THE KINETICS OF OXIDATION OF CYCLOHEXENE IN THE LIQUID PHASE

DISSERTATION

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By

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INTRODUCTION

Up to the present time there has not been reported in the literature a complete consistent picture about the kinetics of oxidation of hydrocarbon compounds.

In this present research it was intended to investigate intensively the kinetics of a hydrocarbon compound and study it with regard to a host of variables.

Cyclohexene was picked due to its rapid rate of oxidation, so that individual runs need not be of too long duration.
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LITERATURE REVIEW

Recent chemical researches in the field of hydrocarbon oxidations have demonstrated that hydroperoxides appear as one of the first products of oxidation\(^{(1-4)}\).

Kinetic studies have shown that subsequent oxidation of the parent hydrocarbon is autocatalyzed by the decomposition of the hydroperoxides which produces radical chain carriers for the chain reaction\(^{(5-9)}\).

The chain reaction leads to the formation of secondary oxidation products such as ketones, aldehydes, acids, alcohols, water, carbon dioxide, etc.\(^{(7-9)}\).

In 1941\(^{(10)}\) it was reported that slow oxidation at 25°C and ordinary pressure of the following hydrocarbons containing double bonds was investigated:
- 3-pentene, cyclohexene, 2-methyl, 2-pentene. After an initial decrease, the pressure falls rapidly and stops at a constant final value.

In 1942\(^{(11)}\) L. Boescken and C. A. Hanegraaff using the Arrhenius-Schaeffer equation

\[
\log K = -\left(\frac{E}{2.3 RT}\right) + B,
\]

found for cyclohexene 129, 15,600 Kcals and 10.4 for K, E and B. The value for K
is at 25.8°C. E is related to ring tension; B, tendency to oxidize.

Hock(12) observed that cyclohexene which has stood for some time (peroxide present) was oxidized much more rapidly than when freshly distilled.
Since the same experimental procedure was followed in the study of the oxidation of cyclohexene in both pyrex and teflon containers, therefore it is more appropriate to start with the experimental procedure and then take up the various systems which were employed in this research for the kinetic studies of the oxidation of cyclohexene.
EXPERIMENTAL PROCEDURES

I. Preparation of the reaction cells:

The experiments were carried out in oxidation cells made from 125 ml. pyrex extraction flasks, fitted at the top with a ground glass joint, connected to a three-way stop cock. One arm of the stop cock was connected to a mercury manometer and the other arm was left open for charging the cell at the start of the reaction (Figure 1).

The flasks were cleaned by filling with cleaning solution for 24 hours, then washed repeatedly with hot water and detergent and then in hot water alone. After repeated washing with distilled water, the operation was ended by an acetone wash.

The upper joint with the three-way 2 mm. capillary stop cock attached to it and the manometer were cleaned in the same fashion by filling with cleaning solution. Great care was taken in cleaning these manometers since the mercury would stick to the walls of the glass and thus no accurate measurement of the pressure changes could be recorded. The rest of the operation of cleaning the top joints was the same as for the flasks.
Diagram of a typical oxidation cell.

FIG. 1
Runs were carried out in pyrex alone and in cylinders made of teflon, placed inside the pyrex cells (Figure 1).

The two components of the oxidation cells, the flask and the upper joints, had their volumes determined separately. The flask with the outer joint \( \frac{34}{45} \) was filled with distilled water at \( 25^\circ C \), up to the bottom mark where the upper joint would fit the lower joint. The same was done with the other half of the cell with the teflon cylinder inside. The net volume of the air space was calculated by subtracting the volume of the hydrocarbon used for a specific run. Then they were washed with acetone and placed in the oven at \( 125^\circ C \) for a period of 24 hours.

When taken out of the oven the cells were left to cool down, the manometers filled with mercury and wrapped around with chromel wire \#22.

Then the upper joint was greased, as well as the three-way stop cock, with high pressure silicone grease.
II. Preparation of cyclohexene:

Cyclohexene used was a research grade of 99.9% purity--Phillips Petroleum Co., Bartlesville, Oklahoma. Cyclohexene was passed through a silica gel column to remove peroxides or hydroperoxides, and then put in small ampules of 5 ml. size. The ampules were washed with soap and water and then distilled water, and finally in acetone, then left in the oven at 125°C for 24 hours.

Upon taking the ampules out of the oven, a clean tube leading from a nitrogen tank (oil-pumped) brought in a stream of nitrogen.

Upon cooling, the cyclohexene was put in these 5 ml. pyrex ampules, which were then flushed with nitrogen, sealed at the top with a torch and kept aside for experimental purposes.

The cyclohexene hydrocarbon was measured with 1 ml. pipettes graduated in 0.1 and 0.01 of a milliliter.

III. The constant temperature baths:

The reaction baths were made out of five-gallon glass jars about 24 cm. in height and 28 cm. in diameter. No attempt was made to insulate the baths. The temperatures of the baths were controlled by a thermo-
regulator, holding 1-2 pounds of mercury, which operated a Thyatron unit. For the lower temperatures, cold water was circulated through copper cooling coils in the baths by a centrifugal pump—Mod. 13M 12F, 60 cycle, 1550 r.p.m., 95 watts (Universal Electric Co., Michigan, U.S.)

(a) To control the temperature at 10°C, the open end of the pump was placed in an ice water reservoir. The water was forced through a nozzle in the pump to the copper coils in the water reaction bath. Enough copper coils were put in the reaction bath so that when the contact was made in the thermoregulator to start the pump, the temperature of the bath would change, but by little—a few hundredths of a degree. The thermoregulator was placed next to the copper coils. The pump usually had to operate for 10-20 seconds before the thermoregulator responded to this small change in temperature.

(b) With the reactions carried out at 15°C, again the water bath was controlled with a Thyatron unit and the open end of the pump described above was placed in a Dewar flask and a large number of copper coils were placed in the ice water bath running through three copper coils in the reaction bath, so the pump was
drawing water from the Dewar flask through 25 feet of copper coils placed in the ice water reservoir through the three copper coils of 5-inch diameter in the reaction bath. This was intended to prevent any severe change in the temperature of the bath right at the moment the contact was made in the thermoregulator.

(c) The temperature of 30°C was hard to control since it was in the neighborhood of the room temperature; even though a heater and cooling coils (copper) were installed, still the temperature could not be controlled better than ± 0.1°C.

The heater, copper cooling coil of one loop of 5-inch radius, thermoregulator and the stirrer were all placed in one spot in the bath.

(d) At 40°C, the heating unit was a 500-watt tubular heater. No cooling coils were installed. The temperature control was good. The best control was obtained whenever the difference between the temperature of the bath and the outside temperature was of the order of 10-7°C.

(e) At 55°C, water had still to be used as bath liquid, since mineral oil was too viscous to be used instead and quick temperature transfer was required for good control of the temperature bath.
Therefore the following scheme was devised:

The heater unit (250 watts) of the 15°C bath, connected to the Thyatron unit, was put in the 55°C bath adjacent to it. Then the Thyatron unit controlling the temperature of bath 55°C had another blade heater of 250 watts placed in the 55°C bath. When the room temperature would rise, then the pump had to be activated more to circulate water through the bath at 15°C, so the blade heater in the 55°C was enough to supply heat for the 55°C bath. When the room temperature came down, the pump operated less, so the Thyatron tube fired and more heat was supplied through the second blade heater and thus the temperature was controlled.

IV. Operation procedure:

After getting the oxidation cells calibrated, washed and dried in the oven as described earlier, the second step was to take them out and let them cool. Then the capillary manometers were filled with mercury by means of a rubber tube attached to the open end of the manometer, the mercury being poured in the tubing. The three-way 2 mm. capillary stop cock would be opened slightly to allow through the manometer the necessary amount of mercury.
(1) Heating unit on the manometers: 

The manometers were wrapped by means of chromel wire #22, with 1 to 2 turns per centimeter of length, so that a certain voltage could be applied to keep the liquid hydrocarbon in the cells from distilling out into the manometers. For the 30°C temperature bath, 6-8 volts were applied at the terminals of the resistance wire. When two cells were used and their wire resistances connected in series, 10-12 volts were applied. When the resistances of three manometers were connected in series 15-18 volts were applied and so on up the line. The maximum number of oxidation cells that were put in one bath at a time was five. 

At 40°C the following voltages were applied to the manometers:

1. For one resistance wire, 8 volts  
2. " two "  " , 14 volts  
3. " three "  " , 18 volts  

The same procedure was followed for the manometers of the cells at 55°C as for 40°C, except that the voltages applied were 3-4 volts higher than those at 40°C.

(2) Starting the reaction: 

After filling the capillary manometers with mercury and wrapping them with resistance wire, the inner joint was greased and the stop cock plug. Then the hydrocarbon volume was measured with a volumetric pipette
of 1 ml. capacity, calibrated in 0.1 ml. and 0.01 ml.

The volumes had to be measured quickly. On the whole it took 12-15 seconds to measure the volume of the hydrocarbon into the teflon cylinder and put on the top joint, which had been greased with high pressure silicone stop cock grease (Dow Corning Co.)

Then rubber bands were stretched out around the "glass ears" on the top and bottom joints, and the cell charged with oxygen in the following manner:

A rubber tube brought in a stream of oxygen from an oxygen tank equipped with a reduction valve, where a pressure of 12-16 cm. was applied and the rubber tube was connected to the open end of the three-way stop cock. Then the stop cock was turned in such a way as to make connection between the inside between the inside cell, the manometer and the outside to let in the stream of oxygen. As soon as the pressure stopped rising in the manometer, the stop cock was turned to shut off the outside and thus it automatically connected the inside of the cell and the manometer.

Rubber bands were then applied around the "ears" of the stop cock to hold it firmly. Then it was placed in the bath and held firmly by means of a clamp tightened around a rubber stopper fitted at the end of the
stem of the three-way capillary stop cock.

The cells in the bath were numbered with red lead pencil and each cell with its number contained a known number of millimols of cyclohexene or a certain concentration of cyclohexene in benzene, depending on the run and its nature.

V. Placement of the cells inside the bath:

The following conditions are required for carrying out a successful oxidation reaction:

1. The cells should be placed as far away from the heater or the copper cooling coils so that no distillation of the hydrocarbon from the teflon cylinder onto the pyrex walls of the oxidation cell occurs.

2. The cells should be at least 2-4 cm. away from the bottom of the bath, as well as from the side wall of the bath, so that a good stream of water always passes between the cells and the walls.

3. The cells should be held away from the walls of the thermostat by vertical glass rods enclosed inside rubber tubes and the upper ends of these rods pulled over the edge of the thermostat by means of rubber bands, as shown in Figure 25 in Chapter III. The lower ends of these rods then exerted a pressure against the cells in the form of a vault-like structure
lying next to another cell. The cells had the formation of an arc inside the bath, keeping in mind that condition (2) must be satisfied.

VI. Problems encountered in these experiments:

1. The cyclohexene could distill on the walls of the oxidation cell and that can cause an increase in the reaction rate.

2. The cell can leak, especially when the cyclohexene is diluted with benzene. The following are the symptoms for detecting leaks:

   (1)Leaks could be due to small pinpoint holes in the cell. So before the start of the reaction the cell should be tested with a Tesla coil.

   (2)Leaks along the stop cock; these could be detected by (a) small fine lines or striations along the core of the stop cock; (b) liquid could be observed in the capillary of the three-way stop cock leading to the outside, and usually the liquid condenses in the capillary if the outer atmosphere is at a lower temperature than the temperature of the bath; (c) every time a reaction was started the stop cock as well as the branches leading from it are thoroughly cleaned before the start of the reaction, so it happened in a
number of instances that the cyclohexene or both the cyclohexene and the benzene might wash off the grease and evaporate completely from the capillary, leaving a white coating of grease along the capillary connecting the three-way stop cock with the atmosphere.

(3) A drop in pressure which is not due to the actual absorption of oxygen by cyclohexene could be due to the water evaporating from the bath and exposing a part of the joint of the cell, and that can cause the vapor of cyclohexene to condense on the walls of the top joint and thus cause rapid increase in rate. The level of the water should be rigidly controlled.

VII. Controlling the height of the water in the bath:

This was achieved by the following method:

A five-gallon jar of distilled water was placed at a five feet higher altitude than the level of the water bath and water siphoned out to a rubber tube that had a pinch clamp by which a certain number of drops of water per minute can drop into the bath, depending on the temperature of the bath. A glass tube was placed at a certain level at which the cells would be under the level of the water till part of the stop cocks are covered. When the water levels got higher
by the dropping of the water from the rubber tube, the glass tube, which is connected to a water suction pump, takes off water and keeps the level of the water constant.

VIII. **Method for computing the amount of oxygen absorbed:**

The amount of oxygen absorbed was computed from changes in pressure, as follows:

If $h_1$ and $p_1$ are the height of the mercury manometer and the atmospheric pressure respectively, in cms. of mercury at time $t_1$,

If $h_2$ and $p_2$ are the height of the mercury manometer and the atmospheric pressure respectively at $t_2$,

If $V$ is the free gas space in the oxidation cell,

Then the amount of oxygen absorbed in millimols ($QO_2$) is:

$$QO_2 = \frac{(h_1 + p_1) - (h_2 + p_2) \times V \times 273 \times 1000}{T \times 22,412 \times 76}$$

The initial partial pressure of oxygen used varied from 15-22 cm. of Hg. This was computed from the equation

Charge of $O_2$ in cm. Hg. $\times \frac{T_1}{T_2} = \text{partial pressure of } O_2$
The ratio of $O_2/N_2$ for uncharged and charged cells is given by,

a) uncharged cell

$$O_2 = \frac{76 \times \frac{1}{5}}{76} = \frac{1}{5} = 0.21 \text{ or } 21\% \ O_2$$

ratio 21/79

b) charged with 10 cm. of $O_2$

$$\frac{(76)(\frac{1}{5}) + 10}{76 + 10} = \frac{10.4}{86} = 0.34 \text{ or } 34\% \ O_2$$

ratio 34/66

c) charged with 15 cm. of $O_2$

$$\frac{(76)(\frac{1}{5}) + 15}{76 + 15} = \frac{16.4}{91} = 0.33 \text{ or } 33\% \ O_2$$

ratio 33/67

Thus the ratio of $O_2/N_2$ was approx. 35:65.

IX. Titration of hydroperoxides or peroxides:

Since the hydrocarbon available had been under storage for an appreciable time, it contained some peroxide or hydroperoxide. The peroxide number (P.N. = milli equivalents of peroxide per liter) was determined before each experiment by the iodine titration method of H. A. Liebhafsky and W. H. Sharkey, J. Am. Chem. Soc., 62, 190 (1940), as modified by Winter memorandum of P. K. Winter, Organic Chemistry Dept., General Motors Res. Dept., August 6, 1941.
CHAPTER I

OXIDATION OF CYCLOHEXENE IN PYREX CONTAINERS

The first system that was adopted to study the kinetics of oxidation of cyclohexene was the pyrex system.

Experimental procedure:

As described before, the experiments were carried out in oxidation cells made from 125 ml. pyrex extraction flasks, each fitted at the top with a ground glass joint leading to an open-end mercury manometer and to a stop cock for introducing oxygen. The ground glass joint was firmly attached to the flask by means of rubber bands, and the stop cock was held firmly by a screw safety clamp. Silicone grease was used as lubricant.

