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**LOW TEMPERATURE AUTOXIDATION OF HYDROCARBONS:
The Kinetics of Tetralin Oxidation.**

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LOW TEMPERATURE AUTOXIDATION OF HYDROCARBONS:
The Kinetics of Tetralin Oxidation.

- by -

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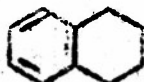
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LOW TEMPERATURE AUTOXIDATION OF HYDROCARBONS: The Kinetics of
Tetralin Oxidation

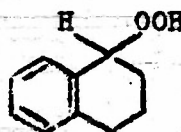
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The liquid phase oxidation of tetralin (I) has been studied by several investigators¹⁻⁶. The recent work of Bamford and Dewar⁶ clearly demonstrated that this oxidation is a radical chain process following the general scheme of Bolland and Gee⁷ for autoxidation reactions. The initial product formed in the reaction is the hydroperoxide (II).



I



II

1,2,3,4-Tetrahydronaphthalene
(Tetralin)

Tetralin Hydroperoxide

and a number of oxygenated products are formed after extensive oxidation⁵. Heavy metal ions have been shown to greatly accelerate

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- (1) S.S. Medvedev, Acta Physicochim., U.R.S.S., **9**, 395 (1938).
 - (2) P. George, E.K. Rideal and A. Robertson, Proc. Royal Soc., **185A**, 288 (1946).
 - (3) (a) P. George, *ibid.*, **185A**, 337 (1946); (b) Trans. Faraday Soc., **42**, 210 (1946).
 - (4) (a) P. George and A. Robertson, Proc. Royal Soc., **185A**, 309 (1946); (b) Trans. Faraday Soc., **42**, 217 (1946).
 - (5) A. Robertson and W. A. Waters, J. Chem. Soc., **1948**, 1574, 1578, 1585.
 - (6) C. H. Bamford and M. J. S. Dewar, Proc. Royal Soc., **198A**, 252 (1949).
 - (7) (a) J. L. Bolland, Proc. Royal Soc., **186A**, 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).

the oxidation of tetralin as well as the decomposition of the hydroperoxide³⁻⁵. 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 these reactions.

In this article, studies are presented on the kinetics of the thermal, free radical initiated (benzoyl peroxide and azo-bis-isobutyronitrile), and heavy metal activated (cobaltous ion) oxidation of tetralin. In an earlier article⁸, a general discussion of the kinetics of autoxidation reactions was presented. By a straightforward mathematical extension of the mechanism presented by Bolland and Gee⁷ for ethyl linoleate oxidation, certain features regarding the extensive autoxidation of hydrocarbons were predicted. These features predicted, that are pertinent to the work presented in this article, may be summarized as follows: (i) the occurrence of steady, maximum rates of hydrocarbon oxidation, (ii) independence of the maximum rate of oxidation on the presence of activators (e.g. heavy metal ions) despite the pronounced effect that these agencies may have on the initial rate of reaction, (iii) the occurrence of steady concentrations of hydroperoxide accompanying the maximum rate of oxidation, (iv) specific dependencies of the maximum rate of oxidation and steady concentration of hydroperoxide on hydrocarbon concentration and temperature of reaction. The studies of tetralin oxidation were undertaken in an attempt to experimentally explore these four items and to demonstrate any unique

(8) A. V. Tobolsky, D. J. Metz and R. B. Mesrobian, J. Am. Chem. Soc., 72, 1942 (1950).

relationship that may exist between the thermal, free radical initiated, and metal activated oxidation reactions.

Tetralin was employed in this work because many of its kinetic features have already been established and because it is readily available. In addition, it is one of the few hydrocarbons that yields a solid, readily purifiable hydroperoxide. As will be discussed later, the availability of the pure hydroperoxide is of considerable aid in establishing a suitable experimental procedure to measure the steady concentration of hydroperoxide in oxidizing systems.

EXPERIMENTAL

Reagents:

Tetralin (Fisher Scientific, purified grade) was washed with conc. 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°/1mm. collected. The purified product gave no response to 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 reflux condenser. Dry air was blown through the solution for 48 hours at 70°C. 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 (boiling range 40-60°) and dried under vacuum at room temperature. It was sometimes found convenient to carry out the second crystallization in the presence of activated charcoal in order to remove discolorations. (m.p. 55.7-56°, yield 7-10% of theoretical). The peroxide content agreed with the theoretical value within the limits of error of iodometric determinations.

Benzene (Mallinckrodt, analytical reagent) was stored over sodium.

Diphenyl (City Chemical, technical grade) was crystallized three times from petroleum ether (b. range 40-60°) and dried in vacuum.

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

Anhydrous cobaltous acetate was prepared by the procedure of Bawn and Williamson⁹. Cobaltous acetate tetrahydrate (Fisher Scientific, tested purity) was ground to a fine powder and dried to constant weight in a vacuum oven at 100° and 1 mm. pressure. The anhydrous material was stored in a desiccator over phosphoric anhydride.

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

Benzoyl peroxide (Fisher Scientific c.p. grade) was used as received.

2,2'-Azo-bis-isobutyronitrile (m.p. 103-104°) was prepared and purified according to the method of Overberger et al.¹⁰ as adapted from the procedure of Thiele and Heuser¹¹.

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

Apparatus

A diagram of the oxygen absorption apparatus is shown in Figure I. Two reaction flasks were used (50 or 125-ml.) depending upon the volume of the solution. The temperature fluctuation in the oil bath was determined with a Beckmann thermometer and found to be constant within $\pm 0.05^\circ$. Silicon oil was used as the manometer fluid since it is inert to oxygen, has a low vapor pressure and due to its low density is more sensitive than mercury to pressure changes.

Procedure:

The procedure employed for measurements of oxygen absorption in the thermal and benzoyl peroxide or azo-bis-isobutyronitrile catalyzed runs was as follows: The reaction flask was cooled to Dry Ice temperature prior to addition of reactants. Each reagent was then

(10) C.G. Overberger, M.T.O'Shaughnessy and H. Shalit, J. Am. Chem. Soc., 71, 2661 (1949).

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

added separately, allowing sufficient time for each component 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 shaking rack maintained 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. The oxygen pressure in the system was maintained constant by frequent manipulation of the level of the gas burette. The runs 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 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 one minute after addition of reactants. The latter procedure was required for metal-catalyzed runs in the presence of added hydroperoxide since the oxidations were rapid and therefore required as short a time as possible for temperature equilibration.

Peroxide Determinations:

The analytical procedure used for all hydroperoxide estimations was essentially the method described by Wagner, Smith and Peters¹². This iodometric procedure appears to be very satisfactory for tetralin hydroperoxide. Although it might be expected that the endpoint for

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

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, titrations of iodine liberated from samples containing hydroperoxide and/or cobalt ion could be titrated with thiosulfate to a colorless endpoint.

Measurement of Hydroperoxide Decomposition

Measured quantities of the solvent or solvents containing cobalt 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 same 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 the Steady Concentration of Hydroperoxide

These measurements were made on multi-component systems consisting of tetralin, tetralin hydroperoxide, solvent, and, whenever used, cobaltous acetate. An initial rate method was used to specify the steady concentration of hydroperoxide. In this procedure, a given amount of pure hydroperoxide was added to the other reagents

0

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, aliquots of the reaction mixture were removed. The first aliquot, taken immediately after addition of the hydroperoxide served to establish the peroxide value at zero time and the second aliquot, removed at a later fixed time interval*, indicated the net increase or decrease in peroxide content of the system. If the amount of peroxide initially added was greater than the steady concentration of the system, a net decrease in peroxide value during oxidation was recorded and vice versa. Through a series of successive measurements a peroxide content was established which showed a minimal change in value between the first and second readings. The data recorded in a typical sequence of runs are summarized in Table I. In view of the fact that the amount of peroxide actually decomposed

0

*The time required for the second reading was chosen 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. 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.

TABLE I

DETERMINATION OF THE STEADY CONCENTRATION OF TETRALIN HYDROPEROXIDE
IN THE OXIDATION OF TETRALIN ACTIVATED BY COBALT ACETATE AT 81°C.
(Tetralin = 1.22 m/l; CoAc₂ = 0.002 m/l in acetic acid).

$[ROOH]_0$ m/l	$[ROOH]_3 \text{ min.}$ m/l	$\Delta ROOH$ m/l
0.0461	0.0486	+ 0.0025
0.0511	0.0533	+ 0.0022
0.0557 ^a	0.0557	0.0000
0.0600	0.0580	- 0.0020

^a Best value for the steady concentration of $[ROOH]$

within the time of the experiment was less than 10 per cent, 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 that any products of peroxide decomposition which may impart an inhibitory effect to the reaction are held to a minimal value. This technique, however, is subject to the usual limitations of initial rate studies inasmuch as it is not possible to evaluate the magnitude of the errors involved.

Dependence of Oxidation Rate on Shaking Speed

In order to determine the proper shaking speed of the reaction vessel shown in Figure 1, studies were made on the dependence of oxidation rate on shaking speed. The results are summarized in Table II for a typical reaction condition. Additional determinations

were made for runs carried out under different conditions of temperature and concentration of reactants. It was found that a shaking rate of 150 strokes per minute was sufficiently rapid to ensure oxidation rates independent of shaking speed.

TABLE II.

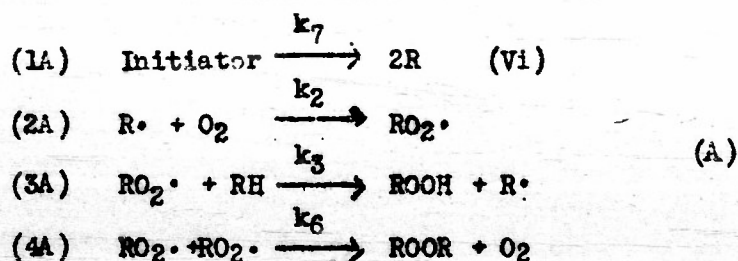
THE EFFECT OF SHAKING SPEED ON RATE OF OXIDATION OF TETRALIN IN CHLOROBENZENE AT 50°C. CATALYZED BY AZO-BIS-ISOBUTYRONITRILE.

Shaking Rate Strokes/min.	Rate of Oxygen Absorption Moles Oxygen Absorbed/35 ml. Solution/min. $\times 10^6$
0	2.0
60	7.28
100	7.28
124	7.30
236	7.20

RESULTS AND DISCUSSION

Oxidations Initiated by Benzoyl Peroxide and Azo-bis-isobutyronitrile

Bamford and Dewar⁶ have demonstrated by photosensitized oxidation studies of tetralin that this reaction follows the general autoxidation scheme of Bolland and Gee⁷. On the basis of this scheme, the oxidation of tetralin, initiated by benzoyl peroxide (BzO_2) or azo-bis-isobutyronitrile (AZEM) at high oxygen pressure (greater than 50 mm. Hg. of oxygen⁶) may be written as follows:



Kinetic analysis of mechanism (A) leads to the following rate expression for oxygen absorption, when the production of radicals occurs only by decomposition of the initiator:

$$-d[O_2]/dt = \frac{k_3 V_i^{\frac{1}{2}} [RH]}{(2k_6)^{\frac{1}{2}}} \quad (1)$$

where V_i is the velocity of the initiation step and $[RH]$ is the hydrocarbon concentration.

If the velocity of initiation may be defined as the rate of unimolecular decomposition of the initiator, times the efficiency, e_i , of initiation of oxidation chains, then equation (1) may be expressed as:

$$-d[O_2]/dt = k_3 (e_i k_7 / 2k_6)^{\frac{1}{2}} [RH] [Initiator]^{\frac{1}{2}} \quad (2)$$

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.

In the case of tetralin oxidation initiated by either BzO_2 or AZEN, Bateman and Morris¹³ have recently shown that e_i is the same for both initiators (i.e., $e_{AZEN}/e_{BzO_2} = 1.01$ at 55°) and is approximately close to unity. Values of e_i greater and smaller than two were found with other olefins, although the theoretical value for e_i , as defined above, should be two. The unimolecular rate constants (k_7) for BzO_2 and AZEN decomposition have been measured by Bawn and Melish¹⁴ using

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

(14) C.E.H. Bawn and S.F. Melish, *ibid.*, **47**, 1216 (1951).

an inhibitor method.

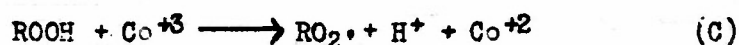
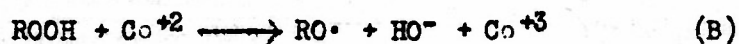
On the basis of equation (2) the rate of tetralin oxidation should be first-order with respect to tetralin concentration and one-half order with respect to initiator concentration. Figure II represents the data obtained by oxidation of tetralin in chlorobenzene solvent at 50° at various initial concentrations of AZEN. The extent of oxidation was maintained at less than 10% in order that the tetralin concentration remain essentially constant. In addition, the total time of each run was small compared with the life time of the catalyst (10% decomposition in 19 hours) at this temperature, so that this concentration also may be considered constant. Figure III represents a logarithmic plot of oxidation rate vs. AZEN concentration as determined from the data of Figure II, whence it is noted that the rate is one-half order with respect to AZEN. The plots represented in Figures IV and V on oxidation rate vs. tetralin concentration at constant AZEN concentration demonstrate that the oxidation rate is also first-order with respect to tetralin concentration. These observations are in agreement with the rate expression given in equation (2).

Oxidations Activated by Cobalt Ion:

Bawn and co-workers^{9,15} have shown that hydrocarbons undergo rapid oxidation in the presence of anhydrous cobaltous acetate in

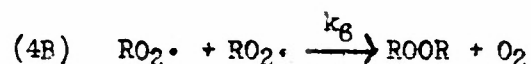
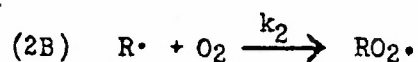
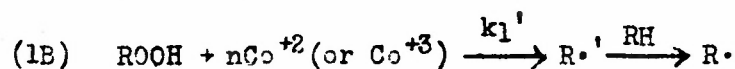
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- (15) (a) C.E.H. Bawn, A.A. Pennington and C.F.H. Tipper, Faraday Society Discussion 10, 252 (1951); (b) C.E.H. Bawn and A.G. White, J. Chem. Soc., 1951, 331, 339, 344; (c) C.E.H. Bawn, Faraday Society Discussion, Sept. 1952 (to be published).
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acetic acid solvent. In certain instances the metal ion can react directly with the hydrocarbon 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 amounts of cobalt ion can promote the decomposition of a large quantity of hydroperoxide, possibly by reactions of the type:



These reactions, however, are very complicated, particularly since the cobalt functions as a complex ion, and oxidations initiated in this manner do not render the relatively straight-forward kinetics obtained with oxidations initiated by BzO_2 or AZEN .

