

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies in Auto-oxidation. V. The Induction Period in Auto-oxidation¹

BY H. N. STEPHENS

Genthe² and many later investigators down to the present time have regarded the early increase of rate with time in auto-oxidations as being due to the formation of an autocatalyst, which has quite generally been assumed to be the intermediate peroxide. This view is supported by a number of observations³ on the effect of peroxides in shortening the induction period but it has been pointed out by the writer that the accelerating effect of peroxides may be interpreted in quite a different way.⁴

If the increase in rate with time is due to autocatalysis the rate of oxidation at a given time ought to be a function of the amount of oxygen which had been absorbed. The present work will show, however, that no such relationship exists in the case of the auto-oxidation of cyclohexene and will indicate that, if autocatalysis plays any part in the increase of rate with time, that part is a minor one. It would be unjustifiable to assume that no contribution can be made by the intermediate peroxide toward auto-acceleration of the reaction, as Bäckström⁵ has shown that the reaction of perbenzoic acid with benzaldehyde is a chain reaction and therefore may serve as an independent origin of chains in the auto-oxidation of the aldehyde. However, as the writer has pointed out elsewhere,⁴ this contribution toward the auto-acceleration can be at best only a very small one, as there is apparently a very small probability of a chain being started in this way.

The writer has favored the alternative interpretation of the induction period,⁴ which assumes that the latter is due to inhibition by small amounts of impurities. On the basis of this view it would be predicted that exhaustive purification of the auto-oxidizable substance ought to eliminate the induction period. The present study of the induction period in the oxidation of cyclohexene has indicated that impurities in the hydrocarbon itself contribute quite largely to the vanishingly small initial rate but even the most exhaustive purifica-

tion failed to remove the induction period entirely. In contrast to this experience, several investigators⁶ have found that carefully purified benzaldehyde shows no induction period, whereas the less pure material used by earlier investigators does. A similar effect upon the oxidation of other substances has also been reported.⁷

Some investigators have reported precisely the opposite effect of purification. Hyman and Wagner⁸ found that isopropylethylene showed a much longer induction period after than before purification. In this case, however, the purification consisted of treatment with 2:1 sulfuric acid, which would unquestionably be attended by formation of some alcohol. A trace of the latter might cause more inhibition than the significant amount of other impurities removed by the sulfuric acid. The effect of exhaustive purification upon benzaldehyde,⁹ which has been reported to be completely inert toward oxygen, offers the one well-authenticated case of its kind and even in this case it is not certain that the apparent inertness is not due to a rapid auto-inhibition^{6c} (p. 2302). The most highly purified cyclohexene has shown no indication of such a behavior.

If pure benzaldehyde actually is inert toward oxygen one might be tempted to conclude that this fundamental inertness is the cause of the induction period. However, when one recalls the fact that the induction period ordinarily observed is removed by purification, it becomes apparent that the latter must be considered quite apart from the effect of exhaustive purification. The induction period shown by benzaldehyde seems to be due to inhibition and it was somewhat of a surprise to find that no amount of purification of cyclohexene would cause it to start oxidizing at its maximum rate.

Experimental

The early work on the oxidation of cyclohexene consisted of a series of attempts to remove all sources of in-

(1) Presented before the Division of Physical and Inorganic Chemistry at the 88th meeting of the American Chemical Society, New York, N. Y., April 22-26, 1935.

(2) Genthe, *Z. angew. Chem.*, **19**, 2087 (1906).

(3) See Milas, *Chem. Rev.*, **10**, 308 (1932).

(4) Stephens, *J. Ind. Eng. Chem.*, **24**, 919 (1932).

(5) Bäckström, *Medd. Vet.-Akads. Nobelinstit.*, [15] **6**, 19 (1927).

(6) (a) Reiff, *THIS JOURNAL*, **48**, 2898 (1926); (b) Bäckström, *ref. 5*, p. 23; (c) Almquist and Branch, *THIS JOURNAL*, **54**, 2294 (1932).

(7) Brunel, *ibid.*, **45**, 1336 (1923); *Ref. 3*, p. 309.

(8) Hyman and Wagner, *THIS JOURNAL*, **52**, 4348 (1930).