The flasks were cleaned by filling with cleaning solution and leaving for 48 hours, then washing repeatedly with hot water and soap and finally in a running stream of hot water for several minutes. They were then rinsed with distilled water, then with acetone,
and dried overnight in an oven at 100-120°C.

The volume of each flask was determined by measuring the volume of water required to fill it. The volume of top ground glass joint was determined in the same way.

All experiments were carried out at 37°C, using a water-filled thermostat. 10 ml. of cyclohexene (98.6 millimols) was used except as specified below.

Results and data:

1. Reproducibility. Two nearly identical reaction flasks were used, and two samples of cyclohexene of the same peroxide number were placed in the thermostat at the same time. The curves for oxygen uptake as a function of time are plotted in Figure 2. The lack of reproducibility shown, together with experience gained in later experiments, indicated that pyrex was not too satisfactory for the kinetic studies of the oxidation of cyclohexene.

2. To investigate the effect of changing the area of the reaction flask exposed to reaction mixture, pyrex beads were introduced into the flask, (a) so that they were completely submerged and (b) so that they
Two experiments with 10 ml of cyclohexene (986 millimols). $PN = 1900$ to test reproducibility.
FIGURE 3

(I) 60 pyrex beads (73.74 cm\(^2\) in surface area) are suspended above the liquid.

(II) 30 pyrex beads (36.87 cm\(^2\) in surface area) are completely submerged under the surface of the liquid.

(III) 60 pyrex beads (73.74 cm\(^2\) in surface area) are introduced so that many of them are halfway submerged.
were completely in the vapor phase (hanging in a perforated pyrex basket). The results of these two experiments are shown on Curves I and II of Figure 3. It is evident that the rates of oxygen uptake are not exactly the same, indicating that pyrex may not be safely used as the material for the reaction vessel.

In other experiments, pyrex beads were so introduced that many of them were half-submerged in the liquid. The results of one of these experiments are shown also in Figure 3 (Curve III). It is evident that the rate of oxygen uptake in the early part of the reaction is markedly increased. This is probably to be explained as a "creep" of hydrocarbon over the surface of the beads, thus exposing more liquid surface to absorption of oxygen, with a consequent increase in rate, and thus another indication of the catalytic effect exerted by the glass surface.

3. To determine the effect of stirring, a reaction flask was equipped with a small glass-encased magnet, which could be turned by a rotating magnet below the thermostat. The rate of oxygen absorption by 25 ml. of 4-methylcyclohexene (P.N. - 1) in this flask was compared with a similar quantity in a flask without a stirrer. At 970 r.p.m. the absorption rate
in the stirred liquid was 1.5 times that in the un-
stirred liquid; at 1850 r.p.m. it was 2.1 times greater. Further increase in stirring rate had no effect on the rate of oxygen uptake. The speed of stirring was determined by direct observation of the rotating magnet, using a stroboscope.

4. Chemical analysis of an old, viscous sample of partially oxidized cyclohexene, by Dr. Earl Malmberg, has shown the existence of carbonyl compounds, about 60% of the total being identified as 2,3-cyclohexene-
1-one. An ultraviolet absorption spectrum showed a strong band at 228 μm. This is close to the 234 μm band of allyl alcohol, and perhaps indicates the presence of 2,3-cyclohexene-1-ol. It is reported in the literature, however, that 2,3-cyclohexene-1-one has an absorption band at 225 μm, and the identification of the 228 μm band as an allylic alcohol type may be incorrect. 2,3-cyclohexene-1-ol and 2,3-cyclohexene-
1-one are the expected products for the oxidation, according to the following reaction scheme (reactions 4 and 2):
\[
\text{C}_{\text{H}} + \text{O}_2 \rightarrow \text{C}_{\text{O}} - \text{H} 
\]

(1)

\[
\text{C}_{\text{O}} - \text{O} - \text{H} \rightarrow \text{C}_{\text{O}} + \text{H}_2 \text{O} 
\]

(2)

\[
\text{C}_{\text{O}} - \text{O} - \text{H} \rightarrow \text{C}_{\text{O}} + . \text{OH} 
\]

(3)

\[
\text{C}_{\text{O}} + \text{C}_{\text{H}_2} \rightarrow \text{C}_{\text{OH}} + \text{C}_{\text{H}} 
\]

(4)

\[
\text{C}_{\text{H}} + \text{O}_2 \rightarrow \text{C}_{\text{O} - \text{O}}. 
\]

(5)

\[
\text{C}_{\text{H}} + \text{C}_{\text{O} - \text{O}} \rightarrow \text{C}_{\text{H}} + \text{C}_{\text{O} - \text{O} - \text{H}} 
\]

(6)

\[
\text{C}_{\text{H}} + . \text{OH} \rightarrow \text{C}_{\text{H}} + \text{H}_2 \text{O} 
\]

(7)
The free hydrocarbon radical formed in reactions (6) and (7) may continue the chain by reactions (5) and (6); the hydroperoxide formed in (6) may decompose by (2) or continue the oxidation chain by (3), (4) and (7). Many additional reactions are possible, since the possibility of removal of hydrogen atoms from other positions on the ring cannot be excluded.

The hydroperoxide formed by reactions (1) and (6) is relatively stable, as shown by the fact that the peroxide number of the stock hydrocarbon used steadily builds up as the bottle is repeatedly opened for removal of samples.

Material balance on the amount of oxygen taken up shows that further reaction of the hydroperoxide occurs. In an experiment the amount of hydroperoxide present after uptake of 56.1 millimols of oxygen was 28 millimols; whereas if all the oxygen had remained as hydroperoxide as the final product 56.1 millimols of hydroperoxide would have been found. In a similar experiment in which glass beads were present, partly submerged, the uptake of 95.0 millimols of oxygen produced 58.5 millimols of hydroperoxide.

Cyclohexene hydroperoxide has been prepared by Criegee, Pilz and Flygare (14) by exposing cyclohexene
and oxygen to ultraviolet light, at 37°C. The yield obtained after 14 hours exposure to light, followed by 10 hours in the dark, was 79% on the basis of the oxygen absorbed. Reactions of the material (b.p. 51° at 0.3 mm.) showed it to have the structure (a) rather than (b). The hydroperoxide could not be preserved in a pure state at room temperature, even in a quartz vessel.

\[
\begin{align*}
(a) & \quad \text{H} - \text{O} - \text{O} - \text{H} \\
(b) & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

5. Increase of cyclohexene hydroperoxide concentration increases the rate of oxygen absorption. This is shown, for example, in Figures 4 and 5 when hydroperoxide is added.

If t-butylisopropylbenzene hydroperoxide is added, there is an initial very rapid reaction, the effect of which quickly disappears, and leaves the reaction proceeding at a slower than normal rate, as shown in Figures 4 and 5. Both these effects are intensified when the glass surface exposed to the liquid is increased. Subsequent addition of the aromatic hydroperoxide has no effect on the rate, although addition of the aliphatic hydroperoxide 1,1,2,2-tetramethylpropyl
FIGURE 4

10 ml. of cyclohexene with P.N. = 20.15
1 ml. of t-butyl isopropyl benzene hydroperoxide

\[ \text{C} - \text{C} = \text{C} - \text{C} - \text{O}_2\text{H} \]

was added at the start of the run.

30 pyrex beads are completely covered by the liquid hydrocarbon.

Again 1 ml. of aromatic peroxide added

As 1 ml. of t-butyl isopropyl benzene hydroperoxide is added, the rate of reaction is large, but subsequent addition produces no effect.
10 ml of cyclohexene PN = 2015

0.009 mol of \((\text{CH}_3)_3\text{C}-\text{C}-\text{O}_2\text{H}\)
added

1 ml of t-butylisopropyl benzene hydroperoxide
added

Time in Hours

Millimols of O\(_2\) Absorbed
hydroperoxide caused a further increase in rate. It is possible that decomposition or reaction of the aromatic hydroperoxide forms an inhibitor which prevents further oxidation. If this inhibitor is assumed to be partially removed by reaction with the aliphatic hydroperoxide, the observed results are readily explained.

The main factor that rendered the pyrex system a futile operation is the surface effects as demonstrated in Figure 3, Curve III, when the beads were half-way submerged.

That means if the amounts of cyclohexene were to vary from 1-20 millimols, for example, the rate would not be proportional to the amounts of cyclohexene, because with various amounts of hydrocarbon the surface area of pyrex to hydrocarbon would change. Actual experiments have indicated that the smaller the amounts of cyclohexene, the greater is the oxidation rate (Appendix A).

So a new system had to be used, and as it turned out, teflon cylinders were the answer to this problem as well as to others.
CHAPTER II

KINETICS OF OXIDATION OF CYCLOHEXENE
IN TEFLOM CYLINDERS

A. Oxidation of cyclohexene without being diluted with an aromatic solvent.

B. Oxidation of cyclohexene in benzene solutions.

Introduction:

The oxidation of cyclohexene in teflon cylinders placed within pyrex cells (Figure 1) is a straightforward operation. Teflon does not exert surface effects. This was a big advantage over pyrex. As it will be shown later, runs could be duplicated easily within the experimental error.

Kinetics of oxidation of cyclohexene without dilution:

The oxidation of cyclohexene has two phases: (a) the induction phase; (b) the after-induction period phase or the steady state phase.

These two phases are shown on Figures 6 and 7, which give a plot of oxygen absorbed against time for two different amounts of cyclohexene at 30°C. It will
FIG. 6

End of the induction period

Oxidation of ...
Oxidation of 8.65 millimols of cyclohexene at 30°C.

Slope = 6.0 x 10^{-3} millimols of O_2/hr.
in the steady state.

End of the induction period.
Oxidation of 13.77 millimols of cyclohexene at 30°C.

Slope = 10.18 x 10^{-3} millimols of O₂/hr.

in the steady state.

End of the induction period
be noticed that the oxidation curve goes through an induction period and then breaks to give a straight line which we shall call the steady state.

The induction period in the oxidation of cyclohexene:

The following factors were investigated with regard to the induction period:

2. The fate of the oxygen absorbed in the induction period.
3. The total amount of oxygen absorbed up to the end of the induction period as a function of the number of millimols of cyclohexene.
4. Dependence of the length of the induction period on the concentration of cyclohexene hydroperoxide.

Since these factors have been investigated at various temperatures, and not all of them have been investigated at one temperature, therefore these factors will be discussed in the order mentioned above.

If the kinetics of the induction period is considered, it will be noticed that if a plot is made of the logarithm of the amount of oxygen absorbed against time (Table I), a linear relationship is obtained, as
Table I

OXYGEN ABSORBED AS A FUNCTION OF TIME
FOR 8.85 MILLIMOLS OF CYCLOHEXENE AT 30°C

<table>
<thead>
<tr>
<th>Number of Hours elapsed</th>
<th>Total Number of Hours Elapsed</th>
<th>Atm.Press. in cms.</th>
<th>Reading of Manometer in cms. of Hg.</th>
<th>Amount of O₂ Used in cms. of Hg. in the Time Interval of Column 1</th>
<th>Millimols of O₂ Used Between Readings</th>
<th>Total Millimols of O₂ Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>74.2</td>
<td>24.06</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>13</td>
<td>74.5</td>
<td>24.08</td>
<td>-0.32</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>23</td>
<td>36</td>
<td>74.6</td>
<td>24.4</td>
<td>-0.42</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>23:45'</td>
<td>23:45'</td>
<td>74.5</td>
<td>23.58</td>
<td>0.92</td>
<td>0.0749</td>
<td>0.0749</td>
</tr>
<tr>
<td>29</td>
<td>52:45'</td>
<td>74.22</td>
<td>23.05</td>
<td>0.81</td>
<td>0.3658</td>
<td>0.1407</td>
</tr>
<tr>
<td>25:30'</td>
<td>78:15'</td>
<td>73.58</td>
<td>23.29</td>
<td>0.41</td>
<td>0.0388</td>
<td>0.1741</td>
</tr>
<tr>
<td>18</td>
<td>96:15'</td>
<td>74.00</td>
<td>22.03</td>
<td>0.56</td>
<td>0.0455</td>
<td>0.2196</td>
</tr>
<tr>
<td>13</td>
<td>109:15'</td>
<td>73.94</td>
<td>21.73</td>
<td>0.63</td>
<td>0.0512</td>
<td>0.2708</td>
</tr>
<tr>
<td>18:30'</td>
<td>127:45'</td>
<td>73.88</td>
<td>20.62</td>
<td>1.17</td>
<td>0.0951</td>
<td>0.3659</td>
</tr>
<tr>
<td>6:45'</td>
<td>134:30'</td>
<td>74.05</td>
<td>20.00</td>
<td>0.45</td>
<td>0.0366</td>
<td>0.4025</td>
</tr>
<tr>
<td>14:30'</td>
<td>149</td>
<td>74.2</td>
<td>18.8</td>
<td>1.05</td>
<td>0.0855</td>
<td>0.488</td>
</tr>
<tr>
<td>9</td>
<td>158</td>
<td>74.17</td>
<td>18.2</td>
<td>0.63</td>
<td>0.0512</td>
<td>0.5392</td>
</tr>
<tr>
<td>16</td>
<td>174</td>
<td>73.87</td>
<td>17.2</td>
<td>1.30</td>
<td>0.1056</td>
<td>0.6448</td>
</tr>
<tr>
<td>24:30'</td>
<td>198:30'</td>
<td>73.63</td>
<td>15.42</td>
<td>2.02</td>
<td>0.165</td>
<td>0.8108</td>
</tr>
<tr>
<td>18</td>
<td>216:30'</td>
<td>74.6</td>
<td>12.7</td>
<td>1.75</td>
<td>0.1425</td>
<td>0.9533</td>
</tr>
<tr>
<td>11:15'</td>
<td>227:45'</td>
<td>74.61</td>
<td>11.42</td>
<td>1.27</td>
<td>0.1032</td>
<td>1.0565</td>
</tr>
</tbody>
</table>
shown for the amounts of 8.85 and 13.77 millimols of cyclohexene, from the curves of Figure 8, Curves I and II.

If the raw data are considered for 8.85 millimols of cyclohexene as an example, we have Table I, where the net cell volume is 153.2 ml., factor 8.14 x 10^-2 millimols of oxygen per 1 cm. change in pressure. Density is 0.808 at 22-23°C. Volume is 0.9 ml. or 3.35 millimols of cyclohexene, temp. 30°C.

From Table II and Figure 9 it will be noticed that \( \frac{d \log O_2}{dt} \) is directly proportional to the number of millimols of cyclohexene. Or \( \frac{d \log O_2}{dt} = k_1 n + c' \).

\( c' \) when considered at 30°C has the magnitude of 3.4 x 10^-3 and at 40°C the value is of the order of -4.5 x 10^-3. Thus it can be deduced that \( c' \) is zero when \( n = 0 \). Or \( \log O_2 = k_1 n t + \log K_2 \)

at \( t = 0 \), \( \log O_2 = \log K_2 \)

Of course, the above reactions were run in the neighborhood of 3-5 P.N. (milli equivalent of peroxide per liter) values, so the intercept of \( \log O_2 \) against time was not appreciably different.