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



then it is apparent that this oxidation will exhibit autocatalysis since the hydroperoxide formed during oxidation will subsequently react with cobalt ion and continue the chain process. The kinetic

expression for the rate of oxidation when peroxide decomposition is negligible compared with its rate of formation is;

$$-d[O_2]/dt = k_3(k_1'/2k_6)^{\frac{1}{2}}[RH][ROOH]^{\frac{1}{2}}[Co^{+2}]^{n/2} \quad (3)$$

It may be seen from equation (3) 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 ion.

As the concentration of hydroperoxide in the system increases with time, the rate of decomposition of hydroperoxide will eventually equal the rate of formation of hydroperoxide and this will then lead to the appearance of a stationary or steady concentration of hydroperoxide⁸. The magnitude of the steady concentration of hydroperoxide $[ROOH]_{\infty}$ will be given by the expression:

$$[ROOH]_{\infty} = \frac{k_3^2 [RH]^2}{2k_1' k_6 [Co^{+2}]^n} \quad (4)$$

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

$$[-d[O_2]/dt]_{\infty} = \frac{k_3^2 [RH]^2}{2k_6} \quad (5)$$

As discussed previously⁸, this rate expression corresponds to the maximum rate of oxidation of tetralin at a given temperature and

hydrocarbon concentration since the rate is independent of the cobalt activator concentration. An equation identical with equation (5) can also be derived for the purely thermal oxidation of tetralin in the advance stage of oxidation where a steady concentration of hydroperoxide has been attained. In this case the initiation step occurs via the thermal decomposition of hydroperoxide.

The experimental verification of equation (5) and also equation (4) for the oxidation of tetralin in acetic acid activated by cobaltous ion will now be discussed.

The rate of oxidation of tetralin at several concentrations of cobaltous acetate at 50°C. is represented in Figure VI. At the lowest cobalt concentration there is an appreciably long inhibition period, 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 the higher cobalt ion concentrations, the time of the induction period and the auto acceleration period are shortened whereas the steady rate attained in all three cases is the same. The inhibition stage noted at the lower cobalt concentrations is believed to be due to the initially slow accumulation of sufficient hydroperoxide in the system to enable the step (ID) 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 should not exhibit any inhibition period. If a small trace of tetralin

hydroperoxide is added to tetralin prior to the start of oxidation run at the low cobalt acetate concentration, the inhibition period is almost completely eliminated. This effect is clearly demonstrated in Figure VII where the rates of oxidation are shown for systems containing small, initial amounts of added hydroperoxide.

Figure VIII represents the dependence of the rate of tetralin oxidation on the concentration of hydrocarbon at 50°. At each concentration of tetralin the rate of oxygen absorption approaches a steady or maximum value. A trace of tetralin hydroperoxide was added to the system prior to each run in order to eliminate the induction period. A logarithmic plot of the steady rates of oxidation from Figure (VIII) versus the tetralin concentration is shown in Figure (IX) whence it is noted that the steady rate of oxidation is proportional to the square of the tetralin concentration. The square dependence of oxidation rate on tetralin concentration and the zero-order dependence on cobalt acetate concentration are in complete agreement with equation (5), derived from the maximum rate theory of oxidation.

In addition to the measurements of oxidation rates, 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. As previously stated, these studies were made by adding pure tetralin hydroperoxide to tetralin in acetic acid containing cobalt ion and determining after a short time interval the relative increase or decrease in peroxide value of the oxidizing system. By this procedure it was possible to eliminate the experimental difficulties encountered by Bawn and co-workers in determining the steady peroxide concentration of oxidizing hydrocarbons in the presence of cobalt ion, wherein a gradual destruction of the cobalt activator (possibly by water formed during reaction) led to a progressive upward drift of the steady concentration of hydroperoxide. The gradual decrease in the activity of the cobalt ion is not reflected in the rates of oxidation, however, since these rates are independent of the activator concentration, eq. (5).

In Figures X and XI are plotted logarithmically the values of the steady concentrations of hydroperoxide versus tetralin concentration and cobaltous acetate concentration, respectively. These studies were carried out at 50°C. under reaction conditions identical with the oxygen absorption measurements.

In agreement with equation (4), 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 concentration ($n=2$ in equation 4) indicates that the decomposition of tetralin hydroperoxide, activated by cobalt ion, is second-order

with respect to the cobalt concentration. 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 decomposition under non-oxidizing conditions.

Accordingly, the rates of decomposition of tetralin hydroperoxide in acetic acid containing benzene (to simulate the tetralin molecule without subsequent oxidation) and cobalt acetate have been determined at 50°C. As shown in Figure XII, the decomposition of tetralin hydroperoxide adheres to a first-order plot down to 90% decomposition of hydroperoxide and the rate of decomposition of peroxide increases with the cobalt concentration. The fact that the cobalt acetate serves as a true activator and is not destroyed by the hydroperoxide is demonstrated by the fact that the decompositions were run at initial molar ratios of cobalt acetate to peroxide as low as 1 to 150. In the absence of cobalt ion, the decomposition of tetralin hydroperoxide at 50°C. is negligibly small. From a logarithmic plot of the decomposition rate of peroxide versus the cobalt acetate concentration given in Figure XII it is seen in Figure XIII that the decomposition is second-order with respect to the cobalt concentration. The cobalt acetate concentration employed in the study of hydroperoxide decomposition was in the same concentration range as that employed in the oxidation studies. At higher concentrations of cobalt (6×10^{-3} m/l.) the slope of the line represented in Figure XIII diminishes toward a value of unity. The decomposition of tetralin

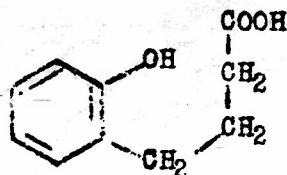
hydroperoxide activated by cobalt acetate may therefore be represented, in the cobalt concentration range employed, by the expression:

$$-d[\text{ROOH}]/dt = k[\text{ROOH}][\text{Co}^{+2}]^2 \quad (6)$$

Thermal Oxidations

The rate of thermal oxidation of pure tetralin at elevated temperatures is shown in Figure XIV. Continuation of the runs shown in this Figure to higher extents of oxidation are not possible since the system ceases to oxidize shortly after the time of the last point given for the runs at each temperature. This effect is demonstrated in Figure XV for oxidations at several concentrations of tetralin since it is noted that the curves pass through a steady region of oxidation and then diminish rapidly. It is seen, however, that the steady rate is proportional to the square of the tetralin concentration as shown in Figure XVI. This dependence has also been noted by several other workers^{1,3}. At first sight it might be assumed that the thermal oxidation of tetralin, in the steady rate stage of oxidation, can be expressed by the maximum rate equation (5). It has been observed, however, that the addition of small amounts of hydroperoxide to tetralin, during the course of an oxidation run, markedly accelerates the rate of oxygen absorption. Determination of the concentration of hydroperoxides during the oxidation of the hydrocarbon gave no indication of the occurrence of a steady concentration of hydroperoxide (the peroxide content increases with time of reaction until

the oxygen absorption passes through the steady state region) as predicted from theory. In addition, it will be shown in the next section that the steady rate of thermal oxidation of tetralin is considerably slower than the maximum rate of oxidation measured by other modes of initiation. On the basis of the evidence thus far accumulated, it would seem that the thermal oxidation of tetralin is accompanied by the simultaneous formation of an inhibitor. In fact, extensively oxidized tetralin can be used in small amounts to inhibit the oxidation of freshly distilled tetralin. Robertson and Waters⁵ have demonstrated that γ -o-hydroxyphenylbutyric acid III is formed as one of the minor products of tetralin oxidation, probably as



γ -O-Hydroxyphenylbutyric Acid

III

a consequence of peroxide decomposition, and that this compound functions as a good inhibitor for oxidation.

Studies on the determination of the steady concentration of hydroperoxide in the thermal oxidation of tetralin using the initial rate technique, are presented in a later section.

Comparison of Oxidations Initiated by Various Agencies

A direct correlation between the rates of tetralin oxidation initiated by BzO_2 or AZBN and oxidation activated by cobalt acetate may be readily presented. If the rate expression given in equation (2) for the free radical catalyzed oxidation is squared and divided by 2, the following is obtained:

$$\frac{1}{2} \left[-d[O_2]/dt \right]^2 = \frac{1}{2} k_3^2 \frac{k_7}{k_6} [RH]^2 [Initiator] \quad (7)$$

where e_i is taken at the theoretical value of 2.0. Division of both sides of equation (7) by the velocity of initiation ($k_7 [Initiator]$), gives:

$$\frac{\left[-d[O_2]/dt \right]^2}{2k_7 [Initiator]} = \frac{k_3^2 [RH]^2}{2k_6} \quad (8)$$

It is noted that the term on the right hand side of equation (8) corresponds to the maximum rate expression derived for autoxidations activated by cobalt acetate (equation 5).

The velocity of initiation of oxidations in the presence of BzO_2 or AZBN can be calculated from Bawn and Melish's data for the decomposition of these two compounds in benzene solvent. Therefore it is possible to directly calculate the right hand term in equation (8) and compare the value obtained with the corresponding value for the maximum rate of oxidation using cobalt activated initiation. The numerical values are summarized in Table III.

TABLE III

Comparison of Maximum Rates of Oxidation ^a				
Temp. °C.	Calculated		Observed	
	BzO ₂	AZBN	CoAc ₂	Thermal
50.0	-	1.4	1.5	-
61.6	3.4	4.6	4.1	-
69.0	8.6	8.2	5.9	0.0135

^a. Maximum rate of oxidation x 10⁵m/l/sec.

At all three temperatures 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 is on the order of 500 to 700 times smaller than the other values. As previously noted this discrepancy can perhaps be attributed to the formation of inhibitors during the course of oxidation.

Comparison of Activation Energies:

The temperature dependence for the AZBN, BzO₂ and cobalt activated oxidation of tetralin is shown in Figures XVII-XIX, respectively. The overall activation energies can be determined for each system from plots of the log rate vs. the reciprocal of absolute temperature as shown in Figures XX and XXI. Figure XXI also includes the data on the temperature dependence for the steady concentration of hydroperoxide $[ROOH]_{\infty}$ and the rate of cobalt

activated decomposition of tetralin hydroperoxide. The latter data are taken from the rate measurements shown in Figure XXII.

In the case of the BzO_2 or AZBN initiated oxidation, the overall activation energy (E_0) from equation (2) is given by the following expressions:

$$E_0 = E_3 + \frac{1}{2} (E_7 - E_6) \quad (9)$$

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 overall activation energy (E_0') from equation (5) is given by the expression:

$$E_0' = 2E_3 - E_6 \quad (10)$$

where E_3 and E_6 are the activation energies of the corresponding rate constants given in mechanism (L).

Equation (9) may be readily transformed to yield the expression:

$$E_0 - \frac{1}{2}E_7 = E_3 - \frac{1}{2}E_6 \quad (11)$$

The magnitude of $(E_3 - \frac{1}{2}E_6)$ in equation (11) should be equal to one-half the magnitude of E_0' given in equation (10). A comparison of $(E_3 - \frac{1}{2}E_6)$ for the three systems as well as the value calculated from the data of Bamford and Dewar⁶ for photo-sensitized oxidation is

given in Table IV.

TABLE IV

Mode of Initiation of Oxidation	$E_7^{(14)}$ (Kcals.)	E_0 (Kcals.)	$E_3 - \frac{1}{2}E_6$ (Kcals.)
AZEN	30.7	24.2	8.8
BzO_2	29.6	25.6	10.8
cobaltous acetate photosensitized ⁽⁶⁾	-	-	8.2 ± 0.6
	-	-	4.3

Whereas the values for $(E_3 - \frac{1}{2}E_6)$ are consistent for the three systems presented in this article, the values are approximately two-fold greater than that 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 of the individual steps in mechanism (A) and this procedure may have avoided errors inherent to the other three methods of measurement.

It is also of interest to compare the activation energy for the cobalt acetate activated decomposition of tetralin hydroperoxide when determined by direct measurement or calculated from the overall temperature dependence for $[-d[O_2]/dt]_{\infty}$ and $[ROOH]_{\infty}$. The overall activation energy for $[-d[O_2]/dt]_{\infty}$ is given by equation (10) and the overall activation energy for $[ROOH]_{\infty}$, (E_H), from equation (4) is given by the expression:

$$E_H = 2E_3 - E_6 - E_1' \quad (12)$$

where E_3 , E_6 and E_1' are the activation energies of the corresponding rate constants given in mechanism (D).

If E_H is subtracted from E_0' , the difference is simply the activation energy, E_1' , for the metal catalyzed breakdown of tetralin hydroperoxide. The values for E_H and E_0' are given in Figure XXI along with the value for E_1' measured directly from studies of the cobalt acetate activated decomposition of tetralin hydroperoxide. The activation energy values are summarized in Table V.

TABLE V

Activation Energies (Kcals.)

E_0'	E_H	E_1'	
		Observed	Calculated ($E_0' - E_H$)
16.4 ± 1.1	-7.6 ± 2.9	21.2 ± 0.9	24.0 ± 4.0

Considering the margin of error in the calculated value of E_1' , the agreement between the two values is good.

It is interesting to note that the overall activation energy for the steady concentration of hydroperoxide is a negative quantity ($E_H = -7.6$ Kcals.). This arises, of course, from the fact that $[ROOH]_{\infty}$ decreases with increasing temperature of oxidation. It would be of considerable interest to investigate oxidations of tetralin activated

by other metal complexes where E_1' would be sufficiently small to enable the value for E_H , as defined in equation (12), to be positive. In such cases, $[ROOH]_{\infty}$ would increase with increasing temperature of oxidation. The bimolecular reaction of ferrous ion with cumene hydroperoxide, for example, is a one-electron transfer process with a measured activation energy of 12.0 Kcals¹⁶. In this case, however, the ferrous ion reacts with the hydroperoxide, mole for mole, whereas the decomposition of tetralin hydroperoxide activated by cobalt acetate in acetic acid is of an obviously more complex nature since the moles of hydroperoxide decomposed is considerably in excess of the moles of added cobalt ion. On the other hand, it has been demonstrated¹⁷ that many other metal complexes can promote the decomposition of large excess of cumene hydroperoxide. These agencies, however, have not been studied as activators for oxidation reactions in the present work.

