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Kinetic Study of the Liquid-Phase Oxidation of Cyclohexene Catalyzed by Manganese Dioxide

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The oxidation of cyclohexene has been studied in the liquid phase over the temperature range 40 to 70°C, using as catalysts three types of manganese dioxide with different specific surfaces. Short reaction periods (up to 60 min) were used to study the initial activity of the catalyst.

The maximum rate of cyclohexene oxidation was 0.5 order with respect to the catalyst in the region of low catalyst weight to hydrocarbon volume ratios; a much lower order was found for high ratios. Above a critical amount of catalyst, the oxidation was completely inhibited due to the quantitative decomposition of hydroperoxide.

The maximum oxidation rate proved to be first order with respect to the concentration of cyclohexene.

The oxidation rate was zero order with respect to the initial hydroperoxide concentration in the range of 3×10^{-3} to 0.5 mole/liter, giving support to the theory that free radicals were produced from the slow decomposition of a catalyst–hydroperoxide complex. Oxidation products such as cyclohexenol and cyclohexenone inhibited the oxidation rate when they were initially present in concentrations greater than 50 μmole/ml.

Apparent activation energies for the oxidation ranged between 11.4 and 13.0 kcal/mole.

Product distribution studies showed that cyclohexenol and cyclohexenone were produced in nearly equal amounts. A degenerate chain branching mechanism is proposed in which the catalyst plays an important role in the initiation and termination steps. Rate equations derived from this mechanism explained qualitatively the experimental observations.

INTRODUCTION

The autoxidation of cyclohexene in nonpolar media catalyzed by various soluble transition metal salts has been reported (*1*). It was concluded that free radicals were initiated from a reaction between the catalyst and the hydroperoxide involving a redox process with the metal. Initiation generally involved the breakdown of a catalyst–hydroperoxide complex and termination of reaction chains by the catalyst occurred to a variable extent depending on the catalyst. The same mode of initiation was confirmed by work on the oxidation of cyclohexene in an acetic acid medium catalyzed by a cobalt salt (*2*). Moreover, a limiting rate phenomenon was observed with increasing catalyst concentration, which suggested that the rates of formation and destruction of hydroperoxide in the system became equal (*3*).

It was found that, for the heterogeneous liquid-phase oxidation of cyclohexene catalyzed by transition metal oxides, the activity of the oxides was closely related to the activity of soluble acetyl-acetonates of the same metal ion (*4*). This could lead to the conclusion that the reaction mechanisms are similar for both types of catalysts.

Initiation by direct interaction of catalysts and cyclohexene was reported (*5*,*6*). However, it was found that the oxidation of cyclohexene catalyzed by MnO_2 would not take place in the complete absence of hydroperoxide (*7*).

The purpose of the present work was to

establish the nature of the initiation and termination steps for the MnO_2 catalyzed oxidation of cyclohexene. To emphasize the role of the catalyst, initial oxidation periods (up to 60 min) were considered.

The chain branched character of the generation of free radicals was confirmed, and the data obtained permitted the proposal of a reaction mechanism for the oxidation process which explained the simultaneous formation and destruction of hydroperoxide.

EXPERIMENTAL METHODS

Apparatus

The reaction was performed in 10 ml tubes with Teflon-coated joints which fitted into an inner joint connected by means of a flexible tube to an apparatus similar to that used by Bolland (*8*). A reaction vessel containing the desired amount of catalyst was placed in an acetone–solid carbon dioxide mixture, and 2 ml of a previously prepared reactant solution were added slowly to the reactor to avoid suspension of the catalyst. The reactor was connected to the system and the gas phase was flushed several times and replaced with dry oxygen. The reactor was attached to a wrist-action shaker to achieve vigorous agitation and plunged into a thermostat, the temperature of which was controllable to within ±2°C.

The volume of oxygen consumed was directly measured at different time intervals from a gas buret. The reactions were carried out at constant pressure which was maintained by the evolution of gas from a small electrolytic cell.