So three runs were devised in which 9.84 millimols of cyclohexene was taken with various hydroperoxide concentrations of 0.13, 0.184 and 0.25 millimols of
TABLE II

THE LOGARITHMIC RATES IN INDUCTION PERIOD AS A FUNCTION OF MILLIMOLS OF CYCLOHEXENE (Temperature 30°C)

<table>
<thead>
<tr>
<th>( \frac{d \log O_2}{dt} \times 10^3 )</th>
<th>Number of Millimols of Cyclohexene</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.09</td>
<td>8.85</td>
</tr>
<tr>
<td>6.4</td>
<td>9.84</td>
</tr>
<tr>
<td>7.2</td>
<td>11.81</td>
</tr>
<tr>
<td>7.65</td>
<td>13.77</td>
</tr>
<tr>
<td>9.18</td>
<td>19.65</td>
</tr>
<tr>
<td>10.7</td>
<td>24.58</td>
</tr>
<tr>
<td>12.3</td>
<td>29.58</td>
</tr>
</tbody>
</table>

TABLE III

THE INTERCEPT OF LOG \( O_2 \) VS. TIME AT \( t = 0 \) AS A FUNCTION OF THE HYDROPEROXIDE CONCENTRATION PER 9.84 MILLIMOLS OF CYCLOHEXENE AT 40°C

<table>
<thead>
<tr>
<th>Millimols of ( O_2 ) at ( t = 0 ), from Intercept of ( \log O_2 ) against ( t ) (x 10²)</th>
<th>Millimols of Hydroperoxide in 9.84 Millimols of Cyclohexene (x 10²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.</td>
<td>13.</td>
</tr>
<tr>
<td>18.</td>
<td>18.4</td>
</tr>
<tr>
<td>19.5</td>
<td>21.0</td>
</tr>
</tbody>
</table>
$\frac{d\text{ln} \left( \frac{2}{3} \right)}{dt}$ for the induction period against number of millimoles of cyclohexene at 30°C.

slope = $3.0 \times 10^{-2}$

Intercept = $3.4 \times 10^{-3}$ at zero millimoles of cyclohexene
The intercept of log $O_2$ vs. time at 760 millimols of $O_2$, as a function of initial hydroperoxide concentration per 0.65 millimols of cyclohexene, for the oxidation of 0.84 millimols of cyclohex at 40°C.
hydroperoxide per 9.34 millimols of cyclohexene and were allowed to oxidize in the same procedure as described before. The intercept of log \( \text{O}_2 \) against time was determined. The antilogarithm of this value varies with the hydroperoxide concentration, as shown in Table III and Figure 10.

So the intercept of the plot of log \( \text{O}_2 \) against time (when \( t = 0 \)) is a function of the hydroperoxide concentration.

\[
(\text{Oxygen at } t = 0) = S (\text{H.P.O.}) + d. \text{ (Figure 10)}
\]

\( d \) is the concentration of unremovable hydroperoxide. So the equation \( \frac{d \log \text{O}_2}{dt} = k_1 n \) if integrated and rearranged to its final form would be

\[
(\text{O}_2) = K_2 10^{k_1nt}
\]

\( K_2 \) is a function of the hydroperoxide at the start of the reaction.

\( k_1 \) is the slope obtained from \( \frac{d \log \text{O}_2}{dt} \) vs. \( n \) (Figure 9).

\( t \) is expressed in hours.

\( n \) is the number of millimols of cyclohexene.

It will be noticed that \( \frac{d \log \text{O}_2}{dt} \) (Figure 9) was not carried below 3 millimols of cyclohexene. The following factors will account for that:

1. Since the amount of hydroperoxide is constant at the end of the induction period, therefore smaller
amounts of cyclohexene will require less oxygen to end their induction period. Therefore not too many points are obtained to carry an accurate plot of log $O_2$ vs. time.

2. It will take the reaction about 36 hours to reach equilibrium with the temperature of the bath, and thus by the time the actual equilibrium has been reached, not too much time is left to plot an accurate log $O_2$ vs. time curve. Till the end of the induction period, the smaller the amounts of cyclohexene the smaller will be the changes in the manometric readings on the cell and thus there is danger of introducing discrepancies in the calculation of $\frac{d \log O_2}{dt}$ for small amounts of cyclohexene.

It is noticed from Table I that the reaction in the first 36-40 hours shows signs of increase in pressure. This could be explained on the grounds that the reaction has not come to equilibrium with the temperature of the bath. The reason is that cyclohexene within the teflon cell is separated by two walls from the thermostat bath, and teflon is a poor conductor of heat and it is placed within a pyrex cell. So when the cell is put in the thermostat, the cyclohexene starts to warm up and thus its vapor pressure increases and so the increase in the pressure on the manometer of
the cell is indicated.

So even though in other experiments there are no signs of increase in pressure, that does not mean that the pressure is not increasing but that the reaction started fast due to a relatively high hydroperoxide concentration, and the increase in pressure was offset by the quick consumption of oxygen and the net result is a decrease in pressure.

So the above equation which is derived from the plot of log $O_2$ against time will always hold after 36-40 hours from the start of the reaction.

3. The last factor and the most important is the fact that when small amounts are used the induction period rapidly vanishes, due to the quick formation of hydroperoxides and that is due mainly to the large surface exposure of cyclohexene per unit millimols to the atmosphere of oxygen above.

The total amount of oxygen in millimols to the end of the induction period:

The total amount of oxygen absorbed to the end of the induction period is proportional to the number of millimols of cyclohexene used. If we examine Figures 6 and 7, we find that 8.35 millimols of cyclohexene has used about 0.45 millimols of oxygen and 13.77 millimols
of cyclohexene has used 0.68 millimols of oxygen to
the end of the induction period.

So if we consider the following table, that has
been computed as shown above:

TABLE IV

NUMBER OF MILLIMOLS OF OXYGEN ABSORBED
TO END OF INDUCTION PERIOD AS A FUNCTION
OF THE NUMBER OF MILLIMOLS OF CYCLOHEXENE
(Temperature 30°C)

<table>
<thead>
<tr>
<th>Number of Millimols</th>
<th>Millimols of Oxygen Absorbed to the End of Induction Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>of Cyclohexene</td>
<td></td>
</tr>
<tr>
<td>1.968</td>
<td>0.08</td>
</tr>
<tr>
<td>3.94</td>
<td>0.2</td>
</tr>
<tr>
<td>4.92</td>
<td>0.22</td>
</tr>
<tr>
<td>8.85</td>
<td>0.45</td>
</tr>
<tr>
<td>9.34</td>
<td>0.50</td>
</tr>
<tr>
<td>9.34</td>
<td>0.48</td>
</tr>
<tr>
<td>11.81</td>
<td>0.62</td>
</tr>
<tr>
<td>13.77</td>
<td>0.68</td>
</tr>
<tr>
<td>17.72</td>
<td>0.60</td>
</tr>
<tr>
<td>19.7</td>
<td>0.518</td>
</tr>
<tr>
<td>29.52</td>
<td>0.350</td>
</tr>
</tbody>
</table>

These data are plotted in Figure 11. It is evident that up to 14 millimols of cyclohexene, the amount of oxygen absorbed to the end of the induction period is proportional to the amount of hydrocarbon used. If all the oxygen is used in forming hydroperoxide, this means that the hydroperoxide concentration is constant.
Total millimols of oxygen absorbed till end of induction period.
at the end of the induction period.

The ratio of the total amount of oxygen to the end of the induction period to the number of millimols of cyclohexene is 5%. In a close examination of Figure 11, it is found that 8 millimols of cyclohexene has absorbed 0.4 millimols of oxygen to the end of the induction period, or: \( \frac{0.4}{8} = 5\% \) at 30°C.

**Kinetics of the induction period at 40°C:**

As discussed previously, the oxidation of cyclohexene goes through an induction period and then reaches a steady state. At 40°C since the reaction goes fast, then we shall consider larger amounts, from 14-24 millimols of cyclohexene.

The reason larger amounts of cyclohexene are being used is that teflon is a poor conductor of heat, as discussed before; whenever a liquid is put in the teflon cylinder inside the oxidation cell, it takes about 40-48 hours to come close to equilibrium. In principle as well as in theory it should take the liquid hydrocarbon an infinite number of hours to reach equilibrium with the bath temperature. Let us consider two runs whereby benzene was used only. In this instance naturally no oxidation will take place to cause any
decrease in pressure. The two runs were carried out with 1 ml. of benzene put in a teflon cylinder as described before and the cells closed and put in a 30°C temperature.

In Experiment I the reading was started after two hours from the time it was placed in the bath, and in Experiment II the reading was started after 1 1/4 hours from the time it was placed in the bath (see Table V).

Actually the pressure continued to increase up to 40-48 hours, but the reaction would have picked up speed by that time so that the error introduced will be negligible compared to the decrease in pressure or the amount of oxygen absorbed. But when small amounts of cyclohexene are taken into consideration, the amount of oxygen absorbed per unit time will be smaller and thus the discrepancy introduced due to the increase in pressure will be felt more. In order to come around this obstacle, the hydrocarbon should be highly dehydroperoxidized and so by the time the reactions start picking up speed the liquid hydrocarbon would have approached equilibrium with the thermostat and so enough points would be recorded during the induction period that a plot of log \( O_2 \) against time is made possible.

Another point to be considered is this: The total
## TABLE V

**CHANGE IN PRESSURE AS A FUNCTION OF TIME IN HOURS IN BENZENE SYSTEM AT 40°C**

### EXPERIMENT I

<table>
<thead>
<tr>
<th>Number of Hours elapsed Between Readings</th>
<th>Total Number of Hours Elapsed</th>
<th>Atm. Pressure Reading on Manometer</th>
<th>Net Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>74.8</td>
<td>6.71</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>74.26</td>
<td>9.00</td>
</tr>
<tr>
<td>12:30'</td>
<td>16:30'</td>
<td>74.68</td>
<td>9.55</td>
</tr>
<tr>
<td>6</td>
<td>22:30'</td>
<td>74.65</td>
<td>9.65</td>
</tr>
<tr>
<td>22</td>
<td>44:30'</td>
<td>74.92</td>
<td>9.90</td>
</tr>
</tbody>
</table>

### EXPERIMENT II

<table>
<thead>
<tr>
<th>Number of Hours elapsed Between Readings</th>
<th>Total Number of Hours Elapsed</th>
<th>Atm. Pressure Reading on Manometer</th>
<th>Net Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>74.8</td>
<td>6.96</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>74.26</td>
<td>10.65</td>
</tr>
<tr>
<td>12:30'</td>
<td>16:30'</td>
<td>74.68</td>
<td>11.2</td>
</tr>
<tr>
<td>6</td>
<td>22:30'</td>
<td>74.65</td>
<td>11.7</td>
</tr>
<tr>
<td>22</td>
<td>44:30'</td>
<td>74.92</td>
<td>11.65</td>
</tr>
</tbody>
</table>
amount of oxygen absorbed to end of the induction period is proportional to the number of millimols of cyclohexene. Thus the greater the number of millimols of cyclohexene, the more oxygen will be needed to end the induction period, and thus it is easier with more points to determine \( \frac{d \log O_2}{dt} \) for a certain large amount of cyclohexene.

**Experimental procedure:**

Some modification was made in carrying out the reactions at 40°C. Since cyclohexene exerts a greater vapor pressure at 40°C than at 30°C, it was necessary to use an outside mercury bubbler, as shown in Figure 25. This was made out of a capillary glass tubing placed under the mercury level at a fixed height and then through a series of T-shaped pyrex tubes connected together with rubber tubes and joined to the open end of the manometers shown in Figures 1 and 25. The main lead was connected to a T-shaped pyrex tube. One outlet led a fine stream of nitrogen, the second outlet led to capillary glass tube in the mercury bubbler and the third outlet of the T-shaped pyrex tube led to the main line feeding the pressure on the open ends of the manometers of the oxidation cell. If it is assumed that \( h_1 \) is the height of the mercury in the bubbler,
h_2 is the height of the mercury in the manometers of the cells, then the total pressure, in cms. of mercury, is \( h_1 + h_2 \). But since \( h_1 \) is constant, therefore the amount of oxygen absorbed could be calculated from the changes in height of mercury \( (h_2) \) in the manometer of the cell.

At this temperature, the following amounts were used: 13.77, 17.71 and 23.61 millimols of cyclohexene. The raw data are tabulated for 1.4 ml. of cyclohexene (Table VI), density 0.808 at 22°C, and thus 13.77 millimols would be obtained. The factor is \( 7.82 \times 10^{-2} \) millimols of oxygen per 1 cm. change in pressure.

Even though the reading was not started till 8 hours from the start of the reaction we note that the second reading showed 0.3 cms. of mercury increase in pressure on the cell. This increase is simply due to the fact that cyclohexene is separated by two walls from the thermostat bath and thus it takes about 40-48 hours to approach the equilibrium value. 0.3 cms. are approximately 0.03 millimols of oxygen and therefore it could be neglected.

If the data in Table VI are plotted on semi-log paper, the result is shown on Figure 12, Curve I, and
### TABLE VI

**OXYGEN ABSORBED AS A FUNCTION OF TIME**

**FOR 13.77 MILLIMOLS OF CYCLOHEXENE AT 40°C**

<table>
<thead>
<tr>
<th>Number of Hours elapsed Between Readings</th>
<th>Total Number of Hours Elapsed</th>
<th>Atm. Press. in cms. of Mercury</th>
<th>Reading of Manometer in cms. of Mercury</th>
<th>Amount of Oxygen Absorbed in cms. of Mercury</th>
<th>Millimols of Oxygen Absorbed Between Readings</th>
<th>Total Millimols of Oxygen Absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>74.77</td>
<td>27.1</td>
<td>0.10</td>
<td>0.0078</td>
<td>0.0078</td>
</tr>
<tr>
<td>23:45'</td>
<td>23:45'</td>
<td>74.82</td>
<td>26.95</td>
<td>0.32</td>
<td>0.061</td>
<td>0.0938</td>
</tr>
<tr>
<td>6:45'</td>
<td>30:30'</td>
<td>74.83</td>
<td>26.62</td>
<td>0.78</td>
<td>0.0938</td>
<td>0.1211</td>
</tr>
<tr>
<td>11:30'</td>
<td>42</td>
<td>74.86</td>
<td>25.81</td>
<td>0.35</td>
<td>0.0938</td>
<td>0.1211</td>
</tr>
<tr>
<td>7</td>
<td>49</td>
<td>74.71</td>
<td>25.61</td>
<td>0.22</td>
<td>0.0938</td>
<td>0.1211</td>
</tr>
<tr>
<td>8:15'</td>
<td>57:15'</td>
<td>74.7</td>
<td>25.4</td>
<td>0.96</td>
<td>0.1072</td>
<td>0.138</td>
</tr>
<tr>
<td>10</td>
<td>67:15'</td>
<td>74.72</td>
<td>24.42</td>
<td>0.96</td>
<td>0.1072</td>
<td>0.138</td>
</tr>
<tr>
<td>6:15'</td>
<td>73:30'</td>
<td>74.52</td>
<td>24.00</td>
<td>0.62</td>
<td>0.1072</td>
<td>0.138</td>
</tr>
<tr>
<td>8:30'</td>
<td>82</td>
<td>74.49</td>
<td>23.00</td>
<td>1.03</td>
<td>0.1072</td>
<td>0.138</td>
</tr>
<tr>
<td>8:30'</td>
<td>90:30'</td>
<td>74.52</td>
<td>21.75</td>
<td>1.22</td>
<td>0.1072</td>
<td>0.138</td>
</tr>
<tr>
<td>7:30'</td>
<td>98</td>
<td>74.4</td>
<td>20.2</td>
<td>1.67</td>
<td>0.1072</td>
<td>0.138</td>
</tr>
<tr>
<td>5:45'</td>
<td>103:45'</td>
<td>74.4</td>
<td>18.91</td>
<td>1.29</td>
<td>0.1072</td>
<td>0.138</td>
</tr>
<tr>
<td>11:15'</td>
<td>115</td>
<td>74.55</td>
<td>16.3</td>
<td>2.46</td>
<td>0.1072</td>
<td>0.138</td>
</tr>
<tr>
<td>25</td>
<td>140</td>
<td>74.68</td>
<td>10.8</td>
<td>5.37</td>
<td>0.1072</td>
<td>0.138</td>
</tr>
</tbody>
</table>

47
I. 13.77 millimoles of cyclohexene
Slope = $13.9 \times 10^{-3}$

II. 17.71 millimoles of cyclohexene
Slope = $19.35 \times 10^{-3}$

III. 23.61 millimoles of cyclohexene
Slope = $25.5 \times 10^{-3}$

The same hydroperoxide concentration, i.e. 0.905 millimols/9.84 millimols of cyclohexene, for the above runs.