(9) Kuhn and Meyer, *Naturwissenschaften*, **16**, 1028 (1928); Wieland and Richter, *Ann.*, **495**, 284 (1932); Raymond, *J. chim. phys.*, **28**, 421 (1931).

hibition both through purification of the hydrocarbon and cleaning of the apparatus employed. Oxidation of 300-cc. samples of the hydrocarbon was carried out in an automatic circulator. Circulation was effected by a piston with ball valve with a piece of iron tubing sealed in the upper part of the plunger, the piston being actuated by a solenoid with intermittent field. The part of the apparatus in which oxidation took place contained no stopcocks and was connected to the high vacuum and oxygen and nitrogen supplies through a specially constructed mercury shut-off valve, the enclosed volume being 1510 cc. Allowing for the 300-cc. sample of hydrocarbon used each time, the volume of oxygen accommodated was 1210 cc. This section of the apparatus was enclosed in a large air thermostat equipped with high-speed fan directed downward toward the heating unit. The temperature was regulated by means of a bi-metallic coil and relay, at $28 \pm 0.1^\circ$. All runs were made by following manometrically the disappearance of oxygen from an enclosed volume at the above temperature. The manometric method was shown to be justified, as negligible amounts of gaseous by-products were formed in the duration of the experiments.

Only the general trend of the effect of purification is of importance; therefore only the last and most satisfactory method of purification will be mentioned.

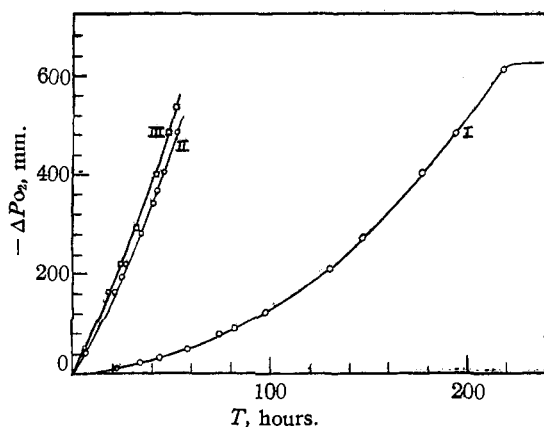


Fig. 1.

Two liter flasks with tall columns equipped with side-arms and condensers were connected in series, leading to accessory receptacles sealed to the circulator. After the whole apparatus had been exhaustively cleaned with hot cleaning solution, washed with hot conductivity water, baked out in high vacuum and filled with oxygen-free nitrogen, both flasks and columns were packed with sodium ribbon from carefully purified sodium. The latter was introduced against a counter current of oxygen-free nitrogen escaping from the apparatus. The flasks were separated by an internally broken bulb in the first side-arm, a by-pass around this bulb being used in preliminary operations and sealed off when its purpose had been served.

Ordinary cyclohexene was fractionated several times through an 80-cm. column packed with iron chain, making generous discards at the beginning and end. The last of these distillations was made in an atmosphere of tank nitrogen.

The main fraction of hydrocarbon was then introduced

into the first of the sodium-packed flasks referred to above and the latter was sealed. In this and similar cases the seal was made while oxygen-free nitrogen escaped from the apparatus. The cyclohexene vapor was prevented from reaching the seal by means of an asbestos wrap soaked with liquid air. The hydrocarbon was then heated to $115\text{--}120^\circ$ in the closed system for one week, cooled, the bulb leading to the second flask broken and the liquid fractionated during the slow escape of nitrogen from an open capillary. A receiver for the first discard was cut off and the open end sealed before distilling the main fraction into the second sodium-packed flask. A similar fractionation from the latter, followed by a low-temperature distillation and complete removal of dissolved gases, completed the purification. The last step was considered necessary in view of the probable presence of hydrogen, which might conceivably have acted as an inhibitor. Three different batches of purified cyclohexene showed boiling points, reduced to 760 mm., of 82.69, 82.72 and 82.68°, respectively. Waterman reports a boiling point of 82.8° at 759 mm.¹⁰

Oxygen was purified by passing over copper oxide at 450° and nitrogen successively over copper oxide at 450° and copper turnings at 400° . Both gases were delivered to the apparatus through tubes containing solid potassium hydroxide and magnesium perchlorate, respectively, and after passing the last stopcock through an efficient liquid air trap.