After a run was over, the reactor with its contents was dipped into the acetone–solid carbon dioxide mixture to arrest any further oxidation prior to analysis, and the catalyst was allowed to settle. The clear liquid phase was removed by a syringe from the reactor for analysis.

Reactants

Cyclohexene (BDH), was purified as described elsewhere (*2*), and stored under nitrogen in the dark cold. Cyclohexenyl hydroperoxide was prepared as described previously (*9*). Monochlorobenzene was used as inert solvent for the dilution experiments of cyclohexene oxidation. 2-Cyclohexene-1-ol, 2-cyclohexene-1-one and cyclohexene oxide were obtained from the Aldrich Chemical Co. Inc.

Analytical Procedures

The same method as described for an oxidized mixture of cyclohexane (*10*) was used in the present work. Part of the sample was titrated for hydroperoxide by the iodometric method (*11*) and the rest was treated with sufficient triphenyl phosphine for quantitative conversion of hydroperoxide into cyclohexenol (*12*). The treated sample was then analyzed for cyclohexene oxide, cyclohexenone, and cyclohexenol by chromatographic methods.

Catalysts

Three different manganese dioxides were used as catalysts.

Catalyst A (Fisher Scientific Co.) was a nonporous low surface area catalyst. The specific surface as determined by BET nitrogen adsorption was 0.9 m^2/g. Its structure, determined by X-ray, corresponded to βMnO_2.

Catalyst B proved to be a nonporous γMnO_2 with a specific surface as determined by BET nitrogen adsorption of 32.0 m^2/g. Further characteristics of this catalyst are given elsewhere (*13*).

Catalyst C was "Special Manganese Dioxide" (Fisher Scientific Co.). X-Ray diffraction analysis showed a disordered structure. After pretreatment with oxygen at 400°C, βMnO_2 was identified. The specific surface as determined by BET nitrogen adsorption was 87 m^2/g; about 77%

of the surface was associated with the internal porosity of the catalyst.

In all three cases, fractions of particle size smaller than 74 μm were used in the experiments.

RESULTS AND DISCUSSION

Effect of the Catalyst Weight to Liquid Volume Ratio

The influence of the catalyst ratio on the oxidation rate of cyclohexene at 60°C was studied for the three MnO_2 catalysts. Product distribution studies were undertaken using catalyst C (high specific surface MnO_2).

Figure 1 shows that the oxidation rates corresponding to catalyst A (low specific surface) increased steadily with catalyst until a certain catalyst ratio was reached after which the rate remained practically constant. For catalyst C, complete inhibition took place originally at a ratio of 9 mg MnO_2/ml, but addition of cyclohexenyl hydroperoxide to the starting solution permitted the increase of the catalyst amount up to values where the rate of oxygen absorption leveled off. The highest catalyst concentration shown for each curve is the maximum catalyst ratio prior to total inhibition.

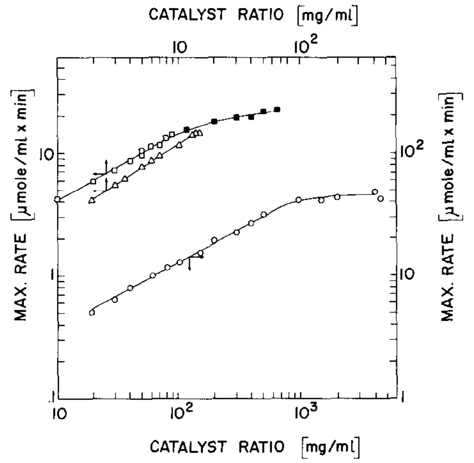


FIG. 1. Log of the maximum oxidation rate of cyclohexene at 60°C as a function of the log of catalyst ratio. (○) Catalyst A, (△) catalyst B, (□) catalyst C (trace hydroperoxide initially present), (■) catalyst C (82 μmole/ml of hydroperoxide initially present).