Temp. 40° C
the same operation is carried out for 17.71 and 23.61 millimols of cyclohexene and are represented by Curves II and III of Figure 12.

On close examination of the above figure it is apparent that for Curves II and III for 17.71 and 23.61 millimols of cyclohexene the logarithmic function breaks at 0.4 and 0.245 millimols of oxygen for 17.71 and 23.61 millimols of cyclohexene respectively. This behavior will be taken up later in regard to the apparent end of the induction period.

If \( \frac{d \log O_2}{dt} \) is plotted against \( n \), the number of millimols of cyclohexene (see Table VII), the result is shown on Figure 13.

The intercept of the curve in Figure 13 occurs at \(-4.3 \times 10^{-3}\) when millimols of HC = 0 as referred to previously, thus indicating the correctness of \( \frac{d \log O_2}{dt} = k_1 n \).

**TABLE VII**

THE LOGARITHMIC RATES AT 40°C AS A FUNCTION OF THE NUMBER OF MILLIMOLS OF CYCLOHEXENE

<table>
<thead>
<tr>
<th>Number of Millimols of Cyclohexene</th>
<th>( \frac{d \log O_2}{dt} \times 10^3 )</th>
<th>Conc. of Hydroperoxide in Millimols per 9.84 Millimols of Cyclohexene</th>
<th>The Intercept of ( \log O_2 ) vs. Time at ( t = 0 ) in Millimols of ( O_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.77</td>
<td>13.9</td>
<td>0.005</td>
<td>0.025</td>
</tr>
<tr>
<td>17.71</td>
<td>18.7</td>
<td>0.005</td>
<td>0.0195</td>
</tr>
<tr>
<td>23.61</td>
<td>25.5</td>
<td>0.005</td>
<td>0.0125</td>
</tr>
</tbody>
</table>
$\frac{d \log \text{O}_2}{dt}$ vs. number of cyclehexene period at 40$^\circ$C.

Slope $= 12$

Intercept for this at $-4.3 \times 10^{-3}$ when millimoles HC = 0.

FIG. 13
\[ \frac{d \log O_2}{dt} \text{ vs. number of millimols of cyclohexene in the induction period at } 46^\circ C. \]

Slope = $15.8 \times 10^{-4}$

Intercept for this curve occurs at $-4.3 \times 10^{-3}$ when millimols HO = 0.
The total amount of oxygen absorbed to the end of the induction period at 40°C:

In the same fashion, if the total amount of oxygen absorbed to the end of the induction period is examined as has been done before, the following table will be obtained:

**TABLE VIII**

MILLIMOLS OF OXYGEN ABSORBED TO THE END OF INDUCTION PERIOD AS A FUNCTION OF THE NUMBER OF MILLIMOLS OF CYCLOHEXENE (Temperature 40°C)

<table>
<thead>
<tr>
<th>Number of Millimols of Cyclohexene</th>
<th>Total Millimols of Oxygen Absorbed to End of Induction Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.93</td>
<td>0.32</td>
</tr>
<tr>
<td>5.9</td>
<td>0.5</td>
</tr>
<tr>
<td>7.87</td>
<td>0.7</td>
</tr>
<tr>
<td>13.77</td>
<td>1.2</td>
</tr>
<tr>
<td>17.71</td>
<td>0.4</td>
</tr>
<tr>
<td>23.61</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The data in Table VIII are plotted as shown in Figure 14, and various regions appear.
Millimoles of oxygen absorbed to the end of the induction period vs. millimoles of cyclohexene at 40°C.

FIG. 14
Regions A, B, C in the figures representing total millimols of oxygen absorbed till end of the induction period: (Refer to Figures 11 and 14).

Before discussing these various regions and bringing up the limiting diffusion rate of oxygen in the liquid phase, let us picture the teflon cylinder and increase the amount of cyclohexene from 1-14 millimols. It will be found, and this will be amply discussed under the steady state reaction, that the rate of oxygen uptake will increase as the number of millimols of cyclohexene is increased up to 14 millimols, and then after that the rate of oxygen uptake will level off to a constant value of $12 \times 10^{-3}$ millimols of oxygen per hour at $30^\circ$C (Figure 18). That means there is a limiting diffusion rate.

With this in mind, we will proceed to explain regions A, B and C, in Figures 11 and 14.

Region A represents the amount of oxygen taken up to the actual end of the induction period, since the limiting diffusion rate exceeds the rate of oxygen uptake in the course of the reaction when the number of millimols of cyclohexene used in a reaction does not exceed 14 millimols.

In Region B a decrease is noted in the total
number of millimols of oxygen used to end the induction period. That is due to the fact that the diffusion rate of oxygen becomes the limiting factor. This is noted not only in Figure 14, but also in Figure 12, in which the breaks in Curves II and III occur when the oxidation curves reach a straight line portion, and that means the end of the induction period. Actually, the induction period has not ended as yet, but the rate of oxygen diffusion came to be the rate-determining step.

When one moves along the cyclohexene axis the total amount of oxygen absorbed to the end of the induction period would drop down in an asymptotic fashion along the cyclohexene axis (Figures 11 and 14). Region C is a critical region whereby the slope of the tangent at the end of the induction period should give the rate for the steady state reaction, and that should be equal to the limiting diffusion rate of oxygen per hour. The best example of that is the plot of oxygen absorbed against time for the oxidation curve of 13.77 millimols of cyclohexene at 40°C, whereby it is hard to tell where the induction period ends and the steady state begins.
Various phases in the course of oxidation of cyclohexene, whereby the limiting diffusion rate appears, or its effect could be felt:

(1) In the steady state; that will be taken up later (Figure 18).

(2) In the plot of log $O_2$ against time. Whenever that plot breaks up it means that the straight line portion of the oxidation curve has been reached. If Figure 12 is examined it will be found that the breaks in Curves II and III occur at 0.4 and 0.245 millimols respectively. That marks the apparent end of the induction period. Curve I in the same figure (Figure 12) would be classified as Region C (Figure 14), because if a plot is made of oxygen absorbed against time, it will be very hard to tell where the induction period ends and the steady state begins. Again, a plot of log $O_2$ against time (Curve I, Figure 12) does not break, but holds all the way up till 1.2 millimols of oxygen is used up.

(3) The third place whereby the limiting diffusion rate of oxygen shows its effect is in Figures 11 and 14, i.e. in the total amount of oxygen absorbed to the end of the induction period as a function of the amount of cyclohexene used.
To explain these factors and get them integrated in one concept, the limiting rate of oxygen diffusion is assumed to be equal to \( V_1 \) millimols of oxygen per hour in the liquid phase. At higher amounts of cyclohexene, 14 millimols and above, the limiting diffusion rate steps in. For various amounts of cyclohexene, that limiting rate will cut them off at various places, but all of them go through an induction period whereby the rate starts slow and then picks up speed.

If at \( t_1 \) the rate of oxygen uptake in the induction period is equal to \( V_1 \) (the maximum rate of oxygen diffusion) for \( n_1 \) millimols of cyclohexene, at the time \( t_1 \), the amount of oxygen that has been absorbed by \( n_1 \) millimols of cyclohexene is \( m_1 \) millimols of oxygen.

Let us assume that \( n_2 \) millimols of cyclohexene is taken (where \( n_2 > n_1 > 14 \)); then the limiting diffusion rate will start to operate at \( t_2 \) when the rate of oxygen uptake is equal to \( V_1 \). Then \( m_2 \) millimols of oxygen would have been absorbed by \( n_2 \) millimols of cyclohexene up to \( t_2 \) hours.

Experiments show that for \( n_2 > n_1 > 14 \) at 40°C, then \( m_1 > m_2 \) and \( t_1 > t_2 \). This is true when the limiting diffusion rate is the controlling factor. Let us see how this principle could be applied:
If Figure 12 is examined it will be found that 13.77 millimols of cyclohexene ($n_1$) will break at 1.2 (that is, equal to $m_1$) millimols of oxygen. If the plot is carried outside the boundaries of the graph, log $O_2$ against time breaks at 130-135 hours ($= t_1$).

For 17.71 millimols ($n_2$) of cyclohexene, it will break at 0.4 millimols of oxygen ($m_2$) and that occurs at $t_2 = 72$ hours.

For 23.61 millimols of cyclohexene ($n_3$), it will break at 0.245 millimols of oxygen ($m_3$) and that occurs at $t_3 = 49$ hours.

Therefore the above inequality is verified, i.e.,

$$n_3 > n_2 > n_1, \quad m_1 > m_2 > m_3, \quad \text{and} \quad t_1 > t_2 > t_3.$$  

But still both $m_2$ and $m_3$ have part of their induction period curves under the limiting diffusion rate of oxygen. Since the plot of log $O_2$ against time gives a straight line, any portion of that straight line could be useful and its slope could be determined, as was carried out in Curves II and III in Figure 12. Thus $\frac{d \log O_2}{dt}$ could be determined for large amounts of cyclohexene, i.e. larger than 14 millimols.

But if 80 millimols of cyclohexene is taken up, not enough points are under the limiting diffusion rate of oxygen to carry out an accurate determination of $\frac{d \log O_2}{dt}$. 

The fate of oxygen that is absorbed during the induction period:

The oxygen absorbed during the induction period goes almost completely into the formation of hydroperoxides, if the following table is considered, for 9.84 millimols of cyclohexene used in the oxidation runs:

**TABLE IX**

HYDROPEROXIDE FORMED AS A FUNCTION OF TIME IN HOURS
9.84 MILLIMOLS OF CYCLOHEXENE
USED IN THE OXIDATION REACTION
(Temperature 40°C)

<table>
<thead>
<tr>
<th>Oxygen Absorbed in Millimols from Start of Reaction</th>
<th>H.P.O. Titrated in Millimols</th>
<th>H.P.O. Conc. per 9.84 (H.P.O.)_{t-(H.P.O.)}, Millimols of Cyclohexene at Start of Reaction</th>
<th>Ratio</th>
<th>Time in Hours Elapsed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.541</td>
<td>1.44</td>
<td>0.005</td>
<td>0.935</td>
<td>139</td>
</tr>
<tr>
<td>1.2431</td>
<td>1.38</td>
<td>0.005</td>
<td>1.1</td>
<td>140</td>
</tr>
<tr>
<td>2.0776</td>
<td>2.217</td>
<td>0.0200</td>
<td>1.055</td>
<td>143:30'</td>
</tr>
<tr>
<td>2.045</td>
<td>1.763</td>
<td>0.017</td>
<td>0.855</td>
<td>143:30'</td>
</tr>
<tr>
<td>2.024</td>
<td>2.33</td>
<td>0.014</td>
<td>1.126</td>
<td>143:30'</td>
</tr>
</tbody>
</table>

So, as it can be seen from the above table, near the end of the induction period the ratio \( \frac{\text{H.P.O.}}{\text{O}_2} = 1 \), while length of the induction period is 140-145 hours for the oxidation of 9.84 millimols of cyclohexene of less than 1 P.N. unit.
The length of the induction period as a function of the hydroperoxide concentration:

This has been studied at 40°C in the following manner:

Two samples of cyclohexene were taken, and for simplicity, let us call one A, and the other B.

A was stored in an ampule, after being deperoxided by passing it through a silica gel column. It was opened and titrated for the hydroperoxide concentration and gave 0.07 millimols of hydroperoxide per 9.84 millimols of cyclohexene.

B, the other sample with the high cyclohexene hydroperoxide content, was prepared as follows: 0.3 moles of cyclohexene of 99.9% purity based on melting point determination was put in a 500 ml. round bottom flask to which was sealed a filter stick at two-thirds the distance from its bottom and extending down to 1.5-2 cms. from its bottom. A stream of oxygen from an oxygen tank with a reduction valve was passed through a train of drying tubes containing calcium chloride.

To the 500 ml. round bottom flask was fitted a condenser into a ground glass joint. During the course of the experiment it was made sure that cyclohexene would not get in contact with any silicone grease or
rubber tubing.

The flask was heated with a heating mantle to 40°C, and the oxygen at about 2 bubbles per sec. was passed through for 12 hours, and then left to cool for two hours while oxygen was still passing at the rate mentioned above.

Then a sample was titrated and thus the concentration of cyclohexene hydroperoxide was determined and gave 0.25 millimols of cyclohexene hydroperoxide per 9.84 millimols of cyclohexene for sample B. Several mixtures of samples A and B were made up, and the length of the induction period determined. The results are shown in Table X.

| TABLE X |
|------------------|------------------|------------------|------------------|
| **LENGTH OF INDUCTION PERIOD** | **AS A FUNCTION OF HYDROPEROXIDE** |
| Millimols of Cyclohexene from Sample A | Millimols of Cyclohexene from Sample B | Cyclohexene Hydroperoxide Conc./9.84 Millimols of Cyclohexene | Length of the Induction Period in Hours |
| 6.388 | 2.952 | 0.130 | 50 |
| 4.92 | 4.92 | 0.184 | 40 |
| 2.952 | 6.838 | 0.21 | 37 |
| 0.934 | 8.356 | 0.25 | 30 |
There were two other runs which were carried with 0.05 and 0.008 millimols of cyclohexene hydroperoxide for 9.84 millimols of cyclohexene. They had induction periods of 85 and 120 hours respectively.

The data are plotted as $t'_0$, the length of the induction period, against the $\log(\text{H.P.O.})_{\text{initial}}$ (Figure 15).

$$\log O_2 = k_1 n t + \log(\text{H.P.O.})_{\text{initial}}$$

since this was originally derived on the basis that $\frac{d\log O_2}{dt} = k_1 n$.

$$\log O_2 = k_1 n t + \log \text{constant}.$$ 

The constant is a function of the hydroperoxide concentration (Figure 10).

$$\log O_2 = k_1 n t + \log(\text{H.P.O.})_{\text{initial}}.$$ 

$log O_2$ in the induction period and up to the end of the induction period $= \log(\text{H.P.O.})$. Right at the start of the steady state, $t = t'_0$ and

$$\log O_2 = \log(\text{H.P.O.}) = \log(\text{H.P.O.})_{\text{steady state}}.$$ 

$$t'_0 = \frac{1}{k_1 n} \cdot \log(\text{H.P.O.})_{\text{steady state}} - \frac{1}{k_1 n} \cdot \log(\text{H.P.O.})_{\text{initial}}.$$ 

$$t'_0 = \text{constant} - \text{constant} \times \log(\text{H.P.O.})_{\text{initial}}.$$ 

A test of this relation is the fact that when $\log(\text{H.P.O.})$ is equal to that of the steady state at the start of the reaction, then $t'_0$ should be zero.
Length of the induction period, \( t_1 \) vs. \( \log(\text{H}_2\text{O}_2)_{\text{initial}} \).