After charging the circulator, the magnetic pump was started, the thermostat brought up to temperature and oxygen introduced up to approximately 600 mm. pressure through the mercury valve. When the oxygen was introduced, the cyclohexene vapor was, of course, swept ahead of it and constant pressure readings were not obtainable until this vapor had time to diffuse throughout the apparatus. This required forty-five minutes or longer, during which time the observed pressure gradually rose to a constant value, which was maintained for several hours.

The general characteristics of the reaction are illustrated by Fig. 1. Curve I represents the first addition of oxygen and curves II and III successive additions after the oxygen had been completely absorbed. It will be obvious from these curves that the reaction is essentially zero order with respect to oxygen—at least down to fairly low pressures of the latter. The last point on curve I corresponds to 608 mm. whereas 611 mm. of oxygen were introduced into the apparatus. This particular curve shows the sharpest break observed but in other cases the rate of disappearance of oxygen did not fall off sharply until its pressure was less than 20 mm. Successive refillings with oxygen yield absorption curves which approach more and more closely to straight lines except for a very slight inflection at the bottom of the curve which persists. The system may be allowed to stand for two months before refilling without appreciably affecting this inflection and it appears to be altogether due to a lag in the diffusion of oxygen.

Several different methods of plotting the oxygen absorption data were attempted in an effort to obtain a straight line relationship. None of these yielded perfectly straight lines but the plots of the logarithm of disappearance of oxygen against the logarithm of time showed only slight inflections.

(10) Waterman, *Rec. trav. chim.*, **48**, 637 (1929).

It is significant that the reaction is essentially, if not exclusively, a liquid phase reaction. Cyclohexene has a vapor pressure at 28° of more than 10 cm. and if any appreciable amount of reaction took place in the gas phase one would expect visible accumulation of oxidation products on the walls of the apparatus. However, a careful examination of the walls, even after experiments of long duration, involving the refilling of the apparatus with oxygen a number of times, indicated at most only traces of oxidation products.

The Effect of Purification.—It has been indicated that the above description of technique refers to later runs. A series of runs in which the precautions taken gradually approached those described yielded curves of regularly increasing steepness and diminishing "inhibition period" but even the most carefully purified material did not start oxidizing at maximum rate. A run carried out in the complete absence of mercury vapor, which was regarded as a possible inhibitor, checked curve I, Fig. 1 very closely, showing that mercury is without affect.

In this latter run the mercury valve connecting the apparatus with the vacuum line, was replaced by a series of internally broken capillaries, which lengthened tremendously the time required to pump the cyclohexene free from gases. At the end of this long evacuation, during which liquid air was kept around the cylinder containing the cyclohexene, a readily observable amount of a white solid had deposited on the inner wall of the tube above the cylinder. After the run had been completed, the tube was washed out with concd. hydrochloric acid and the Marsh test applied to the solution. The presence of arsenic indicated that the deposit must have been arsenic trioxide, which is present in small proportion in Pyrex¹¹ and which must have migrated from the body of the glass.

The Effect of Arsenic Trioxide.—As arsenic trioxide was a possible inhibitor of oxidation, its effect upon the induction period was later investigated. Three small reaction vessels with magnetically actuated plungers were constructed, as nearly as possible of the same dimensions—two of Pyrex and one of quartz. The three vessels were exhaustively cleaned and connected to a system which could be opened through an internally broken capillary to a supply of highly purified cyclohexene. After baking out the whole apparatus, 1 mg. of resublimed c. p. arsenic trioxide was introduced into one of the Pyrex vessels and the latter warmed gently *in vacuo* to vaporize the substance upon the walls. The cyclohexene was then admitted to the system, 10-cc. samples (25°) condensed in each of the reaction vessels and each sealed off in high vacuum.

The oxygen absorptions were measured by connecting the vessels in turn to a suitable system containing a manometer and leading through a capillary to the vacuum and oxygen supply. The capillary was sealed during the introduction of oxygen, when the pressure of the latter reached approximately 600 mm. The reaction vessel was also opened to the system through an internally broken capillary during the admission of oxygen. The enclosed volume was 82.5 cc.