TABLE 1

Catalyst	Type	Catalyst order	Hydrocarbon order	E_a (kcal/mole)
A	βMnO_2	0.54 ± 0.02	1.0 ± 0.1	11.4 ± 1.4
B	γMnO_2	0.63 ± 0.02	1.1 ± 0.1	11.6 ± 1.3
C	βMnO_2	0.57 ± 0.03	0.98 ± 0.2	13.0 ± 1.1

Reaction orders with respect to the catalyst ratio were determined from the slopes of the curves shown in Fig. 1, considering all points at catalyst ratios below the apparent change in mechanism as indicated by the break in the straight lines. The values obtained are presented in Table 1.

Meyer *et al.* (*5*), when studying the influence of the solid surface to liquid volume ratio on the MnO_2 and CoO catalyzed oxidation of cyclohexene, found a reaction order of 0.7 with respect to these catalysts. The idea of heterogeneous initiation and homogenous termination of the chains was accepted, since had the initiation been first order with respect to the catalyst and the termination biradical, an overall order of 0.5 would have been obtained. No explanation was given to justify the discrepancy between the theoretical 0.5 order and the value of 0.7 obtained experimentally. This type of deviation has been reported by other authors (*6,14*) and is also evident in the present study.

For long oxidation chains, the rates of the propagation reactions

$$R^{\cdot} + O_2 \xrightarrow{k_o} RO_2^{\cdot}, \qquad (1)$$

$$RO_2^{\cdot} + RH \xrightarrow{k_p} ROOH + R^{\cdot} \qquad (2)$$

can be considered equal. If oxygen evolved from the biradical termination

$$2RO_2^{\cdot} \xrightarrow{k_t} \text{inert products} + O_2 \qquad (3)$$

is neglected with respect to oxygen absorbed in the propagation, the rate of oxidation can be expressed as:

$$\frac{-d[\mathrm{O_2}]}{dt} = \frac{-d[\mathrm{RH}]}{dt} = k_p[\mathrm{RH}]\left(\frac{R_i}{2k_t}\right)^{1/2}, \tag{4}$$

where R_i stands for the rate of free radical initiation.

It has been established (*15,16*) that for short chain lengths the previous assumptions are not valid any longer. For the simplified mechanism presented above, a more general expression for the rate of oxygen consumption can be derived without introducing these assumptions:

$$\frac{-d[\mathrm{O_2}]}{dt} = \frac{R_i}{2} + k_p[\mathrm{RH}]\left(\frac{R_i}{2k_t}\right)^{1/2}. \tag{5}$$

If the rate of free radical initiation is proportional to the catalyst weight to liquid volume ratio, the increase of the reaction order with respect to catalyst from the value of 0.5 will depend on the influence of the term $R_i/2$.

The opposite effect of reaction orders less than 0.5 with respect to catalyst concentration has also been reported (*1*) and attributed to inhibiting properties of the catalyst.

As shown in Fig. 1, for catalyst A, the oxidation rate reached practically a constant value for catalyst ratios over 1000 mg/ml. This behavior has been widely observed in homogeneously catalyzed oxidations of hydrocarbons (*2,17,18*). Tobolsky *et al.* (*19*) have suggested that the initiation of free radicals in metal catalyzed oxidations is due to degenerate chain branching, and when the rates of formation and decomposition of hydroperoxide in the solution become equal, hydroperoxide reaches a stationary concentration whereupon a limiting oxidation rate is reached.

The rate of hydroperoxide formation during the chain branched oxidation can be written as:

$$\frac{d[\mathrm{ROOH}]}{dt} = \frac{k_p}{(2k_t)^{1/2}}(R_i)^{1/2}[\mathrm{RH}] - R_d, \tag{6}$$

where R_d is the rate of hydroperoxide decomposition.

If, as considered by Kamiya *et al.* (*18*), the rate of free radical initiation is equal to the rate of hydroperoxide decomposition, and if, moreover, these rates are first order with respect to hydroperoxide and *n*th order with respect to catalyst concentration, Eq. (*6*) becomes:

$$\frac{d[\mathrm{ROOH}]}{dt} = \frac{k_p}{(2k_t)^{1/2}}(k_1'[\mathrm{ROOH}][\mathrm{M}]^n)^{1/2} \times [\mathrm{RH}] - k_1'[\mathrm{ROOH}][\mathrm{M}]^n. \tag{7}$$

Equation (7) shows that the rate of hydroperoxide formation may become zero in two different circumstances: first, with the increase of hydroperoxide concentration during oxidation up to a steady state concentration value for a fixed catalyst amount; and second, at a critical catalyst concentration for a fixed initial concentration of hydroperoxide.

