentration of peroxide be maintained in an oxidizing system, it is necessary that the rate of peroxide formation be equal to its rate of decomposition. These rates are also equal to the rate of oxygen absorption. Having previously measured the steady maximum rate of oxygen absorption this rate could then be employed to calculate the time interval wherein less than 10% of the initially added peroxide (at the steady concentration) would have decomposed. Generally, times one-half this value were employed.

(15) L. Bateman and A. L. Morris, *Trans. Faraday Soc.*, **48**, 1149 (1952).

have been confirmed in the present work for oxidations initiated by AZBN. The data are summarized in Table II. The constancy of the figures in the third and sixth columns denotes the agreement of data with equation 1.

TABLE II

OXIDATION OF TETRALIN AT 50°

Rate[a] *vs.* [AZBN][b] Rate, moles/l./sec. × 10⁶	[AZBN], moles/l. × 10²	Rate/[AZBN]$^{1/2}$, mole$^{1/2}$/l.$^{1/2}$/sec. × 10⁵	Rate[a] *vs.* [Tetralin][c] Rate, moles/l./sec. × 10⁶	[Tetralin], moles/l.	Rate/[Tetralin], sec.$^{-1}$ × 10⁵
1.40	0.105	4.51	0.81	1.05	7.67
3.05	.525	4.20	1.69	2.10	8.05
3.37	.788	3.79	2.40	3.15	7.62
3.80	1.05	3.69	2.95	4.21	7.02
4.53	1.50	3.68	3.80	5.25	7.24
			4.09	6.31	6.48

[a] Moles of oxygen absorbed/liter of solution/second. [b] Concentration of tetralin = 5.25 moles/l. in chlorobenzene. [c] Concentration of AZBN = 0.0105 mole/l. in chlorobenzene.

In this study the extent of oxidation and decrease of initiator concentration were maintained at less than 8% in order that the tetralin and AZBN concentrations remain essentially constant.

Additional studies of oxidations initiated by BzO_2 or AZBN at various temperatures are summarized in Table III and will be discussed in section 5.

TABLE III

OXIDATION OF TETRALIN INITIATED BY BzO_2 AND AZBN AT VARIOUS TEMPERATURES

Temp., °C.	Oxidation rate,[a] moles/l./sec. × 10⁵ BzO_2[b]	AZBN[b]
39.2	...	0.13
50.2	...	0.49
61.7	0.70	2.10
69.0	1.74	4.45
78.0	4.67	9.95
89.0	13.9	...

[a] Moles of oxygen absorbed/liter of solution/second. [b] BzO_2 and AZBN concentrations = 0.014 mole/l. in pure tetralin.

(2) **Oxidations Activated by Cobalt Ion.**—Bawn and co-workers[10,16] have shown that olefins and aldehydes undergo rapid oxidation in the presence of anhydrous cobaltous acetate in acetic acid solvent. In some cases the metal ion can react directly with hydrocarbons to initiate oxidation chains, although more generally the role of the metal ion is to generate radicals by reaction with hydroperoxide. It has been postulated that small quantities of cobalt ion can promote the decomposition of a large quantity of hydroperoxide by reactions of the type

$$\mathrm{ROOH + Co^{+2} \longrightarrow RO\cdot + HO^- + Co^{+3}} \qquad \mathrm{(B)}$$

$$\mathrm{ROOH + Co^{+3} \longrightarrow RO_2\cdot + H^+ + Co^{+2}} \qquad \mathrm{(C)}$$

These reactions are complicated, particularly since the cobalt may function as a complexed ion, and oxidations initiated by this agent do not render the relatively straightforward kinetics obtained with oxidations initiated by BzO_2 or AZBN.