Figure 2 contains the oxygen absorption curves (I, II, III) for the above three samples of cyclohexene. The

curve for the quartz vessel includes points from another previous run, illustrating the possibility of obtaining perfect checks when surface conditions, purity, etc., are constant. It is clear from these curves that arsenic trioxide on the glass surface exerts a pronounced inhibitory action and it appears justifiable to conclude that the essential difference between quartz and Pyrex lies in the arsenic trioxide content of the latter.

The large effect of arsenic trioxide upon the induction period, coupled with its insolubility in hydrocarbons, points to the inhibiting effect being localized at the glass surface. However, even the runs in quartz showed a considerable period of vanishingly slow rate and in these cases it is difficult to conceive of a specific inhibitor being associated with the wall—particularly after the rigorous cleaning and baking in high vacuum at red heat. If the excessively slow reaction in the initial stage of the oxidation in quartz is also due to inhibitors at the surface, the inhibitors must have been selectively adsorbed from the cyclohexene.

The view that inhibition takes place largely at the surface of reaction vessels has recently received considerable attention,¹² but if such an inhibition accounted for the induction period observed in the quartz vessel, it ought to have been possible to eliminate it by selective adsorption of the inhibitor on silica gel, before introducing the cyclohexene into the apparatus. To this end, a sample of pure cyclohexene was completely adsorbed on highly purified silica gel, approximately two-thirds condensed off by means of liquid air, the condensate adsorbed on a fresh sample of the gel and about one-half condensed off.

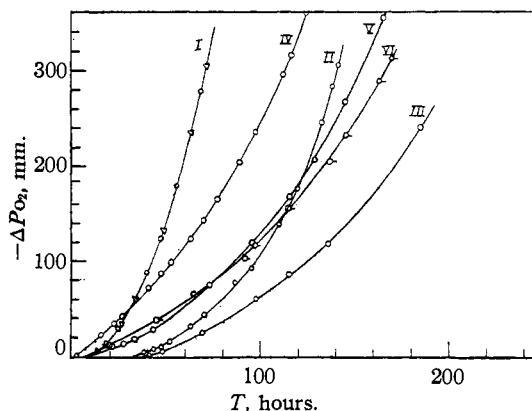


Fig. 2.—Effect of nature and extent of surface: I, quartz vessel; II, Pyrex vessel, III, Pyrex vessel + As_2O_3 ; IV, quartz vessel + 1 g. quartz fibers; V, large Pyrex circulator; VI, large Pyrex circulator + 2 g. of glass wool.

The oxidation of a 10-cc. sample of cyclohexene treated in the above way is shown in curve IIa, Fig. 3, and a comparison of this with curve I, which represents the oxidation of the material before adsorption on silica gel, indicates a large effect opposite to that anticipated. The operation was then repeated, collecting the last fraction of hydrocarbon condensed off the first portion of silica gel and the first fraction from the second adsorption. In order to

(11) This work was done before the present arsenic-free Pyrex was available.

(12) Rideal, *Inst. intern. chim. Solvay, Conseil chim.*, p. 586 (1925). Ref. 6a, p. 2894.

facilitate removal of the firmly retained last fraction, the silica gel was warmed to about 60° , toward the end of the condensation. The condensate was contaminated by a visible amount of water, which, as will be shown presently, exerts an inhibitory effect on the oxidation; therefore, both fractions were dried by vaporizing very slowly through calcium oxide, prepared by calcining reagent calcium carbonate for twelve hours at approximately 900° . Curves II and III in Fig. 3 represent the oxidation of the first and last fractions, respectively. If any concentration of inhibitor took place, it was in the first instead of the last fraction, which would imply a smaller adsorption on silica than for cyclohexene itself. However, neither fraction showed as short an induction period as the material which had not been exposed to silica gel—a fact which suggests contamination with an inhibiting impurity. Such an impurity might conceivably arise from a trace of hydration, dehydrogenation or polymerization at the silica surface but the absence of evidence precludes any definite conclusion. The only thing that can be said with confidence is that the longer inhibition period in curve II as compared with curve III cannot be due to inhibitors which are preferentially adsorbed on silica. By analogy, serious doubt may be expressed as to whether the inhibition period shown in curve III is due to this cause.