Robertson and Waters⁵ have briefly studied the kinetics of the thermal decomposition of tetralin hydroperoxide in tetralin in the range 88° to 135°C. At low peroxide concentrations, the decomposition reaction is essentially unimolecular and exhibits an activation energy of 24.4 Kcals. This activation energy value seems particularly low for the straight-forward unimolecular decomposition of the hydroperoxide since the O-O bond energy of other organic peroxides and

(16) R.J. Orr and H.L. Williams, *Can. J. Chem.*, **30**, 985 (1952).

(17) J.W.L. Fordham and H.L. Williams, *Can. J. of Research*, **B28**, 551 (1950).

hydroperoxides is found to be on the order of 30-38 Kcals.^{14,18}. An attempt has been made to determine the activation energy for the thermal decomposition of tetralin hydroperoxide by the initial rate technique employed for measurements of $[ROOH]_{\infty}$. These studies were made on mixtures of tetralin and tetralin hydroperoxide in diphenyl oxidized in the range 145° to 172°C. By determination of $[ROOH]_{\infty}$ at several temperatures and assuming that the peroxide decomposition is strictly unimolecular, the overall activation energy, E_t , for $[ROOH]_{\infty}$ can be written as (compare eq. 12);

$$E_t = 2E_3 - E_6 - E_1 \quad (13)$$

where E_1 refers to the activation energy for the unimolecular decomposition of tetralin hydroperoxide in tetralin solvent in the absence of metal activators. The measured value for E_t is -19.7 Kcals. as shown in Figure XXIII. When this value is substituted in equation (13), along with the average value of 16.6 Kcals. for $(2E_3 - E_6)$ from Table IV, the magnitude of E_1 is found to be 35.7 Kcals. Although this value more closely approximates the expected activation energy for the rupture of the O-O linkage in an organic hydroperoxide, than the value of Robertson and Waters, nevertheless the experimental determination involved several uncertainties and the value may be in error. The first uncertainty is experimental and is due to the

-
- (18) (a) J.H.Raley, F.F.Rust and W.E.Vaughan, *J.Am.Chem.Soc.*, **70**, 88 (1948).
 (b) M.Szwarc and J.S.Roberts, *J.Chem.Phys.*, **18**, 561 (1950).
 (c) R.E.Rebbert and K.J.Laidler, *J.Chem.Phys.*, **20**, 574 (1952).
 (d) J.W.L.Fordham and H.L.Williams, *Can.J.Research*, **B27**, 943 (1949).
-

relatively long times required for the reactants to reach bath temperature (150° to 172°) in an initial rate experiment. The second uncertainty concerns the application of the initial rate technique to a hydrocarbon system in which the order of the hydroperoxide decomposition reaction can be altered by induced chain decomposition and where the hydrocarbon oxidation reaction is recognized to produce a self-inhibitor. It should be pointed out, however, that while the breakdown of peroxides may exhibit chain induced decompositions in some solvents, in the presence of other solvents (e.g. polymerizable monomers) the radicals formed from the initial breakdown of the peroxide are rapidly converted to solvent type radicals which do not cause induced decomposition. The decomposition of hydroperoxides in solvents such as tetralin which undergo reaction with oxygen may also exhibit a repression of induced decomposition.

SUMMARY

Studies have been performed on the liquid phase oxidation of tetralin. The kinetics of the reaction have been specified for oxidations initiated by free radical producing compounds (benzoyl peroxide and azo-bis-isobutyronitrile) and by a heavy metal activator, cobaltous acetate. It is demonstrated that the oxidation reactions initiated by these agencies are uniquely related and adhere to the maximum rate theory previously proposed for hydrocarbon autoxidation. The thermal oxidation of tetralin at elevated temperatures is accompanied by the formation of self-inhibitors which markedly repress the reaction. The oxidation in the presence of cobalt acetate gives rise to the formation of steady concentrations of tetralin hydroperoxide. The dependence of the steady concentration of hydroperoxide on temperature of reaction and concentration of reactants has been measured by an initial rate technique. From this study it is possible to define in greater detail the oxidation reaction as well as the initiation step involving the decomposition of the hydroperoxide.

Figure 1.
OXYGEN ABSORPTION APPARATUS

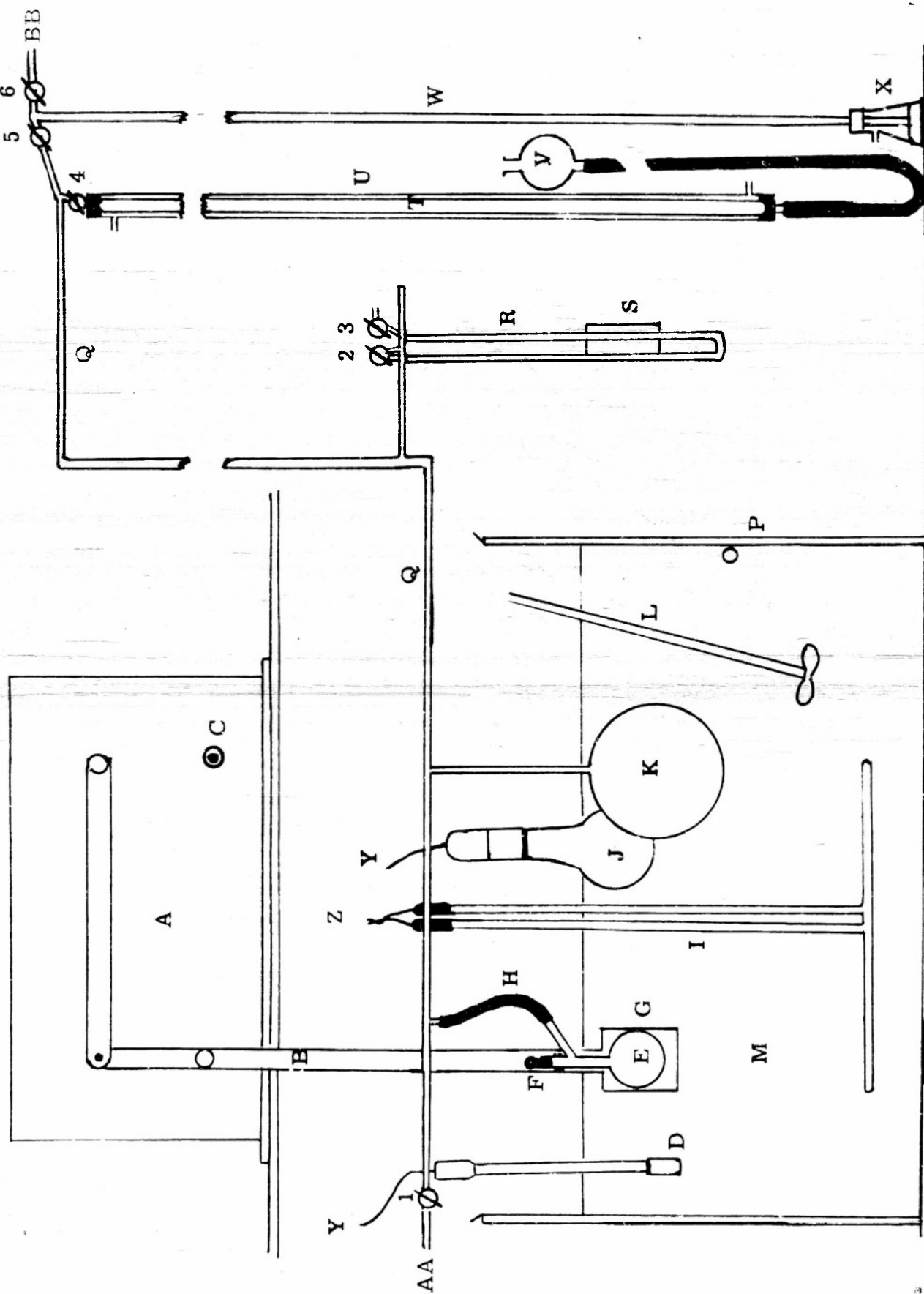


Figure 1 - Oxygen Absorption Apparatus - Legend

- | | |
|--|---|
| A - Shaker Motor | W - Pressure Release Tube |
| B - Shaker Arm | X - (Pressure) Release Valve
(Mercury) |
| C - Shaker Switch | Y - To Relay |
| D - Thermo Regulator | Z - To Powerstat |
| E - Reaction Flask | AA - To Vacuum Pump |
| F - Ground Glass Stopper | BB - To Oxygen Supply |
| G - Shaking Rack | 1-6 - Stopcocks |
| H - Rubber Tubing | |
| I - Heating Coil (Coarse) | |
| J - Heating Lamp (Fine) | |
| K - Oxygen Reservoir (500 ml.) | |
| L - "Lightning" Stirrer | |
| M - Paraffin Oil | |
| O - Metal Bath (Galvanized Iron) | |
| P - Asbestos Board Insulation ($\frac{1}{2}$ " thick) | |
| Q - Capillary Tubing (i.d. 2 mm.) | |
| R - Manometer | |
| S - Manometer Scale | |
| T - Gas Burette (100 ml., 0.1 ml. graduations) | |
| U - Constant Temp. Water Jacket | |
| V - Mercury Bulb | |

Figure 2.

OXIDATION OF TETRALIN AT 50°C.

Rate vs. AZBN Concentration

(Tetralin = 5.25 m/l in Chlorobenzene)

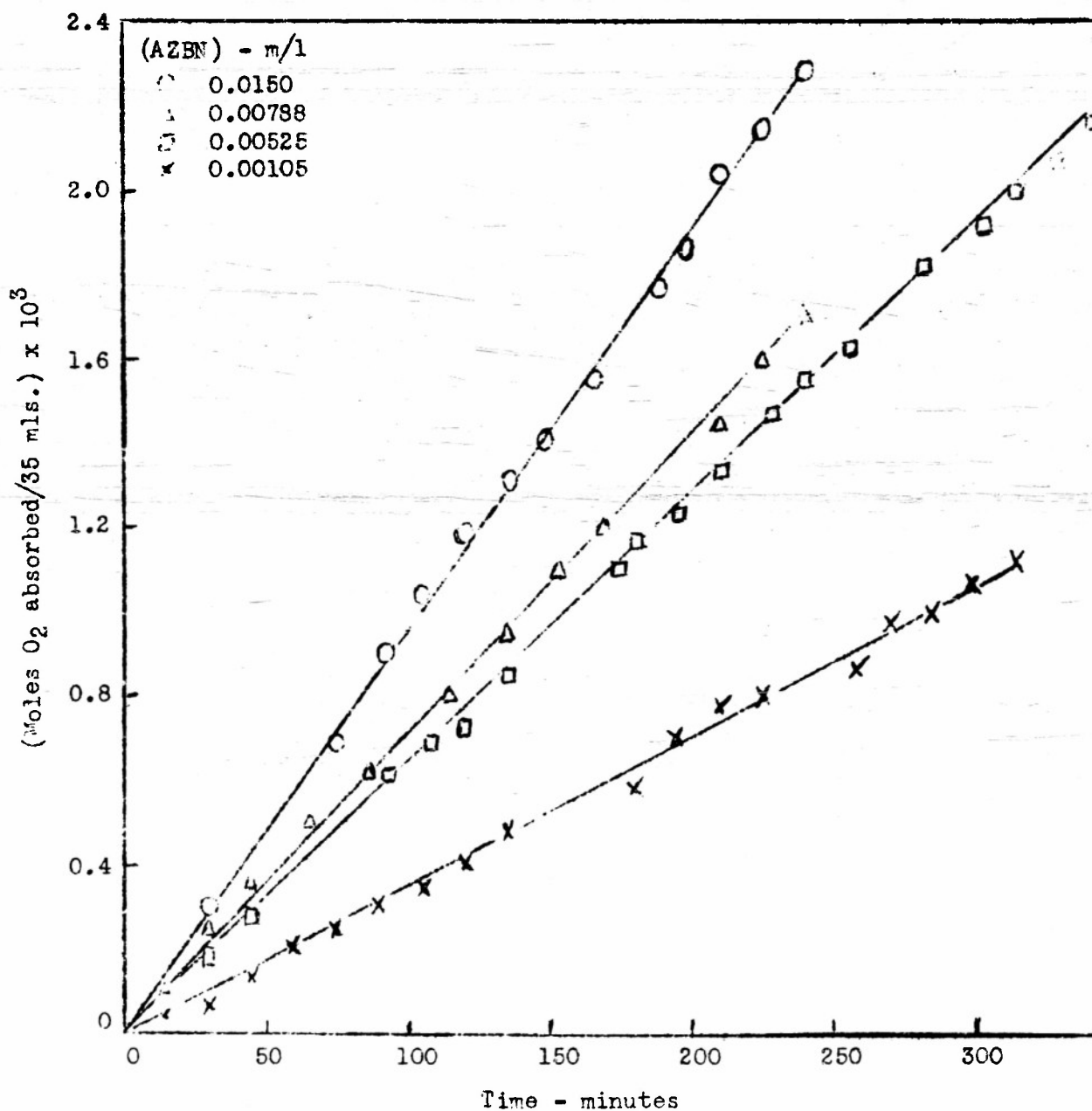


Figure 3.

OXIDATION OF TETRALIN AT 50°C.

Log Rate vs. Log AZEN Concentration

(Tetralin = 5.25 m/l in Chlorobenzene)

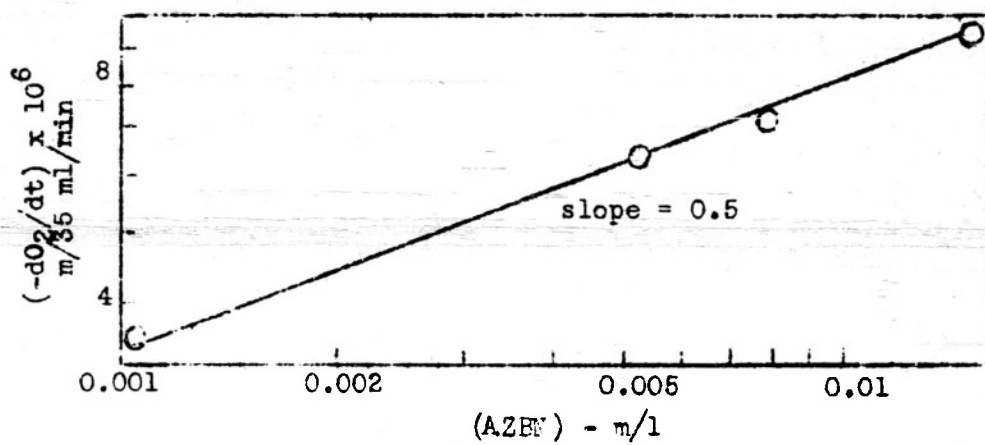


Figure 4.