If the oxidation of tetralin activated by cobalt ion may be represented in the manner

$$\mathrm{ROOH} + n\mathrm{CoAc_2} \xrightarrow{k_1'} \mathrm{Radical} \xrightarrow{\mathrm{RH}} \mathrm{R\cdot} \qquad \mathrm{(1D)}^{17}$$

$$\mathrm{R\cdot + O_2} \xrightarrow{k_2} \mathrm{RO_2\cdot} \qquad \mathrm{(2D)}$$

$$\mathrm{RO_2\cdot + RH} \xrightarrow{k_3} \mathrm{ROOH + R\cdot} \qquad \mathrm{(3D)}$$

$$\mathrm{RO_2\cdot + RO_2\cdot} \xrightarrow{k_6} \mathrm{Products + O_2} \qquad \mathrm{(4D)}$$

it is evident that this oxidation will exhibit autocatalysis since the hydroperoxide formed in step 3D will subsequently react with cobalt ion and continue the chain process. The kinetic expression for the rate of oxidation when hydroperoxide decomposition is negligible compared with its rate of formation is

$$-\mathrm{d[O_2]/d}t = k_3(k_1'/2k_6)^{1/2}[\mathrm{RH}][\mathrm{ROOH}]^{1/2}[\mathrm{CoAc_2}]^{n/2} \qquad (2)$$

It may be seen from equation 2 that the rate of oxidation is proportional to the instantaneous concentration of hydroperoxide in the oxidizing system as well as the concentrations of hydrocarbon and cobalt acetate.

As the concentration of hydroperoxide increases with time, the rate of decomposition of hydroperoxide also increases and eventually equals its rate of formation. The magnitude of the resultant steady concentration of hydroperoxide $[\mathrm{ROOH}]_\infty$ is given by the expression[9]

$$[\mathrm{ROOH}]_\infty = \frac{k_3{}^2[\mathrm{RH}]^2}{2k_1'k_6[\mathrm{CoAc_2}]^n} \qquad [3)$$

On substitution of the value of $[\mathrm{ROOH}]_\infty$ in equation 3 into the hydroperoxide term on the right-hand side of equation 2, the rate of oxidation is given by

$$[-\mathrm{d[O_2]/d}t]_\infty = \frac{k_3{}^2[\mathrm{RH}]^2}{2k_6}$$

Equation 4 represents the steady, maximum rate of autoxidation of tetralin in the advanced stage of reaction where the hydroperoxide has reached its limiting concentration. An expression identical with equation 4 can also be derived for the steady rate of thermal oxidation of tetralin if it is assumed that the initiation step occurs *via* the thermal decomposition of hydroperoxide.[9]

The experimental verification of equations 3 and 4 for the oxidation of tetralin in acetic acid activated by cobalt acetate will now be presented.

The rate of oxidation of tetralin at several concentrations of cobaltous acetate at 50° is represented in Fig. 1. At the lowest cobalt acetate concentration there is an appreciably long period of no measurable oxygen absorption followed by a stage of oxygen absorption exhibiting a constantly accelerating rate of oxidation which after approximately 70 minutes approaches a steady or maximum rate of oxidation. At higher concentrations of cobalt acetate, the duration of the induction period is

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(16) (a) C. E. H. Bawn, A. A. Pennington and C. F. H. Tipper, *Faraday Soc. Disc.*, **10**, 282 (1951); (b) C. E. H. Bawn and A. G. White, *J. Chem. Soc.*, 331, 339, 344 (1951); (c) C. E. H. Bawn, *Faraday Soc. Disc.*, **14**, 181 (1953).

(17) It is assumed here that equation B is operative and rate controlling and that the resultant cobaltic ion is rapidly reduced to the cobaltous ion *via* equation C. The opposite situation where equation C is rate controlling is also possible. In either case, however, the overall effect is the same, namely, that two hydroperoxide molecules are decomposed to produce two radicals and that the initiation process is first order with respect to the hydroperoxide.