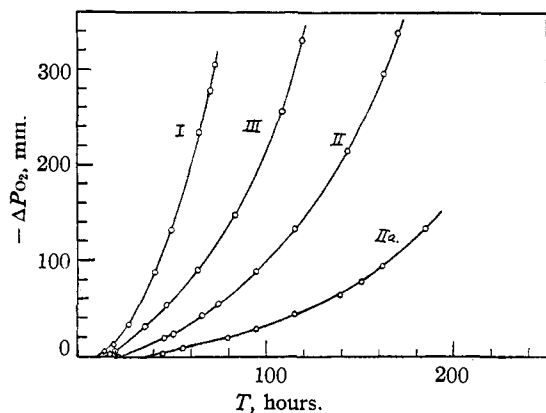


Fig. 3.—Effect of adsorption on silica gel: I, Control; IIa, 1st fraction condensed off silica gel; II, 1st fraction condensed off silica gel (dried); III, last fraction condensed off silica gel; IIa, last fraction condensed off silica gel (dried).

The Effect of Water.—A comparison of curves IIa and II, Fig. 3 indicates the effect of a trace of water (IIa) upon the induction period. The same effect has been observed both in the large Pyrex and the small quartz apparatus when highly purified water was added in very small amounts. In Fig. 4 there are plotted oxygen absorption curves (IV, V) for the large Pyrex circulator, illustrating the effect of the addition of 0.012 g. of water to 300 cc. of cyclohexene (V). Curves I, II and III represent the effect of additions of 0.3 mg. of water to 10 cc. of hydrocarbon two hours after the oxygen had been admitted (II) and of 0.24 mg. of water when the cyclohexene was introduced into the apparatus (III). In the latter run oxygen was admitted a number of hours later, after the water had had ample time to be adsorbed on the wall.

The Effect of Increased Surface.—In the foregoing evidence there have appeared at least two indications that the

auto-oxidation of cyclohexene is initiated at the wall of the reaction vessel, namely, the inhibitory effects of arsenic trioxide and of water. If it is assumed that chains start at the wall, the efficiency of an extremely small amount of arsenic trioxide may be explained on the basis of its favorable location. Also the fact that the effectiveness of a small addition of water is greater if the water is added before oxygen is admitted, indicates that the function of the water is to mask the active surface.

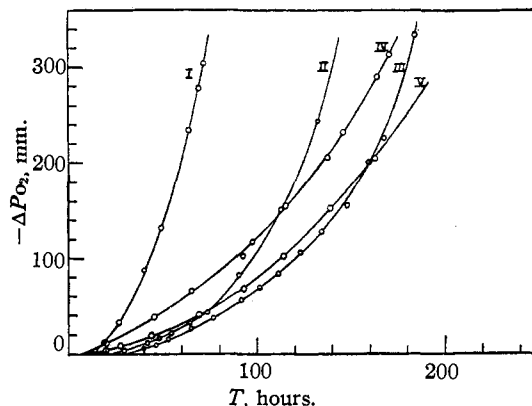


Fig. 4.—Effect of water: I, quartz vessel, no H_2O added; II, quartz vessel + 0.3 mg. H_2O after O_2 ; III, quartz vessel + 0.24 mg. H_2O before O_2 ; IV, large Pyrex circulator—no H_2O ; V, large Pyrex circulator + 0.012 g. H_2O after O_2 .

If such inferences are warranted, one would expect to find an increase in rate if the glass or quartz surface were increased. Curves VI and IV in Fig. 2 illustrate the effect of such increased surface in the large Pyrex circulator and the small quartz vessel, respectively. These are to be compared with curves V and I which represent the normal surfaces of the respective vessels. In the former case 2 g. of glass wool was introduced into the circulator, producing a total surface 4.5 times (minimum value) the original. In the latter, the surface was increased by packing the plunger with 1 g. of quartz fibers, leaving holes in the upper and lower parts so that the hydrocarbon could circulate freely through the packing on each stroke. The increased quartz surface was approximately eleven times (minimum value) the original.