\((\text{H}_2\text{O}_2)_{\text{initial}}\) is expressed in millimols of hydroperoxide per 9.84 millimols of cyclohexene.

0.34 millimoles of cyclohexene used in all experiments.

Temp. 40°C.
From the intercept on the log(H.P.O. x 10) axis, the value of the intercept is 0.94. The antilogarithm of this is 0.871 millimols of hydroperoxide, while if total millimols of oxygen absorbed till end of induction period is 0.841 millimols of oxygen for 9.84 millimols of cyclohexene at 40°C (Figure 14) and we know that every molecule of oxygen absorbed in induction period goes in the formation of hydroperoxide, therefore the above relationship is in good agreement with other experimental data.

"Activation energy" for the oxidation of cyclohexene in the induction period phase:

It was found that \( \frac{d \log O_2}{dt} \) was directly proportional to the number of millimols of cyclohexene,

\[
\frac{d \log O_2}{dt} = k_1 n
\]

From the Arrhenius equation

\[
k = C' e^{-A/RT}
\]

So if the slope of \( \frac{d \log O_2}{dt} \) against number of millimols is considered, \( k_1 \) will be obtained.

At 30°C the slope of \( \frac{d \log O_2}{dt} \) vs. \( n \) is 3.04 x 10^{-4}, and at 40°C is 12.8 x 10^{-4}.

Therefore from the above Arrhenius equation it follows that

\[
2 \times 2.3 \log \frac{12.8}{3} = A \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]
Since \( T_1 = 303^\circ K \)

\[
T_2 = 313^\circ K
\]

\[
\frac{1}{103} \cdot \frac{2 \times 2.3 \times 313 \times 303}{10} \cdot \log \frac{12.8}{5.04} = A
\]

\( A = 27.3 \text{ Kcals} \)

Thus the "activation energy" for the oxidation of cyclohexene in the induction period is obtained.
The steady state condition:

Whether one starts with a low cyclohexene hydroperoxide concentration and lets the reaction go through an induction period, or whether one starts with a higher cyclohexene hydroperoxide concentration than that required for the end of the induction period, when the reaction reaches a steady state, the same steady state slope is obtained, i.e. the same oxidation rate for a particular quantity of cyclohexene. In case of the former, the reaction goes slowly through an induction period, and at any time the rate of oxygen uptake is slower than the oxygen uptake in the steady state.

But if the cyclohexene hydroperoxide is greater than that required for the steady state, the rate of oxidation starts fast depending on the concentration of the hydroperoxide, and then drops down to the steady state.

Rates of oxidation of cyclohexene at 15°C:

Again, the oxidation of cyclohexene goes through an induction period and then reaches the steady state. At this temperature not all of the reactions were
started with low cyclohexene concentration; some of them were started with a higher cyclohexene hydroperoxide concentration than the requirement of the induction period.

Since the reactions discussed before in the steady state went through an induction period, therefore a reaction will be discussed here at this temperature where the hydroperoxide concentration was higher than that required for the reaction to reach the steady state at that particular quantity of cyclohexene.

Let us consider 5.9 millimols of cyclohexene (Table XI). The reaction went without an induction period due to high hydroperoxide concentration (Figure 16), i.e. 1.765 millimols per 9.94 millimols of cyclohexene at the start of the reaction.

It will be noticed from Table XI and Figure 16 that the reaction starts fast and then drops down to the steady state. The rate obtained from this reaction shows the same proportionality to the number of millimols of cyclohexene as if the reaction was made to go through an induction period by low hydroperoxide and then left to reach the steady state rate.

If the rates are determined for various amounts of cyclohexene, the result is shown in Table XII. A plot of the data obtained, i.e. rates against number
TABLE XI

OXYGEN ABSORBED AS A FUNCTION OF TIME
FOR 5.9 MILLIMOLS OF CYCLOHEXENE AT 15°C

<table>
<thead>
<tr>
<th>Number of Hours elapsed Between readings</th>
<th>Total Number of Hours Elapsed</th>
<th>Atm. Pres. in cms. of Hg.</th>
<th>Reading on Manometer in cms. of Hg.</th>
<th>Amount of O₂ Used in cms. of Hg.</th>
<th>Millimols of O₂ Used Between Readings</th>
<th>Total Millimols of O₂ Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>74.88</td>
<td>22.61</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13:30'</td>
<td>18:30'</td>
<td>74.3</td>
<td>22.50</td>
<td>0.19</td>
<td>0.0172</td>
<td>0.0172</td>
</tr>
<tr>
<td>21:15'</td>
<td>39:45'</td>
<td>75.00</td>
<td>21.82</td>
<td>0.48</td>
<td>0.0435</td>
<td>0.0635</td>
</tr>
<tr>
<td>49</td>
<td>88:45'</td>
<td>74.72</td>
<td>21.4</td>
<td>0.70</td>
<td>0.0635</td>
<td>0.1242</td>
</tr>
<tr>
<td>72</td>
<td>160:45'</td>
<td>74.4</td>
<td>20.9</td>
<td>0.82</td>
<td>0.0742</td>
<td>0.1934</td>
</tr>
<tr>
<td>36:15'</td>
<td>197</td>
<td>74.48</td>
<td>20.45</td>
<td>0.37</td>
<td>0.0335</td>
<td>0.2319</td>
</tr>
<tr>
<td>34</td>
<td>231</td>
<td>74.35</td>
<td>19.30</td>
<td>1.28</td>
<td>0.1145</td>
<td>0.3464</td>
</tr>
</tbody>
</table>
of millimols of cyclohexene, the result is shown in Figure 17.

TABLE XII

<table>
<thead>
<tr>
<th>Number of Millimols of Cyclohexene</th>
<th>Rate x 10^4</th>
<th>Peroxide Conc. in Millimols of Peroxide per 9.84 Millimols of Cyclohexene</th>
<th>Nature of the Reaction Rate at Start of Induction Period</th>
<th>Length in Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.968</td>
<td>3.03</td>
<td>0.0125</td>
<td>Small induction period.</td>
<td></td>
</tr>
<tr>
<td>3.936</td>
<td>7.5</td>
<td>0.0125</td>
<td>Long induction period.</td>
<td>500</td>
</tr>
<tr>
<td>5.904</td>
<td>11.25</td>
<td>1.765</td>
<td>Fast</td>
<td>zero</td>
</tr>
<tr>
<td>7.872</td>
<td>14.5</td>
<td>1.765</td>
<td>Fast</td>
<td>zero</td>
</tr>
<tr>
<td>11.79</td>
<td>22.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Table XII above we notice the following:

1. With a small amount of cyclohexene, i.e. 1.968 millimols, the induction period was short, and since in the induction period hydroperoxide is being formed, and is a constant, therefore the amount of oxygen absorbed will be small. Therefore the number of hours required to end that induction period will be correspondingly small.

2. When 3.936 millimols of cyclohexene is used, with low hydroperoxide concentration, and considering
Rates in the st.
cyclohexene at
Slope = 1.6

0 and []
carried on

FIG. 17
Rates in the steady state vs. millimols of cyclohexene at 15°C.

Slope = 1.91 x 10^{-4}

O and □ indicate runs carried out at different times.
the fact that at low temperature reactions go slower, then the 500-hours length of the induction period is explained.

3. When the hydroperoxide concentration is large, there is no induction period, and the reaction starts faster than the steady state rate and then drops down to the steady state condition, apparently the excess of hydroperoxide have decomposed, and then it follows this relationship such that the

\[
\frac{\text{H}_2\text{P}_2\text{O}_5 \text{ formed (millimols)}}{\text{Millimols of O}_2 \text{ absorbed}} = K
\]

in the steady state where \( K \) is less than unity and a function of time and other variables, as will be discussed later.

**Steady state rates in the oxidation of cyclohexene at 30°C:**

The steady state is reached at the end of the induction period. If we examine Figures 6 and 7, we find the rates in the steady state are \( 6.6 \times 10^{-3} \) and \( 10.12 \times 10^{-3} \) millimols of oxygen per hour for 8.85 and 13.77 millimols of cyclohexene respectively. So in the same fashion the rates in the steady state for other amounts of cyclohexene as shown in Table XIII have been determined.

If the data are plotted (Figure 18) we get proportional rates of oxidation as we increase the amounts of cyclohexene up till the limit of 14 millimols. Then
the rate of oxygen diffusion gets to be the determining factor, and so we get the same rate approximately for 17.712, 29.52 and 80 millimols of cyclohexene, as shown in Table XIII and Figure 18.

**TABLE XIII**

**RATES IN THE STEADY STATE PAST THE INDUCTION PERIOD**

(Temperature 30°C)

<table>
<thead>
<tr>
<th>Rates x 10³</th>
<th>Millimols of Cyclohexene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.67</td>
<td>1.96</td>
</tr>
<tr>
<td>3.34</td>
<td>3.94</td>
</tr>
<tr>
<td>3.53</td>
<td>4.92</td>
</tr>
<tr>
<td>5.7</td>
<td>7.87</td>
</tr>
<tr>
<td>6.56</td>
<td>8.85</td>
</tr>
<tr>
<td>6.85</td>
<td>9.84</td>
</tr>
<tr>
<td>7.1</td>
<td>9.84</td>
</tr>
<tr>
<td>9.05</td>
<td>11.81</td>
</tr>
<tr>
<td>10.12</td>
<td>13.77</td>
</tr>
<tr>
<td>11.55</td>
<td>17.72</td>
</tr>
<tr>
<td>11.95</td>
<td>19.9</td>
</tr>
<tr>
<td>11.92</td>
<td>29.58</td>
</tr>
<tr>
<td>12.05</td>
<td>78.72</td>
</tr>
</tbody>
</table>

It is shown in Table XIII and from Figure 18 that the limiting diffusion rate is of the order of $12 \times 10^{-3}$ millimols of oxygen per hour. If Figure 18 is compared with Figure 11, an obvious identity will be shown in that the diffusion rate of oxygen is the important factor after 14 millimols of cyclohexene, and in that the break takes place at the same point in both figures.
At 75.72 millimols of cyclohexene,
rate = 12.05 x 10^{-5}

The rate of oxygen diffusion is the important factor in this region.
Rates of oxidation of cyclohexene in the steady state vs. number of millimoles of cyclohexene at 360°C.

slope = -0.736 x 10^{-3}

diamonds and squares indicate runs carried out at different times.
At 78.72 millimols of cyclohexene, the rate is $12.05 \times 10^{-3}$.

The rate of oxygen diffusion is an important factor in this region.
### Table XIV

**Millimols of Oxygen Absorbed as a Function of Time for 7.97 Millimols of Cyclohexene at 40°C**

<table>
<thead>
<tr>
<th>Number of Hours elapsed Between readings</th>
<th>Total Number of Hours Elapsed</th>
<th>Atm. Pres. in cms. of Mercury</th>
<th>Reading of Manometer in cms. of Mercury</th>
<th>Amount of Oxygen Absorbed Between Readings</th>
<th>Millimols of Oxygen Absorbed Between Readings</th>
<th>Total Millimols of Oxygen Absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>74.5</td>
<td>30.2</td>
<td>0.2</td>
<td>0.016</td>
<td>0.016</td>
</tr>
<tr>
<td>7:45'</td>
<td>7:45'</td>
<td>74.3</td>
<td>30.2</td>
<td>0.2</td>
<td>0.141</td>
<td>0.157</td>
</tr>
<tr>
<td>12</td>
<td>19:45'</td>
<td>74.28</td>
<td>28.38</td>
<td>1.74</td>
<td>0.1132</td>
<td>0.168</td>
</tr>
<tr>
<td>13:30'</td>
<td>33:15'</td>
<td>74.22</td>
<td>28.3</td>
<td>0.14</td>
<td>0.125</td>
<td>0.281</td>
</tr>
<tr>
<td>11:15'</td>
<td>44:30'</td>
<td>74.23</td>
<td>26.9</td>
<td>0.39</td>
<td>0.115</td>
<td>0.518</td>
</tr>
<tr>
<td>11:15'</td>
<td>55:45'</td>
<td>74.43</td>
<td>25.18</td>
<td>1.52</td>
<td>0.123</td>
<td>0.403</td>
</tr>
<tr>
<td>11:30'</td>
<td>67:15'</td>
<td>74.69</td>
<td>23.5</td>
<td>1.42</td>
<td>0.115</td>
<td>0.518</td>
</tr>
<tr>
<td>12:30'</td>
<td>79:30'</td>
<td>74.78</td>
<td>21.1</td>
<td>2.31</td>
<td>0.187</td>
<td>0.705</td>
</tr>
<tr>
<td>12</td>
<td>91:45'</td>
<td>74.96</td>
<td>19.1</td>
<td>1.32</td>
<td>0.1472</td>
<td>0.8522</td>
</tr>
<tr>
<td>13</td>
<td>104:45'</td>
<td>74.88</td>
<td>16.61</td>
<td>2.57</td>
<td>0.203</td>
<td>1.0602</td>
</tr>
<tr>
<td>10:30'</td>
<td>115:15'</td>
<td>74.87</td>
<td>14.25</td>
<td>2.37</td>
<td>0.192</td>
<td>1.2522</td>
</tr>
<tr>
<td>14:45'</td>
<td>130</td>
<td>74.72</td>
<td>11.91</td>
<td>2.49</td>
<td>0.202</td>
<td>1.454</td>
</tr>
</tbody>
</table>

---

44
Illinois of oxygen absorbed
Oxidation of 7.87 millimoles of cyclohexene at 40°C.

Slope = $1.3 \times 10^{-2}$ millimoles of $O_2$/hr.

In the steady state.

End of the induction period.
The steady state in the oxidation of cyclohexene at 40°C:

At the end of the induction period, the reaction reaches a steady state. Table XIV and Figure 19 represent the raw data for 0.8 ml. of cyclohexene, density 0.903, or 7.87 millimols of cyclohexene.

In the same fashion the rates for oxidation of cyclohexene in the steady state were determined (Table XV). If these data are plotted, Figure 20 is obtained.

**TABLE XV**

<table>
<thead>
<tr>
<th>Number of Millimols of Cyclohexene</th>
<th>Rates x 10^3 Millimols O_2/hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.968</td>
<td>4.35</td>
</tr>
<tr>
<td>3.936</td>
<td>7.5</td>
</tr>
<tr>
<td>5.904</td>
<td>11.25</td>
</tr>
<tr>
<td>7.87</td>
<td>15</td>
</tr>
<tr>
<td>9.84</td>
<td>19</td>
</tr>
<tr>
<td>9.84</td>
<td>18.6</td>
</tr>
</tbody>
</table>
Rates vs. number of millimols of cyclohexene.

Slope: $1.87 \times 10^{-3}$

Temp. 40°C.