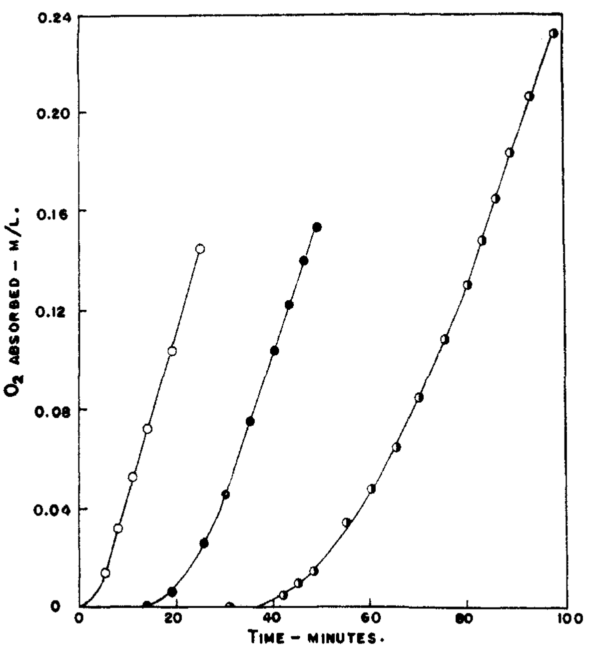


Fig. 1.—Activated oxidation of tetralin, rate *vs.* cobaltous acetate concentration at 50° (tetralin = 3.67 moles/l. in acetic acid), cobaltous acetate (mole/l.): ○, 0.005; ●, 0.002; ◑, 0.001.

shortened whereas *the steady rate ultimately attained is the same in all three cases.* If small amounts of tetralin hydroperoxide are added to tetralin prior to the start of an oxidation run at the low cobalt acetate concentration, the induction period is partly or completely eliminated. This effect is clearly demonstrated in Fig. 2. The induction period is believed to be due to the initially slow accumulation of sufficient hydroperoxide in the system to enable step 1D in mechanism D to serve as the important initiation step in the oxidation reaction. Initiation of oxidation by direct reaction of cobalt ion with tetralin would not give the results shown in Figs. 1 and 2.

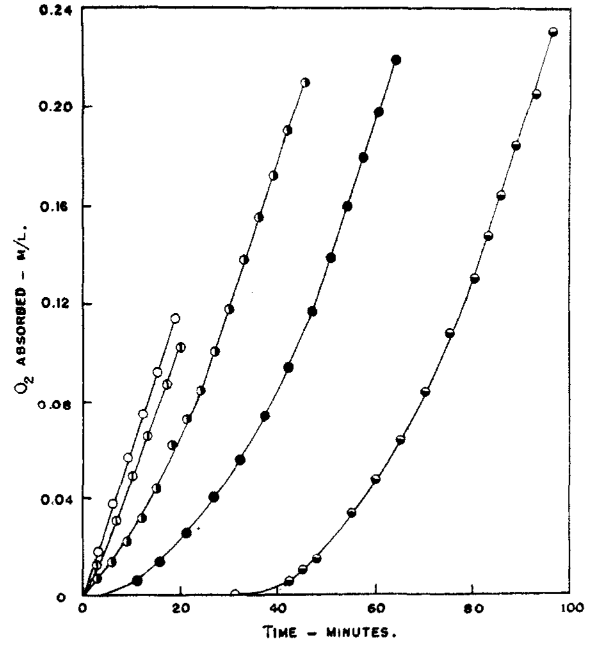


Fig. 2.—Activated oxidation of tetralin, rate *vs.* added ROOH concentration at 50° (cobaltous acetate = 0.001 moles/l.; tetralin = 3.67 moles/l. in acetic acid); added [ROOH] concentration (mole/l.): ○, 0.200; ⦶, 0.100; ◑, 0.020; ●, 0.001; ⊖, 0.

The dependence of the steady rate of oxidation on tetralin concentration is presented in Fig. 3. It is observed that the oxidation rate is proportional to the square of the hydrocarbon concentration in agreement with equation 4.