OXIDATION OF TETRALIN INITIATED BY AZEN AT 50° C.
Rate vs. Tetralin Concentration
(AZEN = 0.0105 m/l in Chlorobenzene)

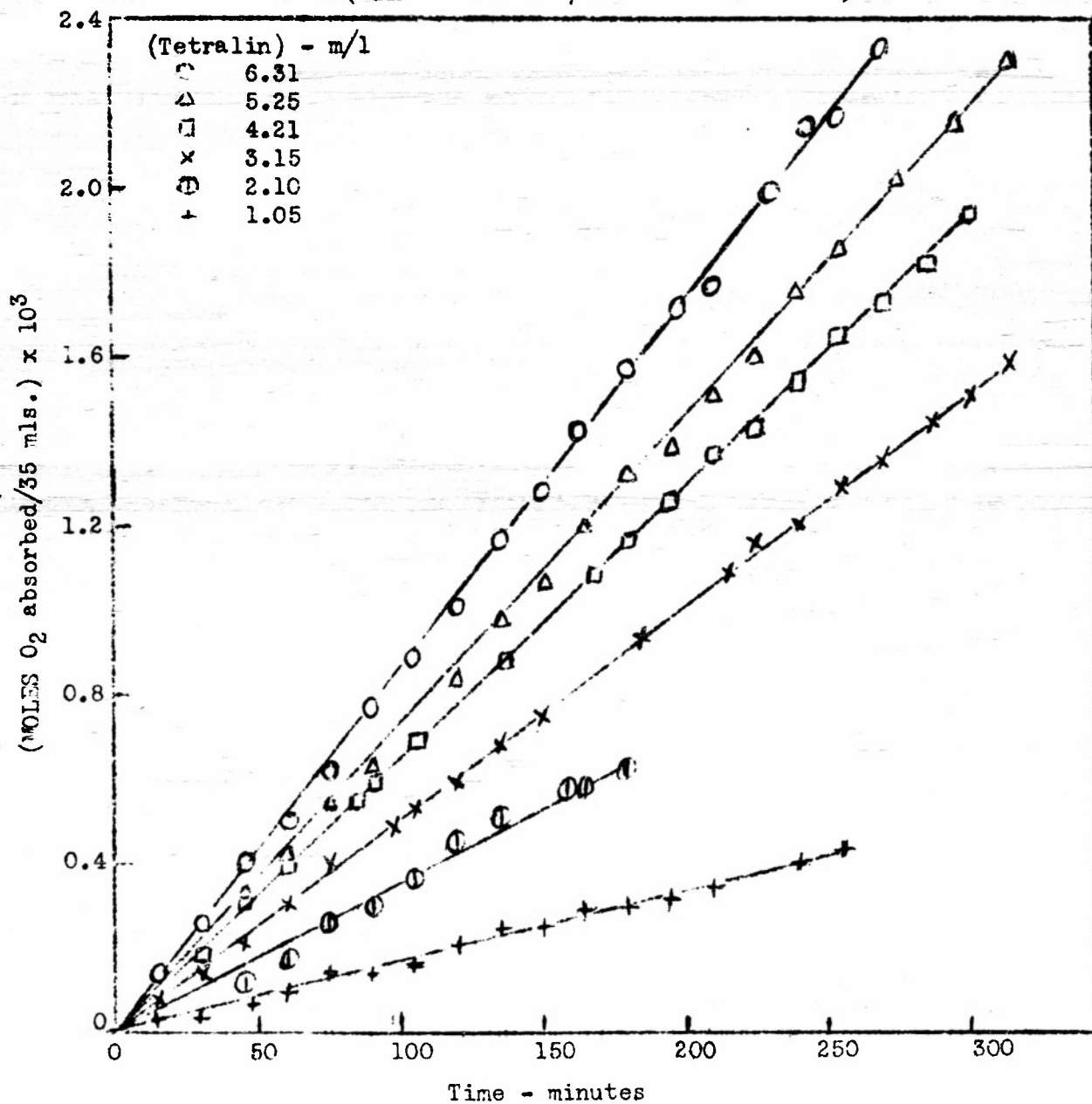


Figure 5.

OXIDATION OF TETRALIN INITIATED
BY AZEN AT 50°C.

Log Rate vs. Log Tetralin Concentration

(AZEN = 0.0105 m/l in Chlorobenzene)

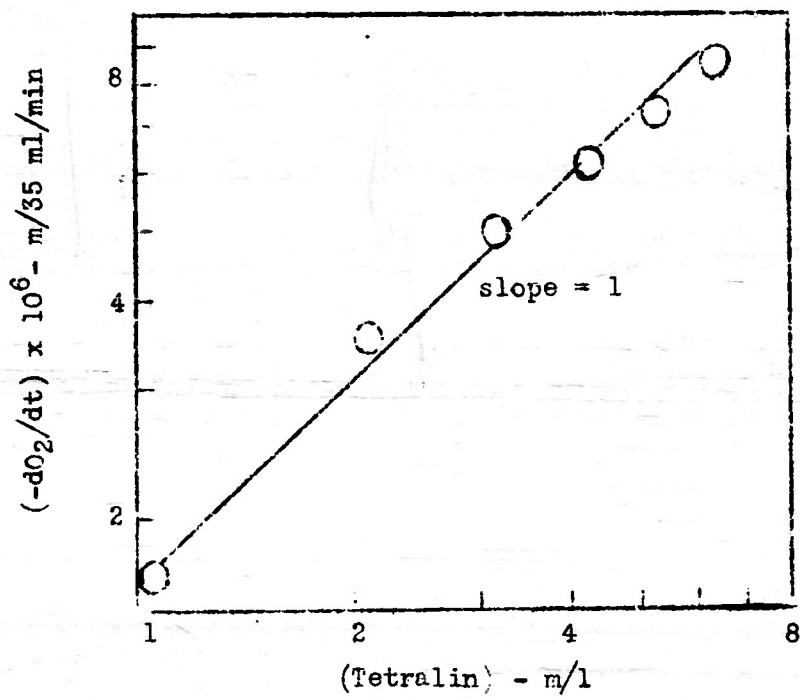


Figure 6.

OXIDATION OF TETRALIN AT 50°C.

Rate vs. CoAc_2 Concentration

(Tetralin = 3.67 m/l in HAc)

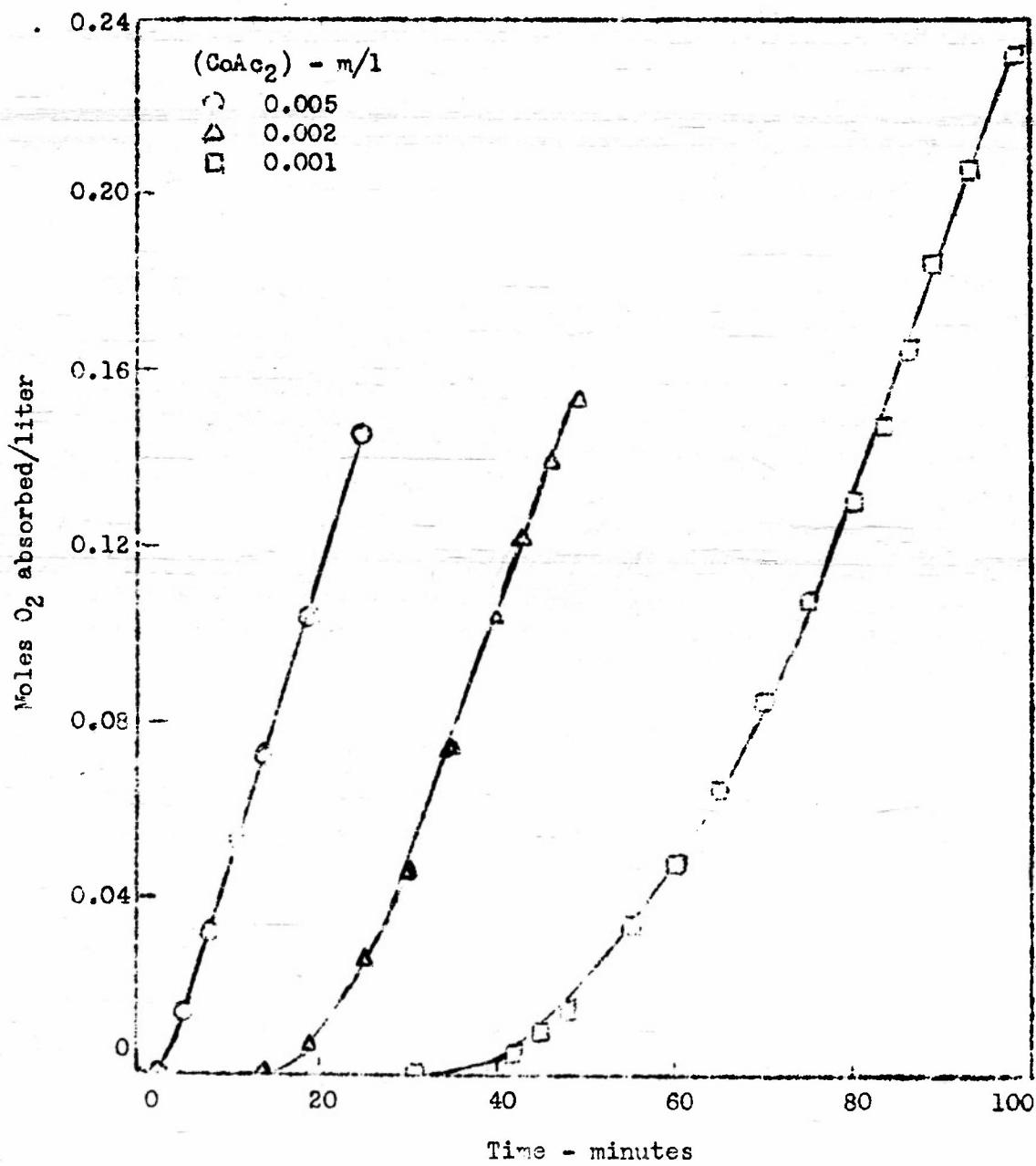


Figure 7.

OXIDATION OF TETRALIN AT 50°C. ACTIVATED BY COBALT ACETATE

Rate vs. Added ROOH Concentration

(CoAc₂ = 0.001, Tetralin = 3.67 m/l in HAc)

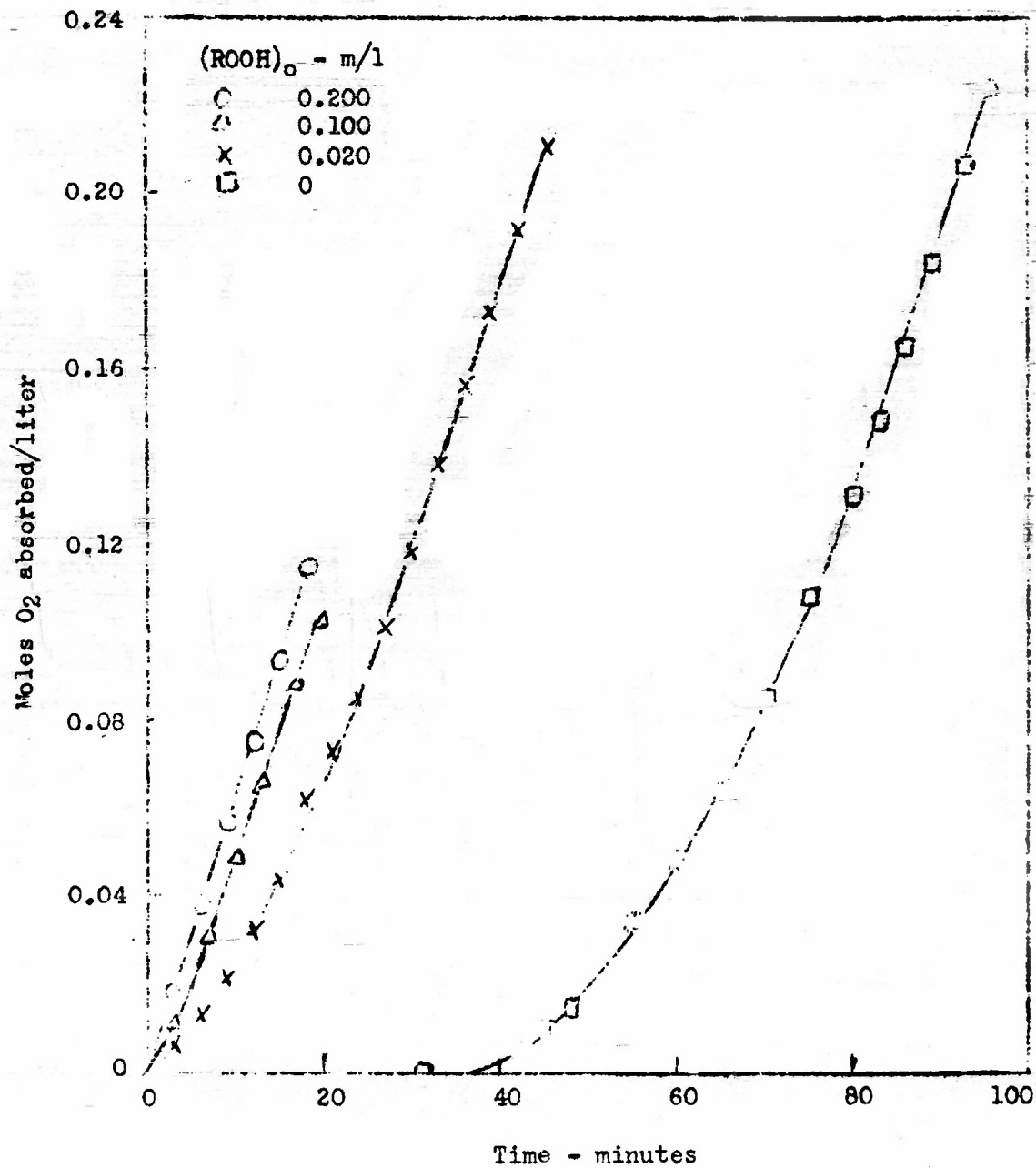


Figure 8.