Rates x 10^2

Millimols of cyclohexene
Balance between oxygen and hydroperoxide formed, as determined by titration:

The reaction was carried out in the usual procedure as described earlier. The changes in pressure were recorded and the number of millimols of oxygen computed, and then the reaction is stopped at $t_1$. The cell was opened and the hydroperoxide titrated and thus the number of millimols of hydroperoxide was determined, by the Winter method as described before and by the direct method of titration, which consisted of the following operations:

0.5 ml.-1.0 ml. of cyclohexene was added to a 250 ml. iodine flask containing 5 ml. of glacial acetic acid containing 3 gms. of sodium bicarbonate and then the flask stoppered and left for about 10-15 minutes so that the carbon dioxide would be evolved and chase out oxygen from the liquid phase within the flask.

Then 2-3 ml's. of potassium iodide was added and the flask left in the dark for another 15-20 minutes. The liberated iodine was titrated with 0.1 N thiosulfate solution, and thus the concentration of cyclohexene hydroperoxide was calculated on the basis of millimols of hydroperoxide per 9.84 millimols of cyclohexene.

If the reactions of peroxides with KI are considered,
the following is obtained:

\[2 \text{HOAC} + \text{ROOR}' + 2 \text{KI} \rightarrow \text{ROR}' + \text{H}_2\text{O} + \text{I}_2 + 2 \text{KOAC}.
\]

\[\text{I}_2 + 2 \text{Na}_2 \text{S}_2 \text{O}_3 \rightarrow \text{Na}_2 \text{S}_4 \text{O}_6 + 2 \text{NaI}.
\]

Thus if 9.84 millimols of cyclohexene required \(V_1\) ml. of 0.1 N thiosulfate, then \(\frac{V_1}{2 \times 10} = \) number of millimols of hydroperoxide per 9.84 millimols of cyclohexene.

The last column in Table XVI, labelled "corrected time," was obtained by adding to the measured time the number of hours which would have been required in a run with no added hydroperoxide to reach the starting hydroperoxide concentration. The latter time interval may be determined by comparing the length of the induction period with no added hydroperoxide with that obtained from the relation shown in Figure 15, giving the length of the induction period as a function of initial hydroperoxide concentration. For the first datum of Table XVI, for example, the length of the induction period from Figure 15 is found to be 30 hours. The length of the induction period for several samples with peroxide concentration of the order of \(3 \times 10^{-4}\) millimols per 9.84 millimols cyclohexene was found to be 140-145 hours. Hence we may conclude that \(140 - 30 = 110\) hours would have been necessary to form the initial amount, 0.25 millimols, of hydroperoxide per 9.84 millimols cyclohexene. To reduce all the experiments to
TABLE XVI
HIDROPEROXIDE FORMED AFTER t HOURS FOR 9.84 MILLIMOLS OF CYCLOHEXENE AT 40°C

<table>
<thead>
<tr>
<th>Oxygen absorbed in Millimols</th>
<th>H.P.O. Concentration H.P.O. Concentrated</th>
<th>H.P.O. Conc. in Millimols per 9.84 Millimols of Cyclohexene</th>
<th>Ratio of $(H.P.O.)_t - (H.P.O.)_0 \div O_2$</th>
<th>Time in Hours</th>
<th>Corrected Elapsed Time in Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.549</td>
<td>1.3</td>
<td>0.25</td>
<td>0.68</td>
<td>90</td>
<td>200</td>
</tr>
<tr>
<td>1.7036</td>
<td>1.935</td>
<td>0.210</td>
<td>1.01</td>
<td>118:15'</td>
<td>221</td>
</tr>
<tr>
<td>1.5410</td>
<td>1.44</td>
<td>0.005</td>
<td>0.935</td>
<td>139</td>
<td>139</td>
</tr>
<tr>
<td>1.2431</td>
<td>1.38</td>
<td>0.005</td>
<td>1.1</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>2.0776</td>
<td>2.217</td>
<td>0.0200</td>
<td>1.055</td>
<td>143:30'</td>
<td>143:30'</td>
</tr>
<tr>
<td>2.024</td>
<td>2.33</td>
<td>0.014</td>
<td>1.126</td>
<td>143:30'</td>
<td>143:30'</td>
</tr>
<tr>
<td>2.12</td>
<td>1.3</td>
<td>0.184</td>
<td>0.772</td>
<td>235</td>
<td>335</td>
</tr>
<tr>
<td>2.249</td>
<td>1.38</td>
<td>0.130</td>
<td>0.778</td>
<td>235</td>
<td>325</td>
</tr>
</tbody>
</table>
a uniform basis, therefore, we must add 110 hours to the measured time (90 hours) which elapsed before the mixture was titrated, and 110 = 200 hours, as recorded in the table. The other experiments with hydroperoxide added initially were treated in the same way.

A plot of the data in Table XVI is shown in Figure 21.

It is seen that in the steady state there always appears to be less hydroperoxide formed than oxygen absorbed, and the following relationship holds for $t > t_o$:

$$
\frac{(H\cdot P\cdot O\cdot)_{t}}{O_2} = -b (t - t_o) + 1
$$

$t_o$ is the length of the induction period.

$b$ is the slope of the line after 140-145 hours.

The above equation gives the ratio of hydroperoxide formed to oxygen absorbed after $t$ hours.

If the reaction is started with a relatively high hydroperoxide value but lower than the requirement for the steady state, then for $t > t_o$,

$$
\frac{(H\cdot P\cdot O\cdot)_{t}}{(H\cdot P\cdot O\cdot)_{t_0}} = -b (t - t_o') + 1
$$

$t_o' = constant - constant \times \log(h\cdot P\cdot O\cdot)_1$.

$i$ = initial hydroperoxide concentration.
\[
\left[ \frac{H \cdot P \cdot O}{O_2} \right] \text{ at time } t
\]
Effect of the partial pressure of oxygen on the oxidation of cyclohexene:

As has been discussed before, the reaction goes through an induction period, then breaks up into a steady state rate. The oxidation rate stays constant and follows a straight line relationship till a low oxygen pressure region is reached and then the rate drops abruptly, as shown in Figure 22. This investigation was carried out at 40°C, with 9.84 millimols of cyclohexene.

This proves that the rate of oxidation is independent of the partial pressure of oxygen up to 40-50 mm. oxygen pressure. The partial pressure of oxygen used to vary from 10-30 cms. at the start of the reaction depending on the nature of the run and the temperature.

The effect of addition of hydroperoxides:

Since cyclohexene hydroperoxide is unstable at room temperature, and starts decomposing as soon as prepared, other hydroperoxides were added and the rate was found to be proportional to the hydroperoxide added at 37°C, as shown in Figure 23. The reactions were carried out in pyrex cells; with the same large number of 98.4 millimols of cyclohexene in both cells the surface effect of the glass is not significant.
Millimols of oxygen absorbed
Millimols of oxygen absorbed
FIG. 23

Rate of Ascorbic acid
hydrogen peroxide oxidized

Time in hours

Time in hours

Ascorbic acid

10

1.4

1.2

0.8

0.4

0.2

2.2

1.8

1.4

1.0

0.6

0.2
Rates as a function of the hydroperoxide concentration at 37°C:

I. Slope = rate = $6.66 \times 10^{-2}$ millimols of O₂/hr., when 0.00647 moles of hydroperoxide is used.

II. Slope = rate = $1.6 \times 10^{-2}$ millimols of O₂/hr., when 0.0175 moles of hydroperoxide is used.
In this series of experiments 1, 1, 2, 2-tetramethyl-propyl hydroperoxide was used. In Figure 23, Curve I, with 0.00647 moles of hydroperoxide added to 98.4 millimols of cyclohexene was given a rate of $6.66 \times 10^{-2}$ millimols of oxygen per hour and Curve II with 0.0175 moles added to 98.4 millimols of cyclohexene gave a rate of $16 \times 10^{-2}$ millimols of oxygen per hour.

Therefore the rates ratio is 2.4. The hydroperoxides ratio is 2.7. It could be concluded that addition of hydroperoxides increase the rate of oxidation proportionally. Or $\frac{dO_2}{dt} = k_4 \text{(H.P.O.)} \text{ added when HC}\neq \text{constant}$.

The activation energy for the oxidation of cyclohexene in the steady state:

From the kinetic equation in the oxidation of cyclohexene in the steady state, $\frac{dO_2}{dt} = k_2 n$. (Fig. 17, 18, 20.)

So if $k_2$ is calculated for various temperatures the following table is obtained:

<table>
<thead>
<tr>
<th>TABLE XVII</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPERATURE COEFFICIENTS FOR THE OXIDATION OF CYCLOHEXENE</td>
</tr>
<tr>
<td>$(k_2 \times 10^3)$</td>
</tr>
<tr>
<td>1.87</td>
</tr>
<tr>
<td>0.715</td>
</tr>
<tr>
<td>0.191</td>
</tr>
</tbody>
</table>
From the slope of the curve, Figure 24, we obtain the following:

\[ 2.303 \times 2 \times \frac{0.9159 \times 10^2}{0.25} = 16.8 \text{ Kcals} \text{ and thus the activation energy for the oxidation of cyclohexene in the steady state is obtained. The value reported in the literature}^{11} \text{ is } 15.600 \text{ Kcals at } 25^\circ\text{C}. \text{ This is in good agreement with the value obtained in this research of } 15.41 \text{ Kcals between } 15^\circ\text{C-30}^\circ\text{C, and } 17.6 \text{ Kcals between } 30^\circ\text{C-40}^\circ\text{C.}

**Conclusion on the kinetics of oxidation of cyclohexene:**

(A) **INDUCTION PERIOD.**

1. The reaction goes through an induction period. The rate follows this relationship: \( \frac{d \log C}{dt} = k_1 n \).

   The values of \( k_1 \) were found to be:

   \[
   \begin{array}{cc}
   k_1 \times 10^4 & T \\
   3.04 & 30^\circ\text{C} \\
   12.8 & 40^\circ\text{C}
   \end{array}
   \]

2. The activation energy for the reaction was calculated to be: \( A = 27.3 \text{ Kcals.} \)

3. The length of the induction period is a function of the hydroperoxide started with initially.

   \[ t'_0 (\text{length of the induction period}) = \text{constant} - \text{constant} \times \log(H.P.O.)_i \]

   \( i \) stands for the initial hydroperoxide concentration.
4. The induction period could be eliminated by the addition of hydroperoxides equal to or greater than that required for the steady state. Thus if the reaction is started with a hydroperoxide content of 5% at 30°C (Figure 11) and 10% at 40°C (Figure 14), the reaction should go straight through steady state right away.

5. The concentration of the hydroperoxide per millimol of cyclohexene is constant at the end of the induction period.

6. All oxygen absorbed during the induction period goes through the formation of hydroperoxides.

(B) STEADY STATE.

1. Whether the reaction goes through an induction period and reaches a steady state, or whether the reaction is started with more hydroperoxide, the final steady state rate is the same.

2. The rate of oxygen uptake in the steady state is proportional to the number of millimols of cyclohexene:

\[ \frac{dO_2}{dt} = k_2 n \text{ when } n \text{ is less than 14.7 millimols of cyclohexene at 30°C.} \]

3. The addition of other hydroperoxides shows that the rate of oxygen uptake is proportional to the addition of hydroperoxides.

4. The reaction rate in the steady state follows a
straight line relationship and then drops down abruptly at very low pressure of oxygen.
CHAPTER III

THE KINETICS OF OXIDATION OF CYCLOHEXENE IN BENZENE SOLUTION

Introduction:

With benzene dilution it was intended to learn the actual kinetics of the reaction as well as its mechanism.

Experimental procedure:

The oxidation cell was cleaned and prepared as described before. Then two pipettes of 1 ml. volume each were used. The pipettes were left in cleaning solution for 12 hours, then in soap solution for two hours, and then washed several times in distilled water. Finally they were washed with acetone and dried in a stream of oil-pump nitrogen for 10 minutes.

Then the following procedure was adopted:

0.1 ml. of cyclohexene and 0.9 ml. of benzene were mixed; 0.2 ml. of cyclohexene and 0.8 ml. of benzene were mixed; and so on down the line... in such a way that the total volume was always 1 ml. of solution at 25°C.

The total pressure was built up on these cells up to one-half atmosphere by using an outside mercury
bubbler as shown in Fig. 25, to the open outside ends of the manometers. Thus the total pressure was equal to \( h_1 \), the height of the mercury in the manometer plus \( h_2 \), the height of the mercury in the bubbler.

In benzene-cyclohexene runs the reaction was more susceptible to leakage, but proper care had been taken to guard against that, by (1) checking the glass ground joints and stop cocks, and (2) by watching the changes in the pressure on the manometers of the cells. When a sudden drop in the pressure used to occur, it was a clear indication of a leak since the rate when in the steady state follows a straight line relation and the rate drops abruptly at low pressure of oxygen.

Factors that could change the rate of the reaction:

1. If the number of millimols of cyclohexene is large where the rate of oxygen diffusion could be the rate determining step. But in the case of benzene-cyclohexene system, the total volume never exceeded 1 ml. for the teflon cylinders that were used and the rate of diffusion is not a factor in the case of cyclohexene up to the limits of 1.4 ml. or about 14 millimols. If the rate of diffusion in the benzene-cyclohexene was entering in, then upon increasing the number of millimols above 14 millimols there was no increase in
the rate (Figure 18), but the fact that 1 ml. of benzene-cyclohexene solution lies below the diffusion limits, then oxygen diffusion could not be a factor.

In the second place, the order of the reaction of benzene-cyclohexene system gave a second order reaction, that only in itself proved the rate to be second order and showed beyond any shadow of a doubt that diffusion of oxygen is not a factor in the benzene system when 1 milliliter of benzene-cyclohexene solution is used.

2. The second factor is distillation. In benzene-cyclohexene system it could be argued that increase of concentration of cyclohexene from 1 millimol to 3 millimols of cyclohexene per 1 ml. of benzene-cyclohexene solution might increase the chances of distillation of cyclohexene and thus it hits the glass wall and makes the reaction go faster than it should be. This argument is not true, since the cells were carefully watched for distillation and it was made sure that nothing distilled over on the pyrex walls.

Distillation rate is determined only by the area of surface exposed, and temperature. Since all three experiments had same surface area, distillation rate would be constant. Hence this argument is invalid.

3. The third argument that could be raised is the problem of leakage. The question could be raised
as to how can one tell that the oxidation cells did not leak, and that was not detected and it thus appeared in the oxidation rates as changes in pressure. This could not be so, for the simple reason that leakage is a function of the pressure within the cell, but examining the data we find that the reaction goes through an induction period and then it stays on that straight line portion of the oxidation curve till approximately all the oxygen is used up and then the rate drops down and tends to approach zero as the oxygen pressure approaches zero, since the case was tested on six independent cases whether with benzene dilution or without dilution, as will be discussed under the effect of the pressure of oxygen on the oxidation rate in a later section. (Fig. 30)

So when cells leaked, the leakage was immediately detected and stopped. When cells leak the pressures drop quickly but never drop to zero when there is a positive pressure on the cells. The leakage used to be detected by small air spaces and striations in the grease layer between the two inter faces of the inner core of the stop cock and the outer case housing it. The ground joints connecting the top and bottom parts rarely leaked.