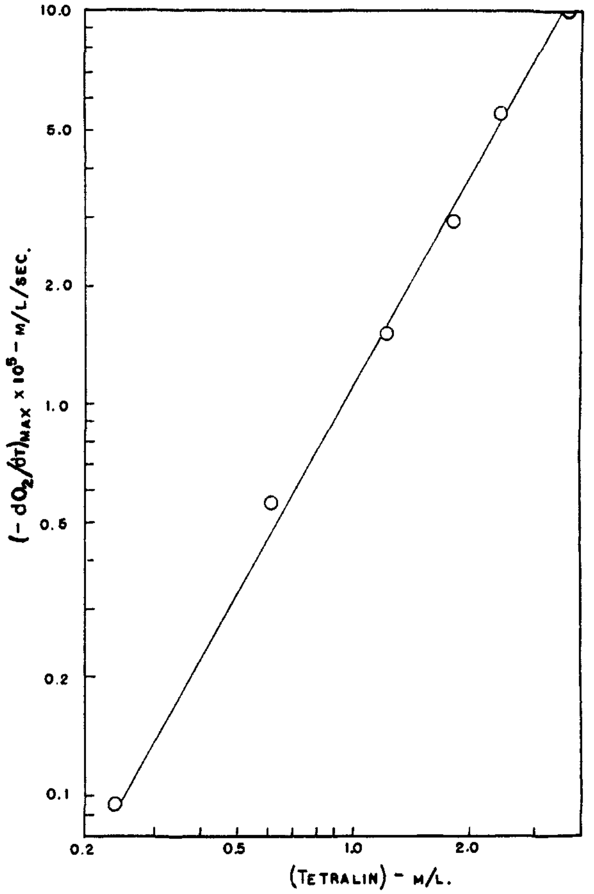


Fig. 3.—Activated oxidation of tetralin, log maximum rate *vs.* log tetralin concentration at 50° (cobaltous acetate = 0.002 mole/l. in acetic acid). The slope of the line is 1.93, in agreement with a second-order dependence of rate on tetralin concentration.

In addition to the measurements of oxygen absorption, studies have also been made of the hydroperoxide concentration of tetralin oxidized in the presence of cobalt acetate. In order to establish the dependence of the steady concentration of hydroperoxide on tetralin and cobalt acetate concentrations, peroxide determinations were made according to the initial rate method described in the experimental section. By this procedure it appeared possible to eliminate the experimental difficulties encountered by Bawn and co-workers[16] who followed the course of hydroperoxide build-up from the pure hydrocarbon. These investigators observed a slow upward drift of hydroperoxide concentration after a rapid build-up to an apparent steady concentration. It is possible that this ef-

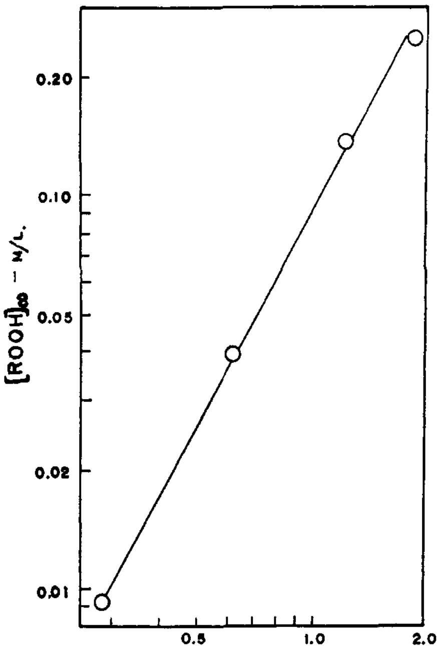


Fig. 4.—Dependence of $[ROOH]_\infty$ on tetralin concentration in the oxidation of tetralin at 50° (cobalt acetate = 0.002 mole/l. in acetic acid). The slope of the line is 1.91, in agreement with a second-order dependence of $[ROOH]_\infty$ on tetralin concentration.