OXIDATION OF TETRALIN AT 50°C. ACTIVATED BY COBALT ACETATE

Rate vs. Tetralin Concentration

(CoAc₂ = 0.002 m/l in HAc)

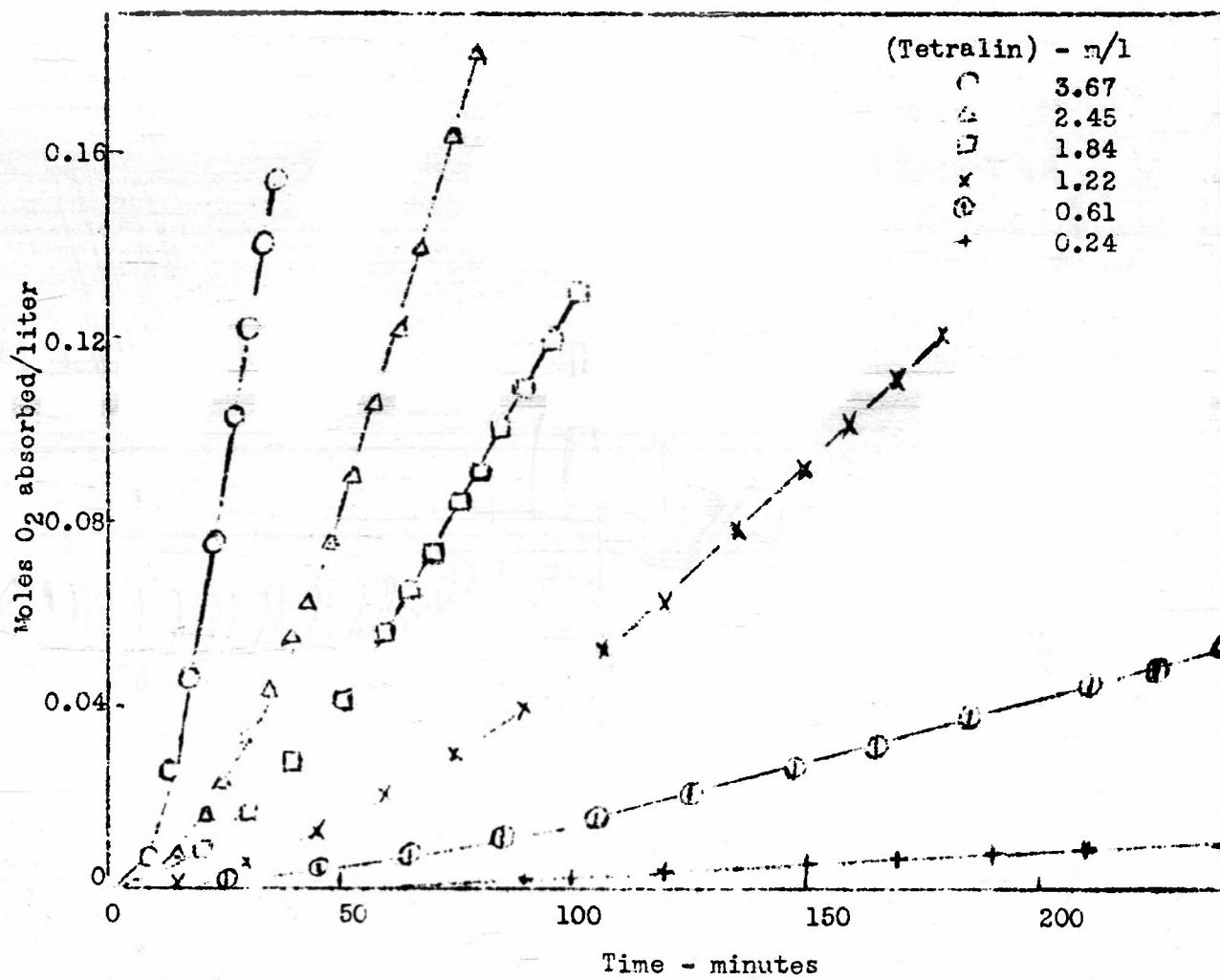


Figure 9.

OXIDATION OF TETRALIN ACTIVATED BY COBALT ACETATE AT 50°C.

Log Maximum Rate vs. Log Tetralin Concentration
(CoAc₂ = 0.002 m/l in HAc)

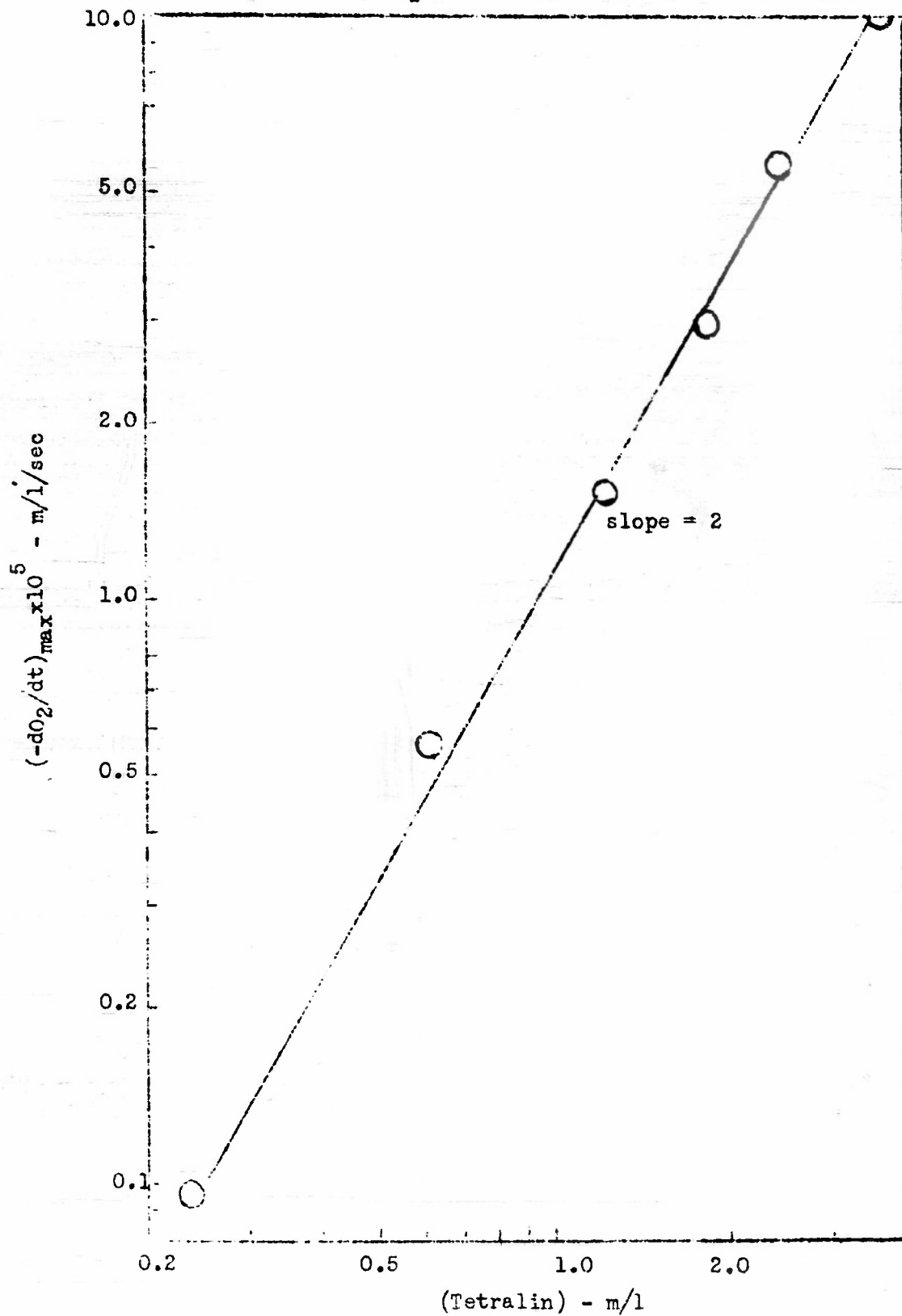


Figure 10.

OXIDATION OF TETRALIN ACTIVATED BY
COBALT ACETATE AT 50°C.

Log(ROOH)_t vs.
Log Tetralin Concentration

(CoAc₂ = 0.002 m/l in HAc)

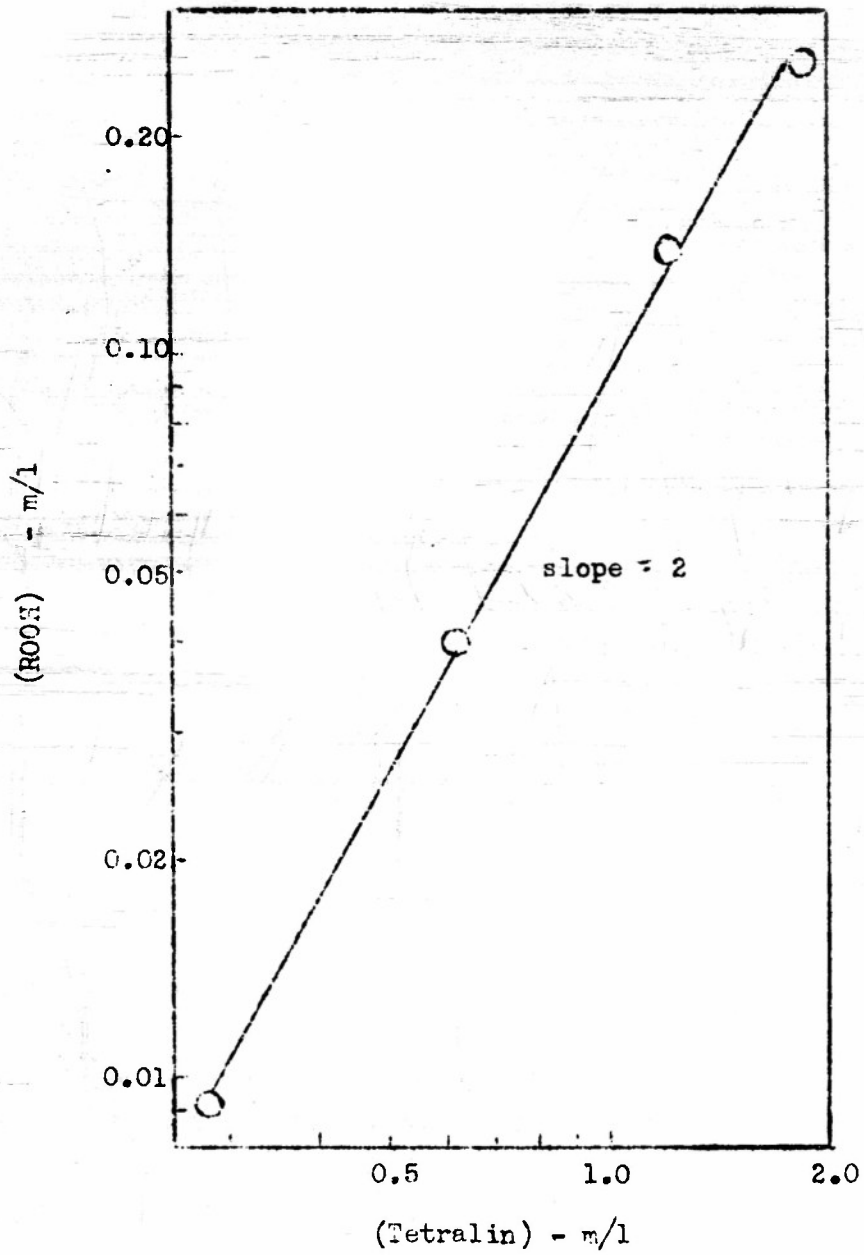


Figure 11.

OXIDATION OF TETRALIN AT 50°C.

Log(ROOH)_t vs.
Log CoAc₂ Concentration
(Tetralin = 1.22 m/l in HAc)

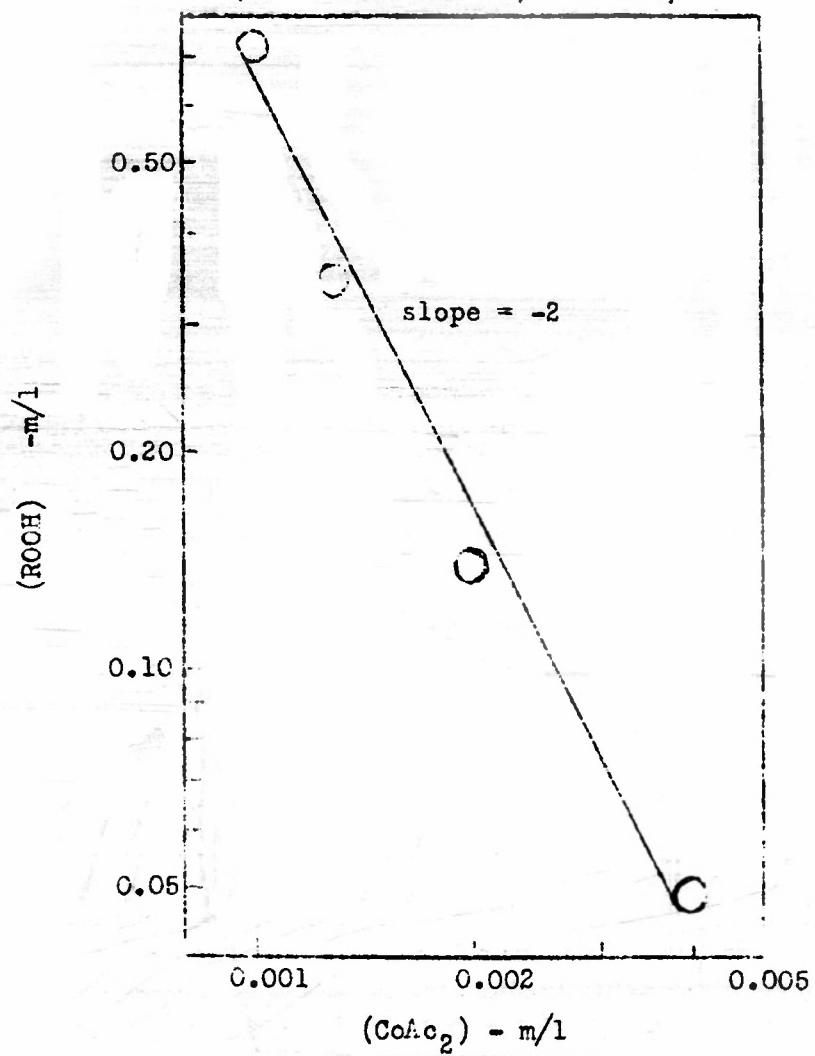


Figure 12.

DECOMPOSITION OF ROOH ACTIVATED BY COBALT ACETATE AT 50°C.