Although the effect of increased surface is very similar in the two examples, by far the more striking effect was observed in the quartz vessel. The disproportionately smaller effect in the Pyrex circulator is probably due to the damping influence of inhibition by arsenic trioxide. It will be noted that the curve for the packed quartz vessel intersects the time axis almost at the origin, thus illustrating the virtual disappearance of the region of immeasurably slow reaction. As oxygen absorption may have started before the zero-point reading was obtained, the true intersection with the time axis is probably earlier than the observed. In each case the increase in rate with time is slower for the packed than for the unpacked vessel.

The disappearance of the inhibition period in the quartz apparatus attendant upon an extension of surface might be explained by incomplete coverage of the large surface by preferentially adsorbed inhibitor. This, however, is in-

consistent with evidence already presented. The only obvious alternative is based upon the assumption that the initial rate is proportional to the area of the solid-liquid interface, but the evidence unfortunately does not permit a precise interpretation.

TABLE I
MAXIMUM RATE OF OXYGEN ABSORPTION PER 10 CC.
C₆H₁₀

Apparatus	Max. rate, cc./hr.
Large Pyrex circulator	0.48
Large Pyrex circulator + glass wool	1.05
Small Pyrex vessel	1.25
Small quartz vessel	1.30
Small quartz vessel + quartz fibers	0.90

Maximum Rates.—Table I indicates the maximum rates of oxygen absorption in several selected runs. These values were obtained by introducing successive samples of oxygen after each was used up, until the maximum rate had been reached or passed. A comparison of the rates in the small Pyrex and quartz vessels indicates that the nature of the surface has very little, if any, effect on the maximum rate, although the extent of surface has a very large effect. The "maximum" given for the increased surface in the large Pyrex circulator is somewhat less than the true maximum, as it was impossible to circulate the cyclohexene rapidly enough with the magnetic pump employed. In view of the large effect obtained in the Pyrex vessel it may seem rather surprising that the packed quartz vessel showed a smaller maximum rate than the unpacked. The explanation of this apparent paradox is probably to be found in the relative spaces within the liquid occupied by the packing. In the large Pyrex apparatus the 2 g. of glass wool occupied only a very small fraction of the volume of the liquid, whereas in the small quartz vessel very little free liquid space was left. If it is now assumed that chains may be terminated at the walls, the low maximum rate in the latter case may be explained. Lenher¹³ has also found it necessary, in his study of the oxidation of ethylene, to assume that chains were both initiated and terminated at the walls.

The Autocatalytic Theory.—It has been mentioned above that the early increase in rate with time commonly has been attributed to autocatalysis by the intermediate peroxide. To test the applicability of this viewpoint in the present work a group of runs have been compared in Table II on the basis of the amount of oxygen absorbed by 10 cc. of cyclohexene, up to the time when the

(13) Lenher, *THIS JOURNAL*, 53, 2420 (1931).

TABLE II
AMOUNTS OF OXYGEN ABSORBED PER 10 CC. OF C₆H₁₀ (25°)
IN PRODUCING RATE OF ABSORPTION OF 0.15 CC./HR./10
CC. C₆H₁₀

Apparatus and Conditions	O ₂ absorbed, cc. N. T. P.
Large Pyrex circulator ^a	13
Large Pyrex circulator	9.1
Large Pyrex circulator + 2 g. glass wool	6.25
Quartz, H ₂ O added after O ₂	4.5
Quartz + 1 g. quartz fibers	2.0
Quartz, no addition	1.5

^a C₆H₁₀ not as highly purified as in other cases.

rate of absorption had reached the arbitrarily selected value of 0.15 cc. per hour per 10 cc. of hydrocarbon. According to the autocatalytic theory the rate would be dependent upon the concentration of peroxide and that in turn upon the amount of oxygen which had been absorbed; therefore the oxygen absorbed ought to be constant for different runs. Table II¹⁴ illustrates how far this is from being the case and indicates that autocatalysis can, at most, play an insignificant part in the early increase in rate with time. If some convenient term descriptive of the increasing rate is still desired, the general term "auto-acceleration" might be used to supplant "autocatalysis."