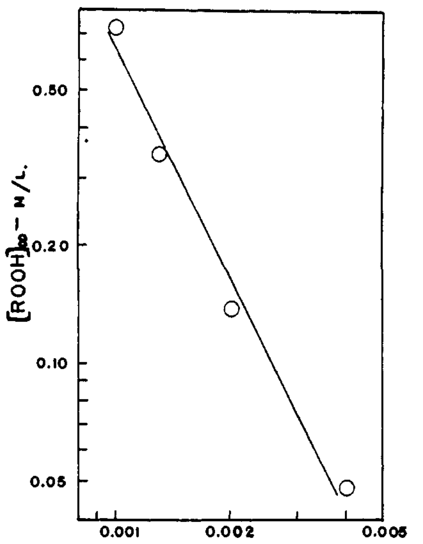
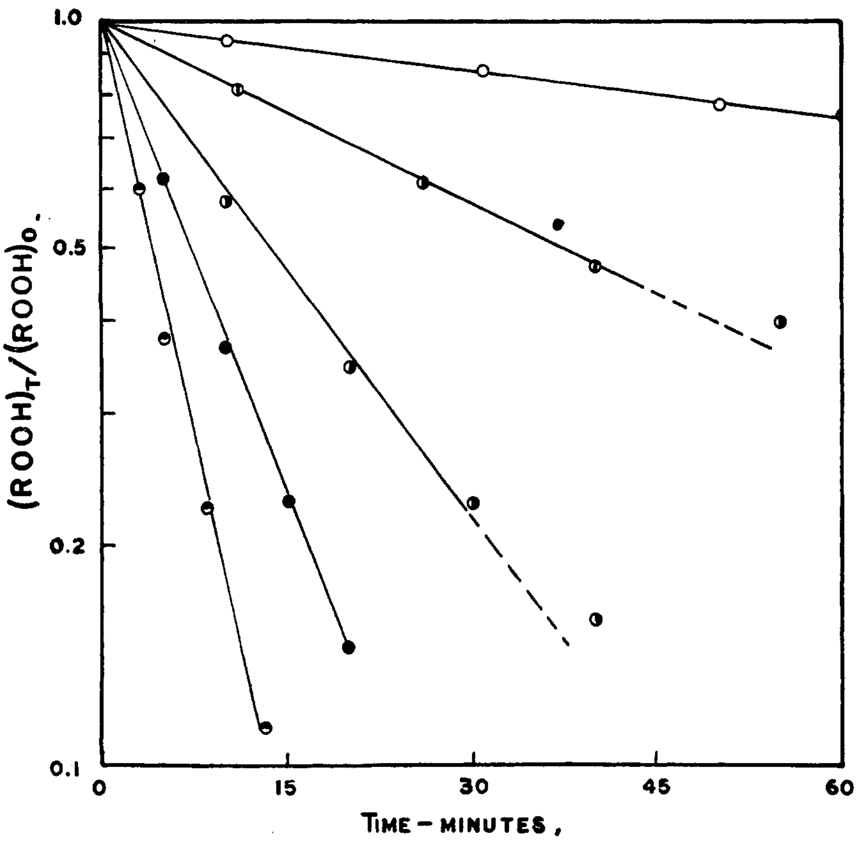


Fig. 5.—Dependence of $[ROOH]_\infty$ on cobaltous acetate concentration in the oxidation of tetralin at 50° (tetralin = 1.22 moles/l. in acetic acid). The slope of the line is −1.97 in agreement with an inverse second-order dependence of $[ROOH]_\infty$ on cobaltous acetate concentration.

fect was due to a gradual destruction of the cobalt activator by water formed during reaction. A gradual decrease in the activity of the cobalt ion would not be reflected in the rates of oxidation, however, since these rates are independent of the activator concentration (eq. 4).