(ROOH₀ = 0.04 m/l in HAc - C₆H₆)

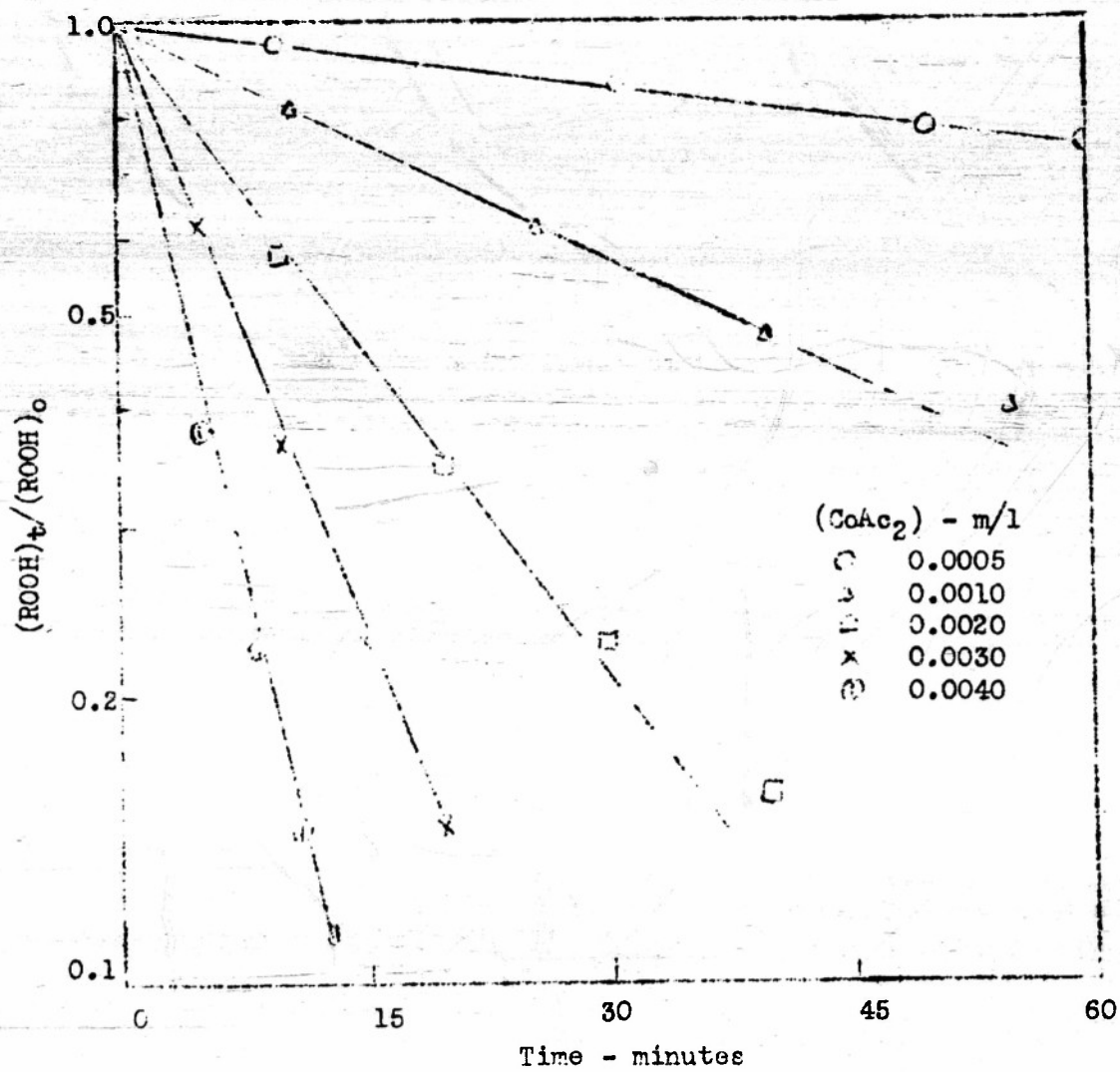


Figure 13.

DECOMPOSITION OF ROOH ACTIVATED BY COBALT ACETATE AT 50°C.

Log Rate vs. Log CoAc_2 Concentration

($\text{ROOH}_0 = 0.04 \text{ m/l}$ in $\text{HAc} - \text{C}_6\text{H}_6$)

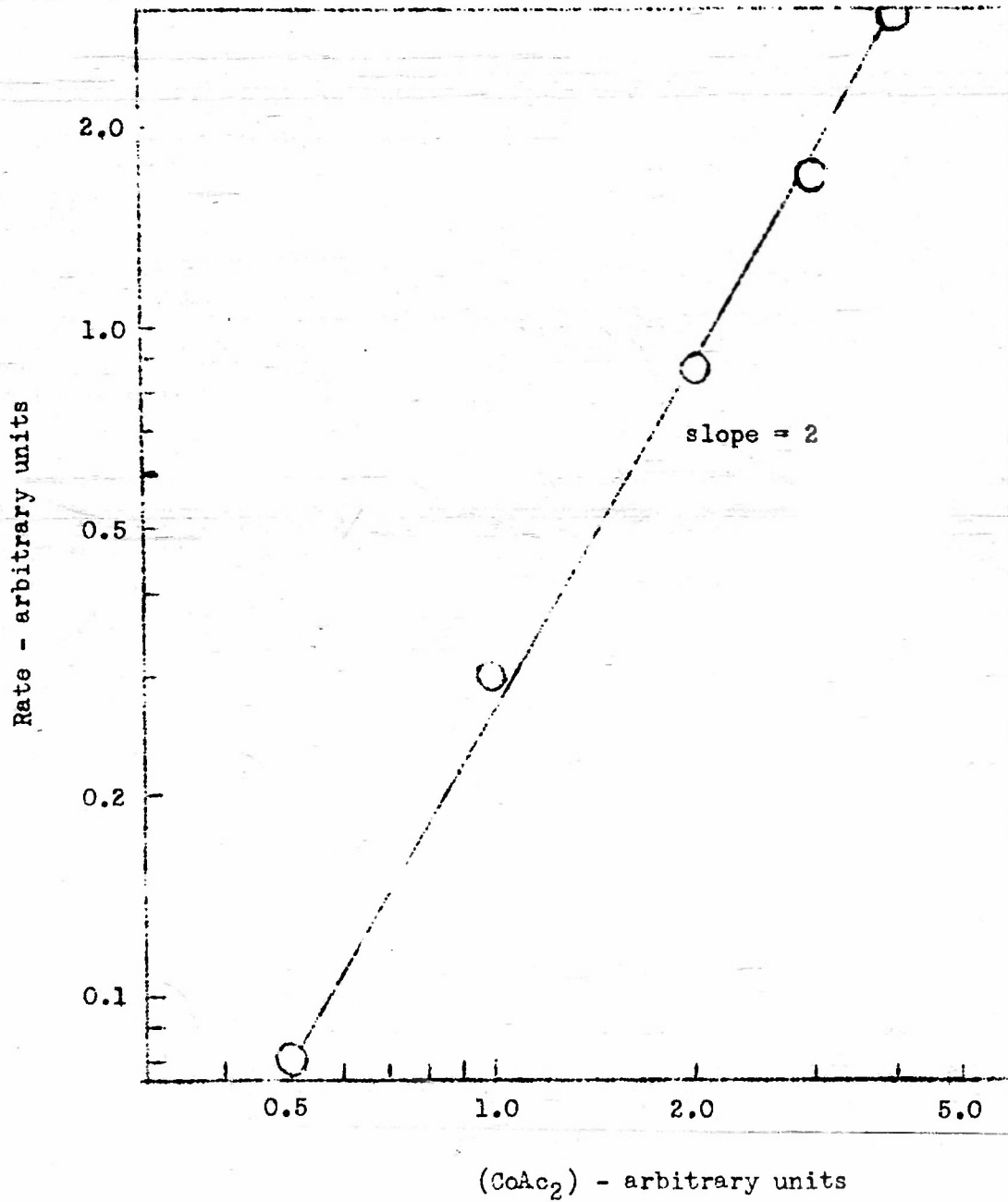


Figure 14.

THERMAL OXIDATION OF TETRALIN AT VARIOUS TEMPERATURES

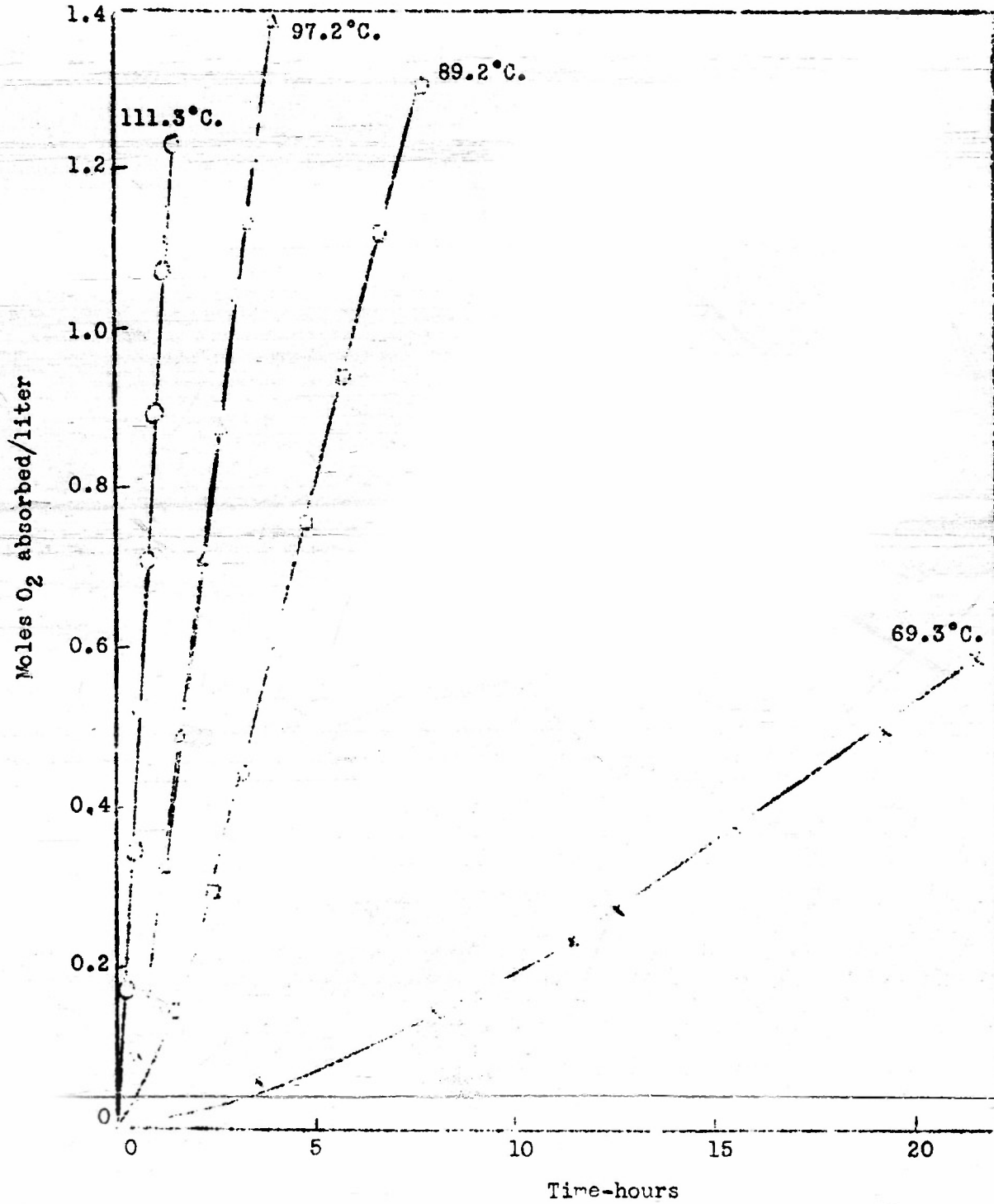


Figure 15

THERMAL OXIDATION OF TETRALIN AT 111°C.

Rate vs. Tetralin Concentration in Diphenyl

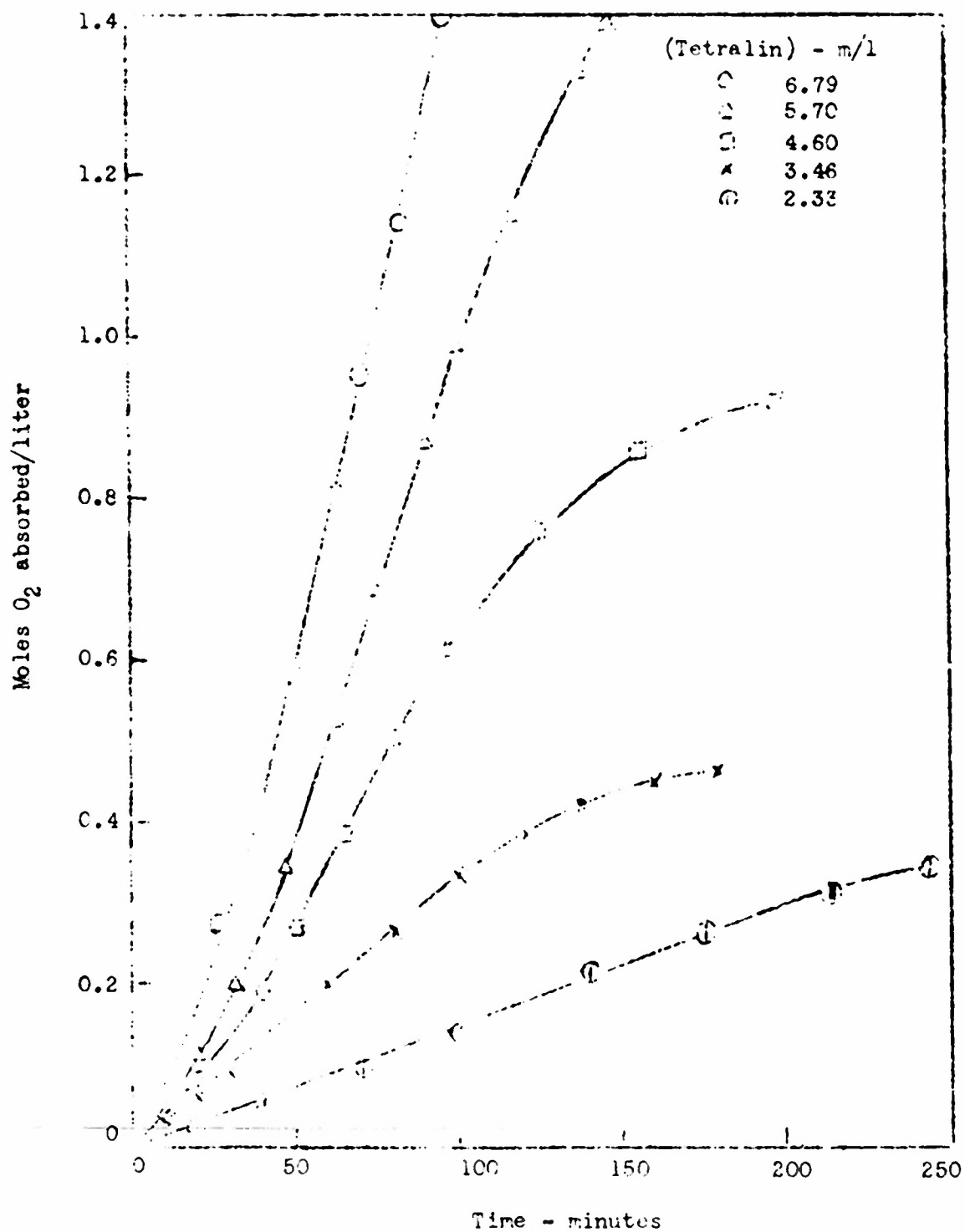


Figure 16.