Many runs were started out at 30°C, unsuccessfully due to the fact that the reaction goes slowly or the rate of oxidation is a slow one and thus more time was
Rubber band
Clamp
Glass rod
Rubber tubing
Clamp
T-shaped 2mm. tubing
Stream of nitrogen
1mm. capillary
Mercury

Diagram showing the supporting glass rods and mercury bubbler.

FIG. 25
needed to carry it through a complete induction period and let it reach a steady state. Thus it gave more time for the benzene-cyclohexene to come in contact with the grease stop cock and thus a leakage used to result.

The way the leakage used to be detected was the sudden drop in pressure on the manometer of the cell. Then the stop cocks were examined and the leaking point used to be verified. So the sudden drop in pressure was not due to any instantaneous rapid reaction. The only concentration that was carried out successfully was 7.87 millimols of cyclohexene per 1 ml. of benzene-cyclohexene solution at 30°C, and the reaction was repeated twice.

Kinetics of oxidation of cyclohexene in benzene system at 40°C;

At 40°C, runs were carried out with low hydroperoxide concentration and the reactions went through an induction period, in which there was a hydroperoxide buildup, then it reached the steady state.

If the reaction is taken up with an induction period for the following two concentrations, 3.9 and 5.9 millimols of cyclohexene per 1 milliliter of benzene-cyclohexene solution, the Tables XVIII and XIX
<table>
<thead>
<tr>
<th>Number of Hours elapsed</th>
<th>Total Number of Hours Elapsed</th>
<th>Atmos. Pressure of Hg.</th>
<th>Reading on Manometer in cms. of Hg.</th>
<th>Amount of Oxygen Absorbed in cms. of Hg.</th>
<th>Millimols of Oxygen Absorbed Between Readings</th>
<th>Total Millimols Absorbed in Between Readings</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>74.25</td>
<td>30.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>24</td>
<td>24</td>
<td>74.28</td>
<td>30.72</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>54</td>
<td>74.33</td>
<td>30.062</td>
<td>0.458</td>
<td>0.0364</td>
<td>0.0364</td>
</tr>
<tr>
<td>55</td>
<td>109</td>
<td>74.29</td>
<td>29.1</td>
<td>1.002</td>
<td>0.0796</td>
<td>0.116</td>
</tr>
<tr>
<td>11</td>
<td>120</td>
<td>74.55</td>
<td>28.6</td>
<td>0.24</td>
<td>0.019</td>
<td>0.135</td>
</tr>
<tr>
<td>23:30'</td>
<td>143:30'</td>
<td>75.1</td>
<td>27.38</td>
<td>0.67</td>
<td>0.0532</td>
<td>0.1882</td>
</tr>
<tr>
<td>12</td>
<td>155:30'</td>
<td>74.86</td>
<td>27.04</td>
<td>0.58</td>
<td>0.046</td>
<td>0.2342</td>
</tr>
<tr>
<td>14:15'</td>
<td>169:45'</td>
<td>75.06</td>
<td>26.62</td>
<td>0.22</td>
<td>0.0175</td>
<td>0.2517</td>
</tr>
<tr>
<td>46:45'</td>
<td>216:30'</td>
<td>74.29</td>
<td>26.01</td>
<td>1.38</td>
<td>0.1096</td>
<td>0.3613</td>
</tr>
<tr>
<td>27:30'</td>
<td>244</td>
<td>74.33</td>
<td>24.61</td>
<td>1.36</td>
<td>0.108</td>
<td>0.4693</td>
</tr>
<tr>
<td>23:30'</td>
<td>267:30'</td>
<td>74.36</td>
<td>23.77</td>
<td>0.81</td>
<td>0.0643</td>
<td>0.5336</td>
</tr>
<tr>
<td>25:30'</td>
<td>293</td>
<td>74.00</td>
<td>23.1</td>
<td>1.03</td>
<td>0.0806</td>
<td>0.614</td>
</tr>
<tr>
<td>42:30'</td>
<td>335:30'</td>
<td>74.32</td>
<td>21.1</td>
<td>1.68</td>
<td>0.1335</td>
<td>0.747</td>
</tr>
<tr>
<td>30</td>
<td>365:30'</td>
<td>74.34</td>
<td>19.85</td>
<td>1.23</td>
<td>0.0976</td>
<td>0.845</td>
</tr>
<tr>
<td>Number of Hours elapsed Between Readings</td>
<td>Total Number of Hours Elapsed</td>
<td>Atm. Press. in cms.</td>
<td>Reading on Manometer in cms. of Hg.</td>
<td>Amount of Oxygen Absorbed Between Readings</td>
<td>Millimols of Oxygen Absorbed Between Readings</td>
<td>Total Millimols of Oxygen Absorbed</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>------------------------------</td>
<td>-------------------</td>
<td>-------------------------------------</td>
<td>------------------------------------------</td>
<td>----------------------------------------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>74.25</td>
<td>33.77</td>
<td>0</td>
<td>0.093</td>
<td>0.093</td>
</tr>
<tr>
<td>24</td>
<td>24</td>
<td>74.28</td>
<td>32.61</td>
<td>1.13</td>
<td>0.0791</td>
<td>0.1721</td>
</tr>
<tr>
<td>30</td>
<td>54</td>
<td>74.33</td>
<td>31.6</td>
<td>0.96</td>
<td>0.0732</td>
<td>0.2453</td>
</tr>
<tr>
<td>20</td>
<td>74</td>
<td>74.46</td>
<td>30.44</td>
<td>0.89</td>
<td>0.0732</td>
<td>0.2453</td>
</tr>
<tr>
<td>35</td>
<td>109</td>
<td>74.29</td>
<td>28.41</td>
<td>2.34</td>
<td>0.193</td>
<td>0.4833</td>
</tr>
<tr>
<td>11</td>
<td>120</td>
<td>74.55</td>
<td>27.41</td>
<td>0.74</td>
<td>0.061</td>
<td>0.4993</td>
</tr>
<tr>
<td>23:30'</td>
<td>143:30'</td>
<td>75.1</td>
<td>24.5</td>
<td>2.36</td>
<td>0.1945</td>
<td>0.6938</td>
</tr>
<tr>
<td>12</td>
<td>155:30'</td>
<td>74.86</td>
<td>23.42</td>
<td>1.32</td>
<td>0.109</td>
<td>0.8028</td>
</tr>
<tr>
<td>14:15'</td>
<td>169:45'</td>
<td>75.06</td>
<td>22.0</td>
<td>1.22</td>
<td>0.101</td>
<td>0.9038</td>
</tr>
<tr>
<td>23:30'</td>
<td>193:15'</td>
<td>74.5</td>
<td>19.91</td>
<td>2.65</td>
<td>0.2181</td>
<td>1.1219</td>
</tr>
<tr>
<td>23:15'</td>
<td>216:30'</td>
<td>74.29</td>
<td>17.91</td>
<td>2.21</td>
<td>0.1821</td>
<td>1.514</td>
</tr>
<tr>
<td>27:30'</td>
<td>244</td>
<td>74.33</td>
<td>15.38</td>
<td>2.49</td>
<td>0.205</td>
<td>1.519</td>
</tr>
</tbody>
</table>
I. Oxidation of 4.4 million of octane

5% of 1 ml. of benzene solution

Step 1: 8 x 10^{-4} milllols of O2/ml.
in the steady state.

II. Oxidation of 4.4 million of

cyclohexane per 1 milliliter of

toluene-cyclohexane solution.

Step 2: 5.4 x 10^{-4} milllols

c/ml. in the

steady state.

Temp. 60°C.
and Figure 26 will illustrate the rates and concentration relationships.

Other reactions were started with high hydroperoxide concentrations of 0.5 and 0.36 millimols per 9.84 millimols of cyclohexene for Curves I and II, respectively, as shown in Figure 27.

It will be noticed that the rate initially starts fast, depending on the initial hydroperoxide concentration, and then the rate drops to the steady state rate and the rate obtained would be the same as if the reaction was made to go through an induction period and then reach a steady state.

It will be noticed that Curve II, Figure 27, shows a break around 35 hours from the start of the reaction. This is due to the fact that readings were made right at the start of the reaction. While the pressure was decreasing due to the absorption of oxygen, that was offset by increase in pressure due to the vapor pressures of both benzene and cyclohexene while the mixture was warming up to reach the temperature of the bath. The reaction with low hydroperoxide concentration, Curve III on the same figure, went through an induction period and gave the same rate as the rest, of $5 \times 10^{-3}$ millimols of oxygen per hour in the steady state, like Curves I and II with slopes of $5.25 \times 10^{-3}$ and $5.5 \times 10^{-3}$.
Oxidation of 1.0 M solutions of oxalate
in 1.0 M solutions of potassium dichromate solution
with different initial pyrophosphate concentrations
at 70°C.
<table>
<thead>
<tr>
<th>Curve number</th>
<th>Initial hydroperoxide concentration in millimols per 9.84 hour x (10^2)</th>
<th>Rate in millimols of cyclohexane of oxygen per hour x (10^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.5</td>
<td>5.25</td>
</tr>
<tr>
<td>II</td>
<td>0.36</td>
<td>5.3</td>
</tr>
<tr>
<td>III</td>
<td>Low peroxide value</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**FIG. 27**
millimols of oxygen per hour respectively. So it is obvious from Curves I, II and III in Figure 27 that whether the reaction with low hydroperoxide concentration goes through a long induction period or whether the reaction is started with hydroperoxide concentration high, the same steady state rates are obtained.

If 7.87 millimols of cyclohexene is considered (Figure 23), the rate is $14 \times 10^{-3}$ millimols of oxygen per hour. It will be noticed that 0.57 millimols of oxygen end the induction period. So the important step to watch out for in carrying out these reactions is the fact that it should be made sure that the reaction is carried far enough in the steady state, because sometimes for an unknown reason the reaction gives a short straight line in the induction period with benzene dilution. So it should always be made sure that the reaction has well passed the induction period.

One important thing to be remembered from Figure 23 is the smoothness of the straight line portion of the graphs which is due to the fact that manometers were well cleaned and the mercury never had the chance of clinging to the sides of the walls. Thus an accurate recording of the manometer pressures on the cells was obtained and that should appear in the accuracy
Millimoles of oxygen absorbed

![Graph showing millimoles of oxygen absorbed against concentration.

The graph includes a line labeled 'Red. of Ind. Oxidation'.
Oxidation of 7.87 millimols of cyclohexene per 1 milliliter of benzene-cyclohexane solution at 40°C.

Slope = $1.40 \times 10^{-2}$ millimols of $O_2$/hr. in the steady state.

End of the induction period
of the plot.

So down the line the rates for the following concentrations were determined at 40°C in the steady state reactions for other concentrations:

### TABLE XX

(40°C)

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Rate x 10³</th>
<th>Velocity</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millimols of Cyclohexene</td>
<td>(Millimols of O₂/hr.)</td>
<td>Constant of the Reaction</td>
<td>Constant of (k₃ x 10⁴) the Reaction</td>
</tr>
<tr>
<td>per Milliliter of Solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.984</td>
<td>0.232</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>3.936</td>
<td>3.23</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>4.92</td>
<td>5.25</td>
<td>2.17</td>
<td></td>
</tr>
<tr>
<td>4.92</td>
<td>5.5</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td>4.92</td>
<td>5.0</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>5.904</td>
<td>8.0</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>6.888</td>
<td>11.2</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>7.372</td>
<td>14.</td>
<td>2.26</td>
<td></td>
</tr>
</tbody>
</table>

So if log \( \frac{-dc}{dt} \) is plotted against log c the slope is 2, and the result is shown on Figure 29. This follows from the kinetic equation \( \frac{-dc}{dt} = k₃ c^n \).

In all the above reactions it was made sure that the induction period had completely ended and the reactions were left to go through long steady state to acquire many readings so that when the slope is determined it will be summed up through many points, and this increases the accuracy of the rate determination.
<table>
<thead>
<tr>
<th>Number of Hours elapsed Between Readings</th>
<th>Total Number of Hours Elapsed</th>
<th>Atm. Press. in cms.</th>
<th>Reading on Manometer in cms. of Hg.</th>
<th>Amount of O₂ absorbed in cms. of Hg. between Readings</th>
<th>Millimols of O₂ used Between Readings</th>
<th>Total Millimols of O₂ Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>74.88</td>
<td>39.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13:15'</td>
<td>13:15'</td>
<td>74.92</td>
<td>38.7</td>
<td>0.44</td>
<td>0.0346</td>
<td>0.0346</td>
</tr>
<tr>
<td>6:15'</td>
<td>19:30'</td>
<td>74.92</td>
<td>38.8</td>
<td>0.03</td>
<td>0.00236</td>
<td>0.0398</td>
</tr>
<tr>
<td>6</td>
<td>25:30'</td>
<td>74.75</td>
<td>37.4</td>
<td>1.44</td>
<td>0.1131</td>
<td>0.15</td>
</tr>
<tr>
<td>10:30'</td>
<td>36</td>
<td>74.76</td>
<td>35.3</td>
<td>2.09</td>
<td>0.1645</td>
<td>0.3145</td>
</tr>
<tr>
<td>6:30'</td>
<td>42:30'</td>
<td>74.62</td>
<td>33.4</td>
<td>2.04</td>
<td>0.161</td>
<td>0.4755</td>
</tr>
<tr>
<td>7</td>
<td>49:30'</td>
<td>74.62</td>
<td>30.1</td>
<td>3.5</td>
<td>0.26</td>
<td>0.7355</td>
</tr>
<tr>
<td>10</td>
<td>59:30'</td>
<td>74.78</td>
<td>27.94</td>
<td>2.0</td>
<td>0.1568</td>
<td>0.8923</td>
</tr>
<tr>
<td>12</td>
<td>71:30'</td>
<td>74.64</td>
<td>25.4</td>
<td>2.68</td>
<td>0.211</td>
<td>1.103</td>
</tr>
<tr>
<td>12:30'</td>
<td>84</td>
<td>75.00</td>
<td>24.38</td>
<td>0.66</td>
<td>0.052</td>
<td>1.155</td>
</tr>
<tr>
<td>4:30'</td>
<td>88:30'</td>
<td>74.98</td>
<td>24.28</td>
<td>0.12</td>
<td>0.00941</td>
<td>1.1644</td>
</tr>
<tr>
<td>6:30'</td>
<td>95</td>
<td>74.96</td>
<td>24.15</td>
<td>0.15</td>
<td>0.0118</td>
<td>1.1762</td>
</tr>
</tbody>
</table>
### TABLE XXII

**7.87 MILLIMOLS OF CYCLOHEXENE PER 1 MILLILITER OF BENZENE-CYCLOHEXENE AT 55°C**

<table>
<thead>
<tr>
<th>Number of Hours elapsed Between Readings</th>
<th>Total Number of Hours Elapsed</th>
<th>Atm. Press. in cms. of Hg.</th>
<th>Reading on Manometer in cms. of Hg.</th>
<th>Amount of Oxygen used Between Readings in cms. of Hg.</th>
<th>Millimols of O₂ used Between Readings</th>
<th>Total Millimols of O₂ Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>75.11</td>
<td>29.42</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6:15'</td>
<td>6:15'</td>
<td>75.11</td>
<td>28.3</td>
<td>1.12</td>
<td>0.0828</td>
<td>0.0828</td>
</tr>
<tr>
<td>11:15'</td>
<td>17:30'</td>
<td>74.83</td>
<td>24.4</td>
<td>4.18</td>
<td>0.31</td>
<td>0.3928</td>
</tr>
<tr>
<td>3</td>
<td>20:30'</td>
<td>74.98</td>
<td>23.00</td>
<td>1.25</td>
<td>0.0925</td>
<td>0.4853</td>
</tr>
<tr>
<td>4</td>
<td>24:30'</td>
<td>74.83</td>
<td>20.8</td>
<td>2.35</td>
<td>0.174</td>
<td>0.6593</td>
</tr>
<tr>
<td>3</td>
<td>27:30'</td>
<td>74.74</td>
<td>20.5</td>
<td>0.39</td>
<td>0.0288</td>
<td>0.6881</td>
</tr>
<tr>
<td>5:30'</td>
<td>33</td>
<td>74.72</td>
<td>19.3</td>
<td>1.22</td>
<td>0.09</td>
<td>0.778</td>
</tr>
<tr>
<td>10:45'</td>
<td>43:45'</td>
<td>74.72</td>
<td>14.3</td>
<td>5.0</td>
<td>0.37</td>
<td>1.148</td>
</tr>
<tr>
<td>7:15'</td>
<td>51</td>
<td>74.48</td>
<td>13.85</td>
<td>0.69</td>
<td>0.051</td>
<td>1.199</td>
</tr>
<tr>
<td>I. Oxidation of 5.9 millimols of cyclohexene per 1 milliliter</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>of benzene-cyclohexene solution.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1. Oxidation of 5.0 milliliters of cyclohexene per 1 milliliter.