The values of the steady concentrations of hydroperoxide, $[ROOH]_\infty$, *versus* tetralin concentration and cobaltous acetate concentration, are represented on a logarithmic scale in Figs. 4 and 5, respectively. These studies were carried out at 50° under reaction conditions identical with oxygen absorption measurements. It is seen that the steady concentration of hydroperoxide is proportional to the square of the tetralin concentration and inversely proportional to the square of the cobalt acetate concentration. The inverse, *square* dependence on cobalt acetate concentration ($n = 2$ in equation 3) indicates that the decomposition of tetralin hydroperoxide activated by cobalt acetate is second order with respect to the latter. An independent verification of the order of reaction involved in the cobalt activated decomposition of tetralin hydroperoxide may be obtained from direct study of this process under



Fig, 6.—Decomposition of tetralin hydroperoxide activated by cobaltous acetate at 50° (initial ROOH concentration = 0.04 mole/l. in equimolar benzene–acetic acid), cobaltous acetate (moles/l.): ⊖, 0.0040; ●, 0.0030; ◑, 0.0020; ⦶, 0.0010; ○, 0.0005.

non-oxidizing conditions. The rates of decomposition of tetralin hydroperoxide in acetic acid containing cobalt acetate and benzene, in place of tetralin, have been determined at 50°. As shown in Fig. 6 the decomposition of tetralin hydroperoxide at various molar ratios of hydroperoxide to cobalt acetate adheres to a first-order plot. Analysis of the data in Fig. 6 indicates that the decomposition rate is dependent upon the square of the cobalt concentration (in the range 5×10^{-4} to 4×10^{-3} moles/l.) in agreement with the results given in Fig. 5 on the dependence of $[\mathrm{ROOH}]_\infty$. The data in Fig. 6 leave no doubt that cobaltous acetate serves as a true activator for tetralin hydroperoxide decomposition since the decompositions can be run at molar ratios of cobalt acetate to hydroperoxide as low as 1 to 80.

Since the over-all rate of decomposition of tetralin hydroperoxide activated by cobalt acetate can be expressed by the equation

$$-\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t = k_1'[\mathrm{ROOH}][\mathrm{CoAc_2}]^2 \qquad (5)$$

it is of interest to compare the value of k_1' determined by direct studies of hydroperoxide decomposition with the corresponding value of k_1' calculated from measurements of $[\mathrm{ROOH}]_\infty$ and the maximum rate of oxidation. If equation 4 is divided by equation 3, the following expression is obtained

$$[-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t]_\infty/[\mathrm{ROOH}]_\infty = k_1'[\mathrm{CoAc_2}]^n \qquad (6)$$

The observed value of k_1' and that calculated from equation 6 are given in Table IV.

TABLE IV

COMPARISON OF THE OVER-ALL RATE CONSTANT FOR TETRALIN HYDROPEROXIDE DECOMPOSITION AT 50°

Tetralin = 1.84 moles/l.; $\mathrm{CoAc_2}$ = 0.002 mole/l. in acetic acid

$[-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t]_\infty$, moles/l./sec.	$[\mathrm{ROOH}]_\infty$, moles/l.	k_1' (calcd.), l.^{2}/moles^2/sec.	k_1' (obs.),[a] l.^{2}/moles^2/sec.
2.93×10^{-5}	0.140	52	40

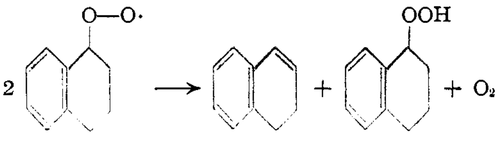
[a] Decomposition run in tetralin–acetic acid solvent under purified nitrogen at an initial tetralin hydroperoxide concentration of 0.04 mole/l.

The rather close agreement between the two values of k_1' indicates that the velocity of initiation of tetralin oxidation is very nearly equal to the rate of hydroperoxide decomposition provided the observed oxidation rate is the true maximum rate of oxidation. As will be shown later, the maximum rate of oxidation can be measured by other means and the various values compare favorably.