Discussion

It has been shown that the auto-oxidation of cyclohexene is essentially zero order with respect to oxygen—a fact which suggests some rate-determining factor independent of the concentration of oxygen. It has also been shown that the reaction is strongly influenced by the solid surface area. These two characteristics are most simply explained by assuming that the rate determining factor is the rate of activation of hydrocarbon molecules and that the process of activation occurs at the wall. There can be no confusion here between the respective effects of solid-liquid and liquid-gas interfaces, although Bailey¹⁵ has recently pointed out that this confusion does exist in works purporting to show that the rate of oxidation of benzaldehyde is dependent upon the area of the solid-liquid interface. In this work an increase in the solid-liquid interface was necessarily accompanied by an increase in the liquid-gas interface and Bailey has assumed that it is in the latter region that the reaction is initiated. It must be conceded that the effect of surface in the

(14) It has unfortunately been impossible to study the effect of additions of peroxide due to the impossibility of obtaining it in even a reasonably pure state.

(15) Bailey, *J. Chem. Soc.*, 114 (1930).

small quartz apparatus with fiber-packed piston might be questioned on a similar basis, as the piston rose above the surface of the liquid on each stroke and thus caused an increase in the liquid-gas interface. However, the glass wool used to increase the surface in the large Pyrex circulator was completely and continuously submerged in the liquid, yet a similar effect was observed in this case. Also, the inhibitory effects of arsenic trioxide and of water offer contributory evidence in favor of the solid-liquid interface being the region in which chains are initiated.

Now if chains are initiated at the wall, it is easy to see why there should be a period of vanishingly slow rate in Pyrex vessels, because the arsenic trioxide present at the wall would be in a favorable position to interrupt the chains at the first link. In a quartz vessel, however, this inhibition period has no such obvious explanation—particularly in view of the fact that the evidence is opposed to the idea that inhibitor in the liquid is selectively adsorbed at the surface. The hydrocarbon might be assumed to be firmly adsorbed or to undergo some change at the active points, thus providing a temporary shield; but this assumption is inconsistent with the fact that an 11-fold increase in quartz surface increases tremendously the initial rate. A larger area would be just as effectively shielded as a smaller one by such a process.

Apparently the only satisfactory explanation is based upon the assumption that the initial rate is simply the rate of the surface reaction, with no propagation of chains or, at most, with a relatively low probability of propagation. The increase in rate would then be due to an increasing probability of chains being propagated. In the quartz vessel it appears necessary to assume that the wall itself must be conditioned in some way so that hot molecules of reaction product may be allowed to pass on their energy to other hydrocarbon molecules instead of dissipating it at the surface upon which they are formed. The probability that such a dissipation of energy is im-

portant is emphasized by the fact that the maximum rate in the packed quartz vessel is strongly suppressed—a fact which seems explainable only on the basis of interruption of chains by the surface itself.

Granted the validity of the above interpretation, the maximum rate of oxidation in a given piece of apparatus will depend upon the available surface area at which chains may be initiated. It will be limited by the free space within the liquid in which chains may be propagated.

The attainment of maximum rate will depend upon the following factors:

(1) Destruction of inhibitors on the wall, such as arsenic trioxide in the case of Pyrex vessels.

(2) Conditioning of the wall in such a way as to allow hot molecules of product to act as the first links in chains instead of having their energy dissipated at the wall. The primary factor in maximum rate would thus be maximum probability of a chain resulting from a surface activation.

(3) Destruction of inhibitors present in the body of the liquid, so that chains, already initiated, may attain their maximum length.

(4) The time required for attainment of maximum rate will be determined by the balance between initiation and interruption of chains at the surface. If the former increases from a minimum efficiency while the latter decreases from a maximum we have a plausible explanation of the lag observed in the attainment of maximum rate in the fiber-packed vessels.

Summary

A detailed study of the various factors which contribute to the induction period in the auto-oxidation of cyclohexene, leads to the conclusion that the phenomenon is due almost, if not quite, exclusively to inhibitory effects, which retard the attainment of maximum rate. The evidence is entirely opposed to the older theory which attributes the increase in rate with time to autocatalysis.

MINNEAPOLIS, MINN.

RECEIVED JULY 5, 1935