II. Oxidation of 1.5 milliliters of cyclohexene per 1 milliliter.

II. Oxidation of 7.87 millimols of cyclohexene per 1 milliliter.

Step 7.0 to 10.0 millimols of O2/hr. in the steady state.

Stage 0.36 x 10^-5 millimols of O2/hr. in the steady state.
Oxidation of cyclohexene at 55°C with benzene dilution:

Since the manometers of the cells were of uniform length and could not hold enough mercury for the pressure exerted by the oxygen, nitrogen and other gaseous vapors, together with the vapor pressures of benzene and cyclohexene, a mercury bubbler was used as in the case of the 40°C temperature runs and as has been discussed before in Figure 25.

Kinetics of oxidation of cyclohexene in the steady state at 55°C:

If two raw data for the oxidation of cyclohexene are considered, from Tables XXI and XXII, the curves in Figure 30 will be obtained.

If the rates are calculated for the rest of the remaining concentrations, we will obtain the following table:

TABLE XXIII

RATES AS A FUNCTION OF CONCENTRATION AT 55°C

<table>
<thead>
<tr>
<th>Rate x 10^3</th>
<th>Concentration in Millimols per 1 ml.</th>
<th>k_3 x 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Velocity</td>
</tr>
<tr>
<td>3.00</td>
<td>3.936</td>
<td>k_3 average: 5.0475</td>
</tr>
<tr>
<td>12.</td>
<td>4.92</td>
<td>5.17</td>
</tr>
<tr>
<td>19.</td>
<td>5.904</td>
<td>4.96</td>
</tr>
<tr>
<td>23.5</td>
<td>7.872</td>
<td>5.46</td>
</tr>
</tbody>
</table>


Concentration expressed as millimoles of cyclohexane per 1 milliliter of solution.

Temp. 55°C

$y = \frac{1}{3}x + \frac{1}{2}$
A plot of the data in Table XXIII as \( \log -\frac{dc}{dt} \) against \( \log c \) is shown in Figure 31. Again the slope is 2, showing a dependence upon the square of the cyclohexene concentration.

Oxidation of cyclohexene by dilution with benzene at 30°C:

At 30°C, the reaction was hard to carry out since the reaction is rather slow and that means the oxidation cells had to be left a longer time in the thermally controlled bath, and that meant a longer time for benzene and cyclohexene to be in contact with stop cock grease and thus it results in leakage.

Another factor was the fact that 30°C temperature is close to room temperature and that meant a dual heater and cooling circulating pump had to be used. This fast switch in temperature from heating to cooling caused serious distillation on the walls of the glass, which catalyzes the oxidation rate.

The only concentration that carried through successfully was 7.87 millimols of cyclohexene per 1 ml. of benzene-cyclohexene solution.

The data in Table XXIV are plotted as oxygen absorbed against time and the result shown in Figure 32.
<table>
<thead>
<tr>
<th>Number of Hours Elapsed Between Readings</th>
<th>Total Number of Hours of Hg.</th>
<th>Atm. Press. in cms.</th>
<th>Reading on Manometer in cms. of Hg.</th>
<th>Amount of O$_2$ used Between Readings in cms. of Hg.</th>
<th>Millimols of Oxygen Used Between Readings</th>
<th>Total Millimols of Oxygen Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>74.65</td>
<td>29.75</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>24:30'</td>
<td>24:30'</td>
<td>74.64</td>
<td>29.6</td>
<td>0.16</td>
<td>0.0129</td>
<td>0.0129</td>
</tr>
<tr>
<td>37</td>
<td>61:30'</td>
<td>74.25</td>
<td>29.79</td>
<td>0.20</td>
<td>0.0161</td>
<td>0.0290</td>
</tr>
<tr>
<td>23</td>
<td>84:30'</td>
<td>74.28</td>
<td>29.6</td>
<td>0.16</td>
<td>0.0129</td>
<td>0.0419</td>
</tr>
<tr>
<td>30</td>
<td>114:30'</td>
<td>74.33</td>
<td>29.37</td>
<td>0.18</td>
<td>0.0145</td>
<td>0.0564</td>
</tr>
<tr>
<td>20</td>
<td>134:30'</td>
<td>74.6</td>
<td>27.98</td>
<td>1.12</td>
<td>0.094</td>
<td>0.1504</td>
</tr>
<tr>
<td>35</td>
<td>169:30'</td>
<td>74.29</td>
<td>27.61</td>
<td>0.68</td>
<td>0.0548</td>
<td>0.2052</td>
</tr>
<tr>
<td>11</td>
<td>180:30'</td>
<td>74.55</td>
<td>26.58</td>
<td>0.77</td>
<td>0.0627</td>
<td>0.2679</td>
</tr>
<tr>
<td>24</td>
<td>204:30'</td>
<td>75.1</td>
<td>23.7</td>
<td>2.33</td>
<td>0.1880</td>
<td>0.4559</td>
</tr>
<tr>
<td>11:15'</td>
<td>215:45'</td>
<td>74.86</td>
<td>22.38</td>
<td>1.56</td>
<td>0.126</td>
<td>0.582</td>
</tr>
<tr>
<td>14:30'</td>
<td>230:15'</td>
<td>75.06</td>
<td>20.2</td>
<td>1.98</td>
<td>0.16</td>
<td>0.742</td>
</tr>
</tbody>
</table>

TABLE XXIV

OXYGEN ABSORBED AS A FUNCTION OF TIME AT 30°C FOR 7.87 MILLIMOLS OF CYCLOHEXENE PER 1 MILLILITER OF SOLUTION
Oxidation of 7.87 ml per 1 milliliter of solution at 50°C.

Slope = 11.45 x $\frac{O_2}{\text{hr. - in}}$

FIG. 32
Oxidation of 7.87 millimols of cyclohexene per 1 milliliter of benzene-cyclohexene solution at 30°C.

Slope = 1.45 x 10^{-3} millimols of O_2/hr. in the steady state.
TABLE XXV

RATES AS A FUNCTION OF TEMPERATURE AT 30°C

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Rate x 10^3</th>
<th>k specifically x 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.872</td>
<td>11.45</td>
<td>1.84</td>
</tr>
<tr>
<td>7.872</td>
<td>11.9</td>
<td>1.925</td>
</tr>
</tbody>
</table>

The velocity constant was calculated from the kinetic equation: \(-\frac{dc}{dt} = k_3 c^n = k_3 c^2\).

**Effect of the pressure:**

The reaction follows a straight line relationship until practically all the oxygen is used up and the reaction drops down practically to zero as all the oxygen is used up. As can be seen from Figure 30, Curve I, the reaction is independent of the pressure. Actually the reaction follows a straight line relationship and starts dropping sharply. So it could be assumed that the reaction rate is independent of pressure up to a certain limit. But when the rate drops it does so in a sharp fashion. The partial pressure of oxygen at that limit is between 3-4 cms. of mercury.
In $k$ vs. $\frac{1}{T}$ for the oxidation of cyclohexene in benzene.

$\ln k \times 10^4$ $\frac{1}{T}$ °C

1.798 351°C
2.121 651°C
5.15275 551°C

Average 7.125 Kcal
Activation energy for oxidation of cyclohexene in benzene:

As it will be noticed from the plot of log $k_3$, the specific velocity constant, against reciprocal of temperature (Figure 33), the activation energy seems to vary greatly between 40°C and 55°C. The great increase in the activation energy is due to the instability of the cyclohexene hydroperoxide. At high temperatures it decomposes fast and that sets a fast chain reaction and a large increase in the specific velocity constant and thus an increase in the activation energy. Another evidence comes from the time limit of the length of the induction period. While it is of the order of 80 hours at 40°C (Figures 26 and 23), it practically vanishes at 55°C and the reaction starts right away (Figure 30).

Comparison between the kinetics of the oxidation of cyclohexene and cyclohexene-benzene system:

1. Both of them go through an induction period.
2. In both cases, the induction period could be eliminated by the addition of hydroperoxide at the start of the reaction. The amount of hydroperoxide added should be equal to or more than the hydroperoxide
requirement for the end of the induction period. In both cases, the rate obtained in the steady state would be the same as if the reaction went through an induction period and then reached the steady state. But the individual rates differ when comparing the rates obtained in cyclohexene to those obtained in cyclohexene-benzene solutions; i.e., if \( n \) millimols of cyclohexene gives a rate \( R_1 \) in the steady state, and if \( n \) millimols of cyclohexene per 1 ml. of benzene-cyclohexene solution gives \( R_2 \) in the steady state, then upon examining the data \( R_1 \) is not equal to \( R_2 \). But the same \( R_1 \) would be obtained whether the reaction goes through an induction period and then reaches a steady state or whether the induction period is eliminated by starting the reaction with a hydroperoxide concentration equal to that of the steady state requirement. If the hydroperoxide concentration is larger than the requirement for the steady state, then the reaction will start fast and upon the decomposition of the excess of hydroperoxide, the rate drops down to that of the steady state.

3. In both cases the oxidation rate is independent of the pressure up to a certain limit. Then the rate drops sharply or abruptly at very low oxygen pressures, i.e. between 40-30 mm. of oxygen pressure.
4. (a) In absence of benzene the rate is proportional to the number of millimols of cyclohexene:

\[ \frac{dO_2}{dt} = k_2 n \]

(b) In benzene solutions the rate varies as the square of the concentration:

\[ \frac{dO_2}{dt} = k_3 c^2 \]

5. In absence of benzene, the rate of oxidation is proportional to the hydroperoxide concentration:

\[ \frac{dO_2}{dt} = k_4 (H_2P.O.) \]

Keeping the number of millimols of cyclohexene constant. After the excess hydroperoxide has decomposed the rate drops down to that of the steady state.

Comparison between the activation energy of oxidation of cyclohexene with benzene dilution and without benzene dilution:

(A) The activation energy of the oxidation of cyclohexene, without benzene dilution.

1. The activation energy for the oxidation of cyclohexene is 15.41 Kcals and 17.6 Kcals between 15°C-30°C and between 30°C-40°C respectively. The activation energy for the oxidation of cyclohexene in the steady state is 16.8 Kcals, as calculated from the slope in Figure 24.
The activation energy for the oxidation of cyclohexene in benzene solutions in the steady state.

1. The activation energy for the oxidation of cyclohexene in benzene solutions in the steady state is 3 Kcals between 30°C-40°C, but the activation energy gets to be 11.25 Kcals between 40°C-55°C.

Reproducibility of these reactions:

1. INDUCTION PERIOD.

In this region there is slow reaction right at the start of the run, so there will be small change in pressure, and thus a greater chance for introducing error.

Also, it takes about 40-48 hours for the reaction to reach complete equilibrium.

So in order to avoid the two above mentioned factors, the following things have to be taken care of:

1. Start the reaction with very low peroxide concentration and thus by the time the reaction starts picking up speed, it would have reached equilibrium with the bath.

2. The reaction should be carried through a complete induction period until the oxidation curve reaches a steady state.
(3) Many readings should be taken during the induction period, so that when $\log O_2$ is plotted against time, the line would be drawn through many points and thus increase the accuracy of finding $\frac{d \log O_2}{dt}$ for a particular number of millimols of cyclohexene.

(4) When $\log O_2$ vs. time is plotted, it should be made sure that the plot is made within the boundaries of the induction period. The only way to know that is to plot millimols of oxygen vs. time, and follow the regions where each part starts and ends.

If all these points are taken care of, there will be no trouble at all in reproducing the data.

Reproducibility of these reactions:

2. THE STEADY STATE.

The steady state reactions are more straightforward, in the sense that the change in pressure per unit time is much larger than that of the induction period. Thus there is little discrepancy introduced by a small error brought about by the pressure measurements. But still the following precautions have to be observed:

(1) No distillation should occur and measures against that have been discussed. Distillation could be avoided if proper steps like keeping the cells away from the heaters as well as the walls of the bath are
taken.

(2) No leakage should take place, and symptoms for leakage have been discussed.

(3) No vibrations in the cells should take place.

(4) The volumes of the hydrocarbon should be accurately measured and the cells closed quickly so as to prevent loss of hydrocarbon through evaporation. The operation time, that is from the time the volume of hydrocarbon is measured from the 1-milliliter pipette till the cell is closed, should not take more than 15 seconds for the measurement of the cyclohexene reactions.

When the cell is to be charged with oxygen, the rubber tubing should be connected first to the open outlet of the three-way stop cock, the pressure of oxygen applied through a reduction valve of about 10-20 cms. and then the three-way stop cock is open, thus making the three connections of the inner cell, the manometer and the incoming oxygen line.

As soon as the mercury stops rising in the cell manometer, the three-way stop cock is turned to shut off the connections between the outside and the cell. But by doing so automatically the manometer and the inner cell are connected. The cell is fastened and put in the bath.
(5) The stop cock should not be overgreased so that the opening would not be clogged.

If the above conditions are taken care of, there will be no trouble in reproducing the experiments. Duplication runs, as well as triplication runs, were carried out at various stages in the course of these experiments, as indicated in previous tables and figures.

With benzene-cyclohexene solution, the maximum allowable time for measuring both the volume of benzene and cyclohexene into the teflon cylinder and closing up the cell should not exceed the 25-28 seconds limits.

(6) As a safeguard it should be made sure that the reactions are well carried through the steady state, for two reasons: (a) to make sure that the induction period is completed; (b) to obtain more points to carry out an exact plot for the rates calculation.
APPENDIX A

In Figure 34, there are three runs that are carried out in pyrex containers. It is obvious that the smaller the amounts of cyclohexene, the greater is the oxidation rate; thus another indication of the catalytic effect of the surface of pyrex. So this made it impossible to vary the amounts of cyclohexene and study the respective oxidation rates.
Curves I, II and III represent the oxidation of 2.95, 5.9 and 59.0 millimols of cyclohexene respectively at 37^\circ C.
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