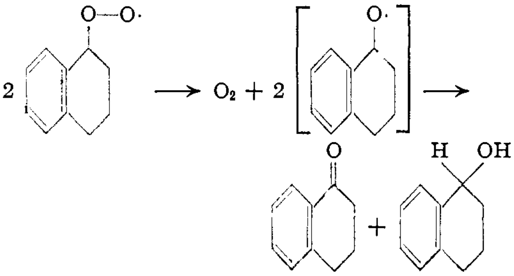
From the present work it is possible to speculate upon the nature of the termination step, equation 4D. One possible reaction is

$$2\mathrm{RO_2}\cdot \longrightarrow \mathrm{ROOR} + \mathrm{O_2} \qquad (E)$$

However, ditetralyl peroxide (ROOR) has not been reported as an oxidation product of tetralin.[5a] Bamford and Dewar[6] have suggested that the interaction of two $\mathrm{RO_2}\cdot$ radicals may proceed as


(F)

On this basis a hydroperoxide molecule is reformed in the termination step. This would not be consistent with the present work since termination in this manner would not lead to a steady concentration of hydroperoxide. Vaughan and co-workers,[18] on the other hand, have proposed that the interaction of two tertiary $\mathrm{RO_2}\cdot$ radicals (where R is *t*-butyl) gives rise to the formation of two alkoxy radicals, $\mathrm{RO}\cdot$, with the loss of an oxygen molecule. For the interaction of two secondary $\mathrm{RO_2}\cdot$ radicals derived from tetralin, the resultant $\mathrm{RO}\cdot$ radicals may be short-lived and interact further to produce tetralone and tetralol


(G)

It is interesting to note that along with oxygen, these compounds are the major products of tetralin hydroperoxide decomposition[5a]

(3) **Thermal Oxidation.**—The rate of thermal oxidation of tetralin has been studied in the temperature range 69–120°. The data obtained were similar to those reported by other workers.[5b,19] The rates of oxygen absorption were initially autocatalytic and then approached a steady rate which, from studies in diphenyl solvent, were found to be dependent upon the square of the tetralin concentration. Although it might appear that these steady rates conform with equation 4, it will be shown in the next section that they are considerably slower than the maximum rates of oxidation observed for oxidations initiated by other means. The retardation effect is possibly due to the formation of a self-inhibitor (γ-*o*-hydroxyphenylbutyric acid) which has been isolated in small amounts from thermally oxidized tetralin.[5a]

(4) **Comparison of Oxidations Initiated by Various Agencies.**—A direct correlation between the rates of tetralin oxidation activated by cobaltous acetate or initiated by $\mathrm{BzO_2}$, or AZBN may be readily presented. If equation 1 derived for free radical initiated oxidation is squared, divided by 2 and rearranged, the following is obtained (when e_1 is taken at its maximum theoretical value of 2.0)

$$\frac{[-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t]^2}{2k_7[\mathrm{Initiator}]} = \frac{k_3{}^2[\mathrm{RH}]^2}{2k_6} \qquad (7)$$

It is noted that the term on the right-hand side of equation 7 is identical with the maximum rate expression derived for oxidations initiated thermally or activated by cobaltous acetate (equation 4).

The rate constants, k_7, for the decomposition of $\mathrm{BzO_2}$ and AZBN in benzene have been accurately determined by Bawn and Mellish.[20] It is therefore possible to compare the calculated (eq. 7) values of

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(18) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughan, *Faraday Soc. Disc.*, **10**, 242 (1951).

(19) S. S. Medvedev, *Acta Physicochim.* (*U.S.S.R.*), **9**, 395 (1938).

(20) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

the maximum rates of oxidation with the observed values for thermal initiation or cobaltous acetate activation. These results are summarized in Table V.