THERMAL OXIDATION OF TETRALIN AT 111°C. IN DIPHENYL

Steady Rate vs. (Tetralin)²

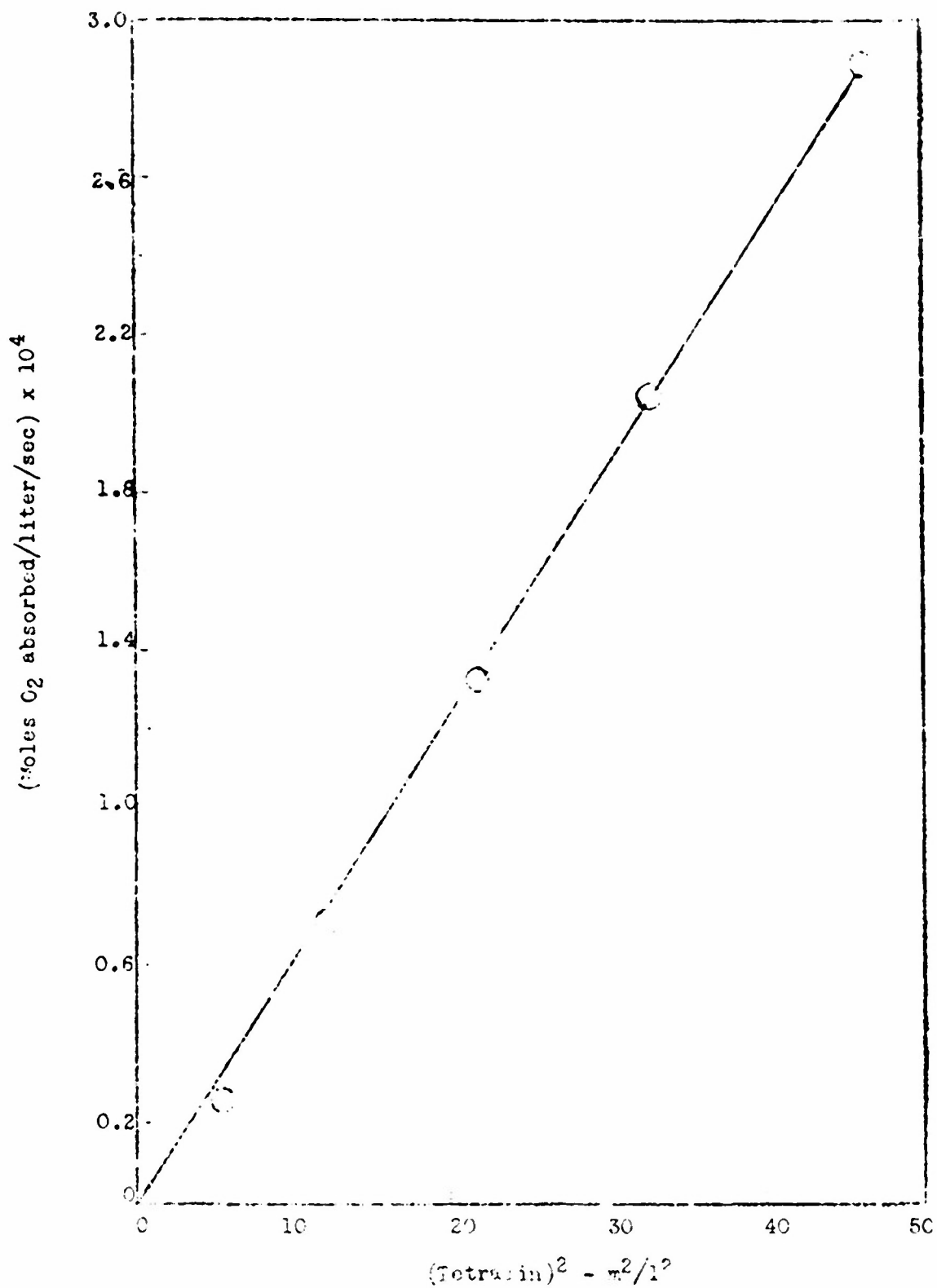


Figure 17.

OXIDATION OF TETRALIN INITIATED BY AZEN AT
VARIOUS TEMPERATURES

(AZEN = 0.0147 m/l)

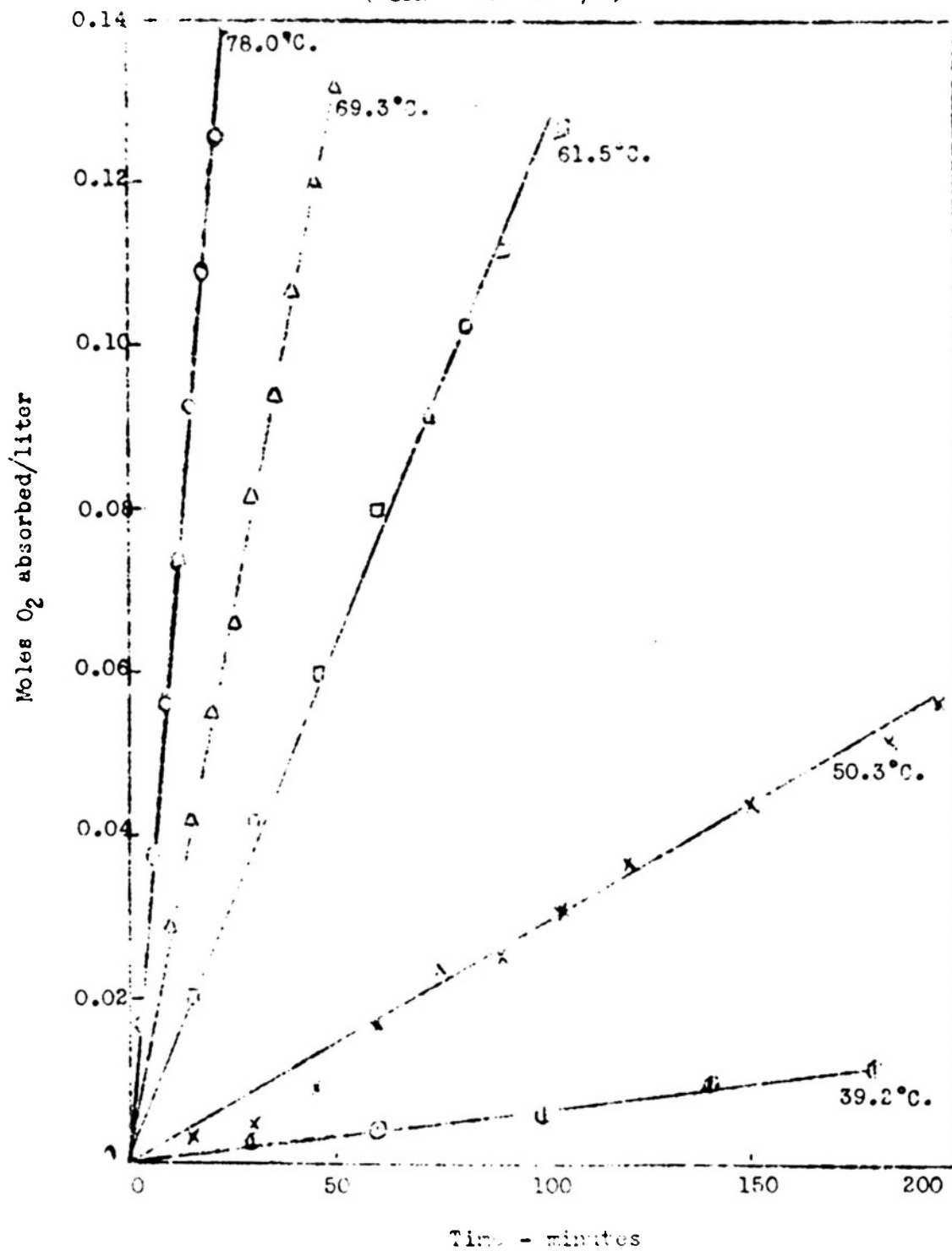


Figure 18.

OXIDATION OF TETRALIN INITIATED BY BENZOYL PEROXIDE
AT VARIOUS TEMPERATURES

($BzO_2 = 0.0147 \text{ m/l}$)

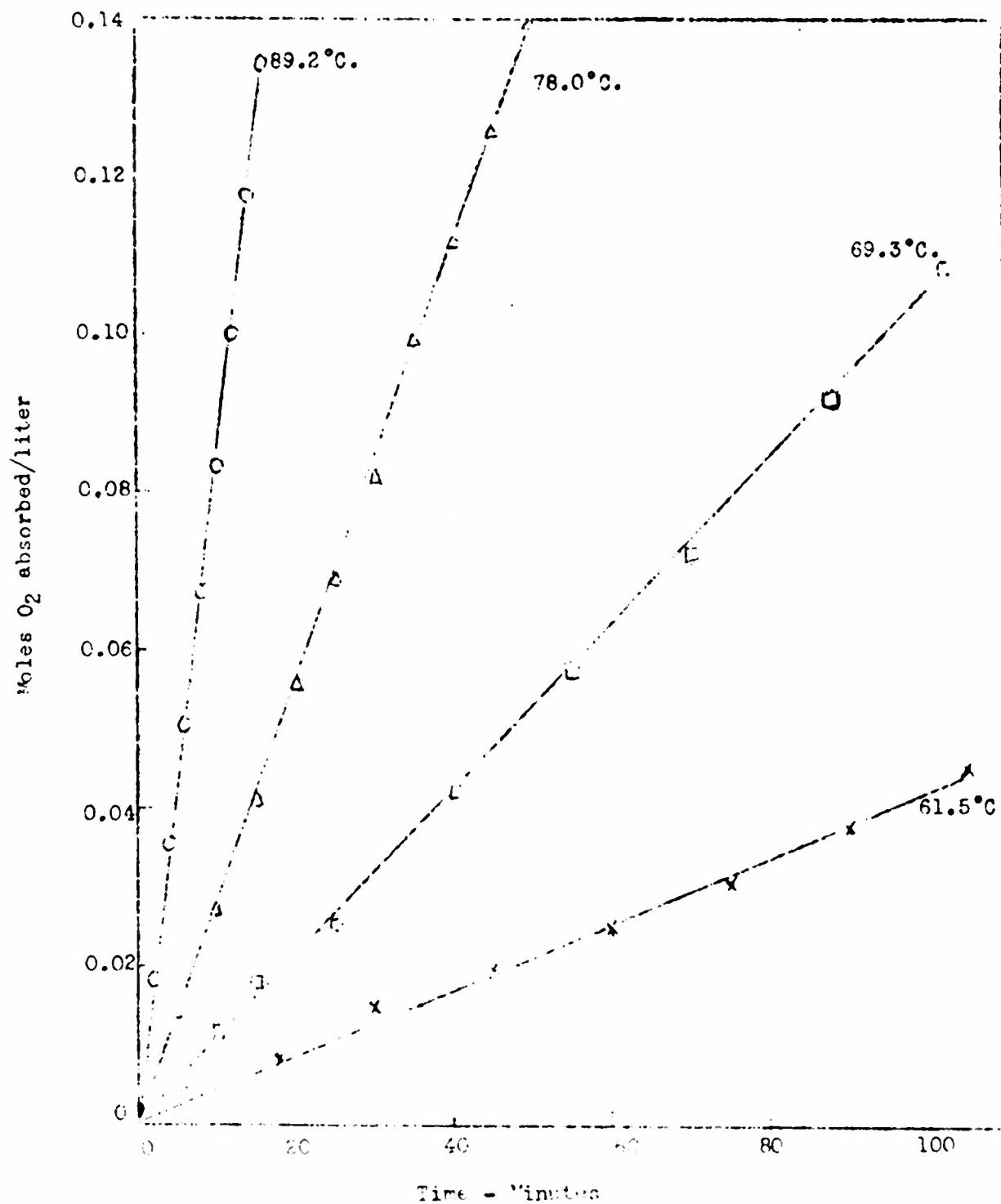


Figure 19.