TABLE V

COMPARISON OF MAXIMUM RATES OF OXIDATION[a]

Temp., °C.	Calcd.		Obsd.	
	BzO_2	AZBN	$CoAc_2$	Thermal
50.2	...	1.4	1.5	....
61.7	3.4	4.6	4.1	....
69.0	8.6	8.2	5.9	0.0135
81.0	...	...	14.8	....

[a] Maximum rate of oxidation $\times 10^5$ moles of oxygen absorbed/liter of solution/second.

In the temperature range studied, the agreement between the two calculated values of the maximum rate of oxidation and the observed value for cobalt acetate activated oxidation is very close. The value for the rate of oxidation measured for the thermally oxidized tetralin, however, is approximately 1/600 as large as the other values. As previously stated, this discrepancy can perhaps be attributed to the formation of inhibitors during the course of thermal oxidation.

(5) **Comparison of Activation Energies.**—For oxidations initiated by BzO_2 or AZBN, the over-all activation energy (E_0) from equation 1 is given by

$$E_0 = E_3 + {}^1/_2(E_7 - E_6) \qquad (8)$$

where E_3, E_6 and E_7 are the activation energies of the corresponding rate constants given in mechanism (A); and for cobalt acetate activated oxidation, the over-all activation energy (E_0') from equation 4 is given by

$$E_0' = 2E_3 - E_6 \qquad (9)$$

where E_3 and E_6 are the activation energies of the corresponding rate constants given in mechanism (D). Equation 8 may be readily transformed to yield the expression

$$E_0 - {}^1/_2E_7 = E_3 - {}^1/_2E_6 \qquad (10)$$

The magnitude of ($E_3 - {}^1/_2E_6$) in equation 10 should be equal to one-half the magnitude of E_0' given in equation 9. A comparison of ($E_3 - {}^1/_2E_6$) for these three systems as well as the value obtained by Bamford and Dewar[6] for photosensitized oxidation of tetralin is given in Table VI.

TABLE VI

COMPARISON OF ACTIVATION ENERGIES

Mode of initiation	E_7, kcal.[a]	E_0, kcal.[b]	$E_3 - {}^1/_2E_6$, kcal.
AZBN	30.7	24.2 ± 1.5	8.8
BzO_2	29.6	25.6 ± 0.8	10.8
Cobaltous acetate	..	....	8.2 ± 0.6[c]
Photosensitized	..	....	4.3

[a] Taken from reference 20. [b] Calculated from the data in Table III. [c] Calculated from the data in Table V.

Whereas ($E_3 - {}^1/_2E_6$) is in fair agreement for the three systems studied in the present work, the values are approximately twofold greater than those obtained by Bamford and Dewar. This discrepancy may perhaps be attributed to the fact that these authors performed their studies at only two temperatures in order to determine activation energies. It should be pointed out, however, that Bamford and Dewar performed direct measurements of the rate constants k_3 and k_6 and this procedure may have avoided errors inherent to the other three methods of measurement.

It is also possible to compare the activation energy for the cobaltous acetate activated decomposition of tetralin hydroperoxide when determined by direct measurement or calculated from the over-all temperature dependence of $[-d[O_2]/dt]_\infty$ and $[ROOH]_\infty$ (see equations 5 and 6, respectively). The calculated and observed values are 24.0 ± 4.0 and 21.2 ± 0.9 kcal., respectively. These were determined from four measurements in the range 50–81°. The activation energy for $[ROOH]_\infty$ as defined by equation 3 was found to be -7.6 ± 2.9 kcal. This over-all activation energy is a negative quantity due to the fact that $[ROOH]_\infty$ decreases with increasing temperature for the cobalt acetate activated system. It would be of interest to investigate oxidations activated by other metal compounds where the activation energy for the decomposition of the hydroperoxide is sufficiently small to enable the temperature dependence for $[ROOH]_\infty$ to be positive. Under such conditions the steady concentration of hydroperoxide should *increase* with increasing temperature of oxidation.

BROOKLYN, N. Y.