OXIDATION OF TETRALIN ACTIVATED BY COBALT ACETATE

Rate vs. Temperature

($\text{CoAc}_2 = 0.002$, Tetralin = 1.22 m/l in HAc)

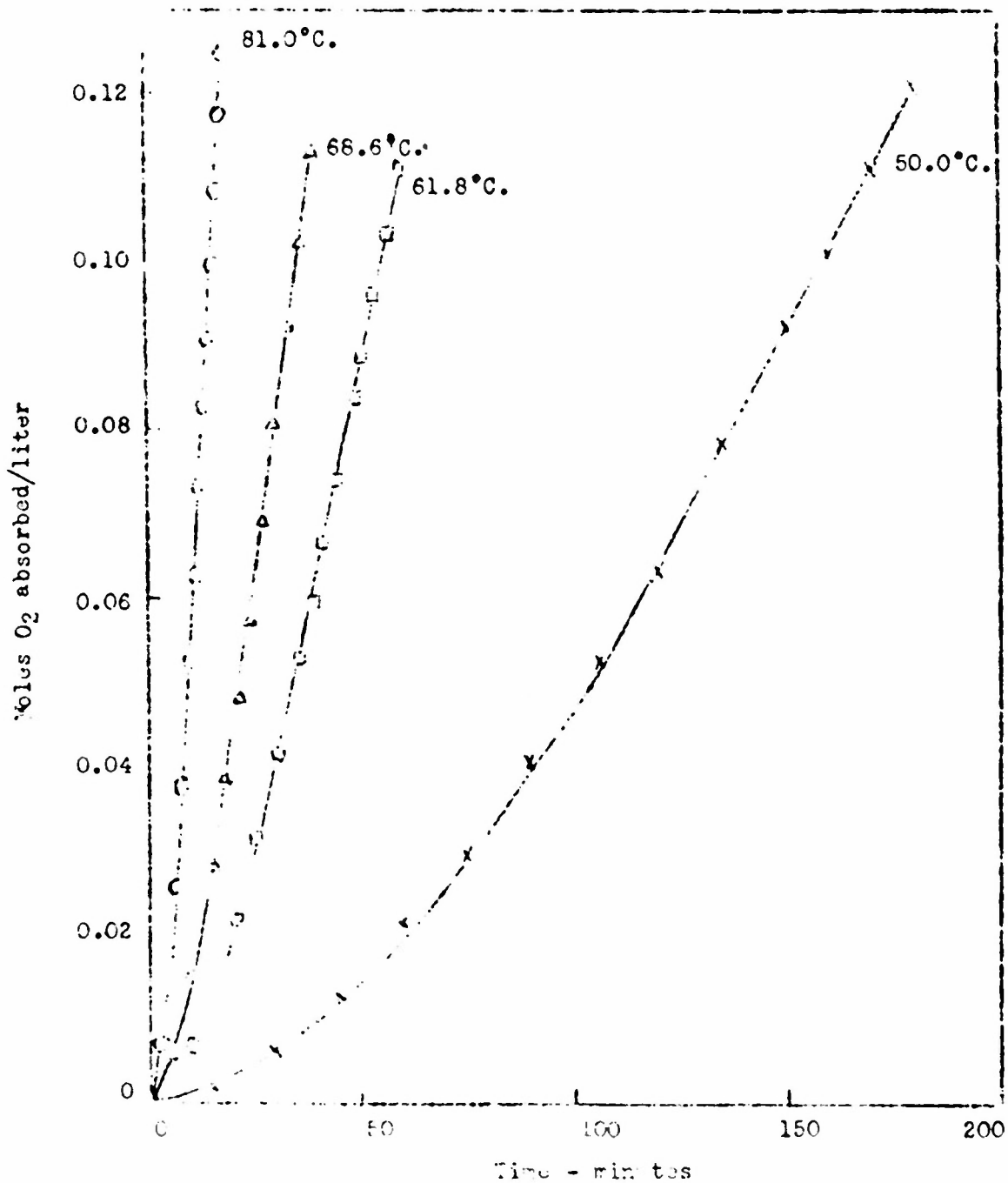


Figure 20.

THE TEMPERATURE DEPENDENCE OF THE RATE
OF TETRALIN OXIDATION INITIATED BY
BENZOYL PEROXIDE AND AZEN

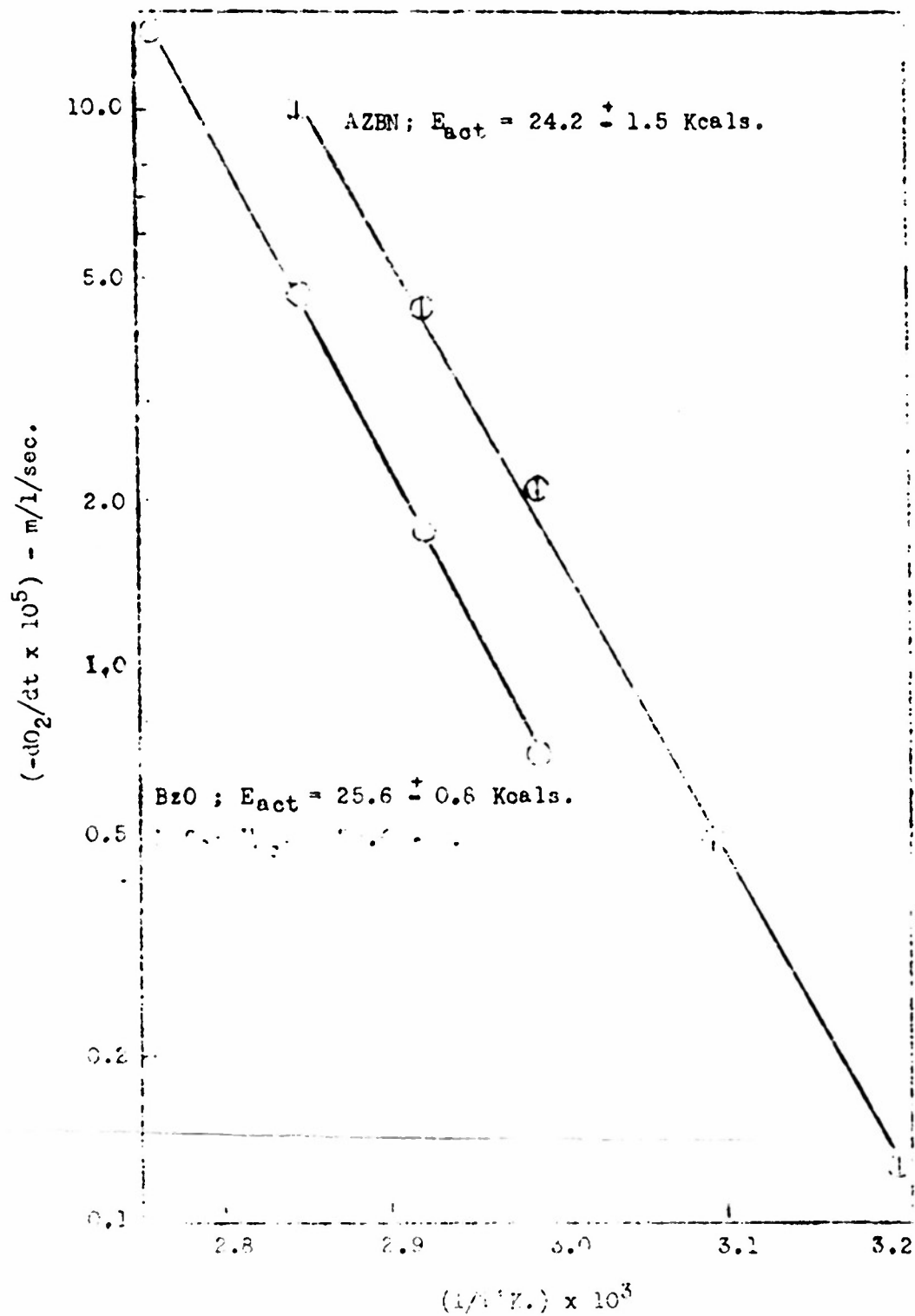


FIGURE 21.

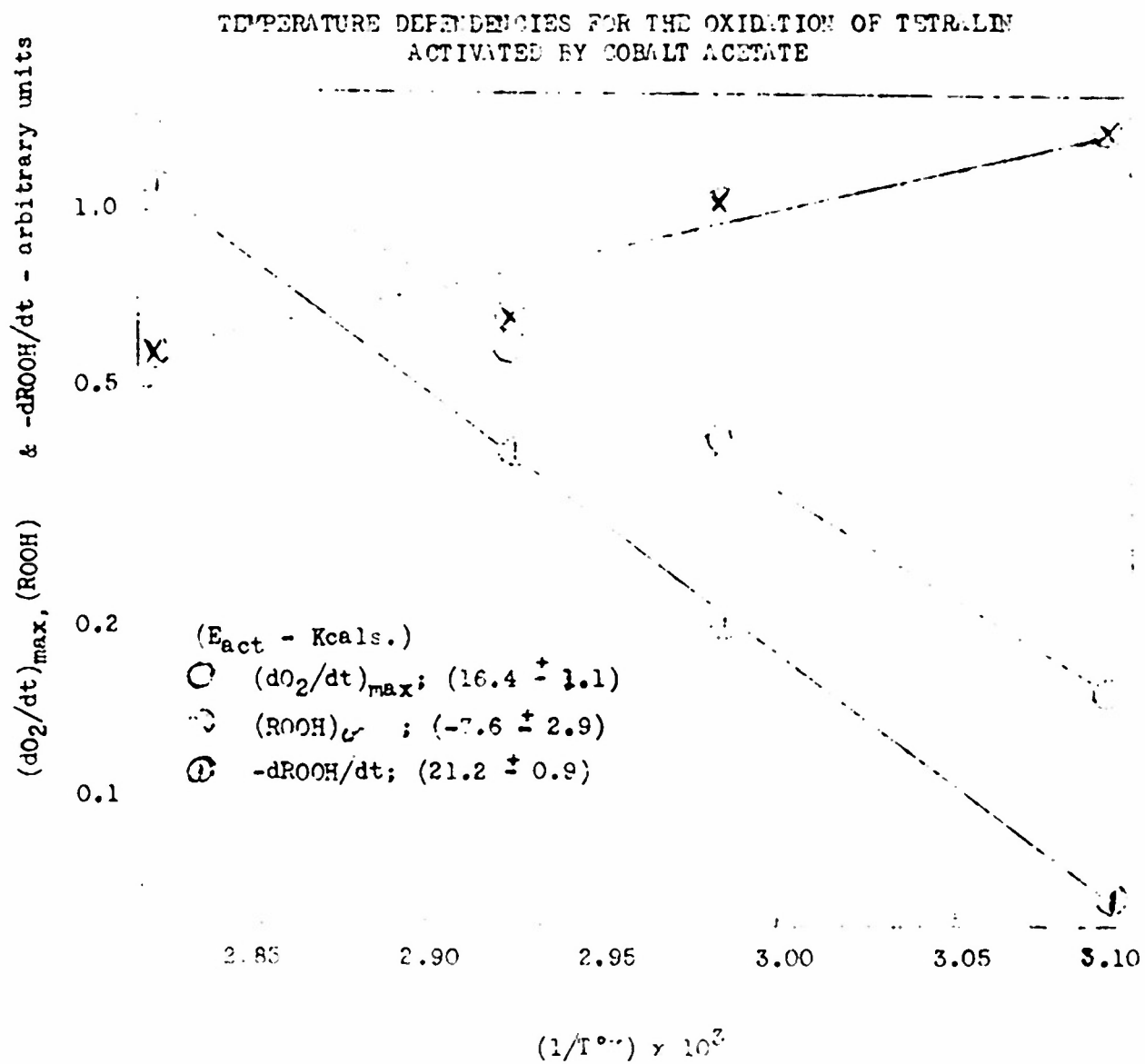


Figure 22.

DECOMPOSITION OF ROOH ACTIVATED BY
COBALT ACETATE AT VARIOUS TEMPERATURES

($\text{ROOH}_0 = 0.04$, $\text{CoAc}_2 = 0.002$ m/l in HAc)

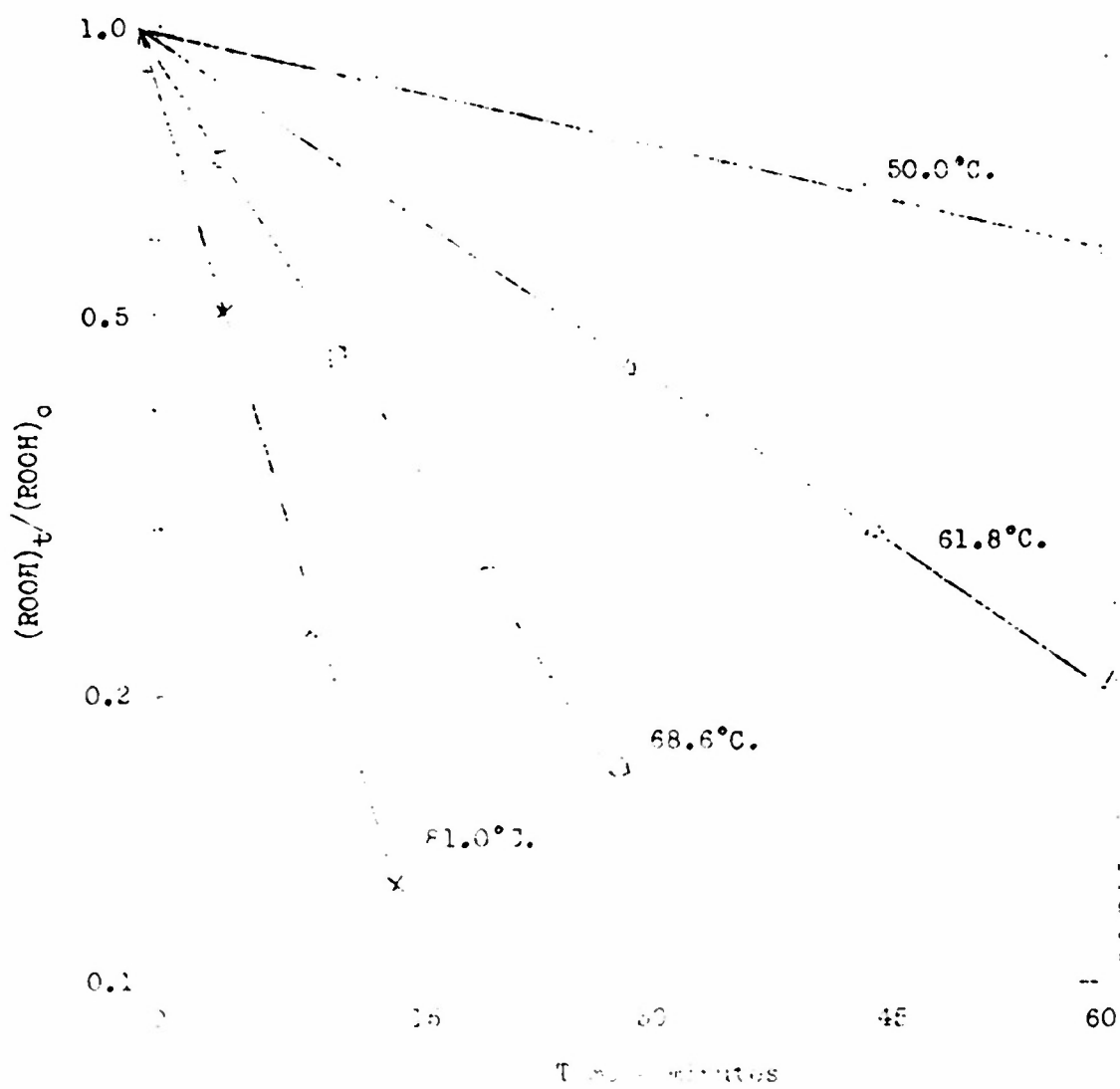


Figure 23

AUTOXIDATION OF TETRALIN

$\log [\text{ROOH}]_x$ vs. $1/T^\circ\text{K.}$

(Conc. RH = 0.345 m/l in Diphenyl)