The first situation has proven to be true for the cobalt catalyzed autoxidation of tetralin in a medium of acetic acid (*17,18*), giving support to Tobolsky's theory. A steady state concentration of hydroperoxide was obtained complying with the equation:

$$[\mathrm{ROOH}]_\infty = \frac{k_p^2[\mathrm{RH}]^2}{2k_1'k_t[\mathrm{M}]^n}, \tag{8}$$

from which the limiting theoretical rate of oxidation becomes:

$$-\left(\frac{d[\mathrm{O_2}]}{dt}\right)_\infty = \frac{k_p^2[\mathrm{RH}]^2}{2k_t}. \tag{9}$$

However, more often the rate-controlling step for the production of free radicals is the slow decomposition of a preformed catalyst–hydroperoxide complex (*1,20,21*). The same is true for the rate of hydroperoxide decomposition in metal catalyzed systems (*9,22*). In this case, R_i and R_d will become practically independent of hydroperoxide for relatively low peroxide concentration. Therefore, once the oxidation has started, hydroperoxide will not reach a steady state concentration and the hydroperoxide rate will become zero only with a sufficiently high (critical) initial concentration of catalyst.

If it is assumed that R_i and R_d are linearly related as:

$$R_i = \alpha R_d, \tag{10}$$

where α is the fraction of hydroperoxide decomposed yielding free radicals, then the limiting rate of oxidation will be given as:

$$-\left(\frac{d[\mathrm{O_2}]}{dt}\right)_\infty = \alpha \frac{k_p^2[\mathrm{RH}]^2}{2k_t}, \tag{11}$$

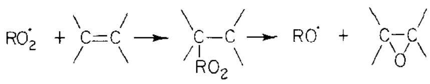
if only biradical termination is considered.

Equation (11) indicates that the limiting rate of oxidation in this case will be proportional to the square of the hydrocarbon concentration without the necessity of a steady state hydroperoxide concentration. The value of α which is less than one for many systems, prevents the limiting rate from reaching the theoretical maximum value given by Eq. (9).

In the present work the limiting rate found for catalyst A was about ⅓ of the theoretical rate given by Eq. (9) when using values of $k_p^2/2k_t$ obtained after extrapolating to 60°C those given by several authors for cyclohexene (*23,24,25*). The limiting-rate value found for catalyst A was similar to the one reported for the oxidation of cyclohexene in an acetic acid medium catalyzed by a cobaltous salt at 60°C (*2*).

In Fig. 1 the curve corresponding to catalyst C shows that for catalyst ratios over 10 mg/ml the rate of oxidation levels off from the 0.5 order observed for smaller ratios. However, the rate did not become independent of catalyst before complete inhibition was effective. A similar behavior has been reported (*26*) and attributed to a less efficient use of the catalyst as a result of agglomeration. In the present case, an increasing inhibiting effect of the catalyst due to termination of peroxy radicals on the surface of the solid is thought to be responsible for the observed rate decay.

Product distribution studies indicated that the oxidation products were cyclohexenyl hydroperoxide, cyclohexenol, cyclohexenone and cyclohexene oxide. The oxide was not analyzed quantitatively since its concentration was never greater than 1.6 μmole/ml in the reaction periods (up to 60 min) studied, a very low value compared with minimum concentrations of about 20 μmole/ml for alcohol and ketone. As reported for the oxidation of cycloalkenes (*24*), cyclohexene oxide is formed through the reaction:



(12)

It was found that in the whole range of time and catalyst ratios covered, the molar concentrations of alcohol and ketone produced are very similar. Therefore, it can be concluded that for times up to 60 min, the catalyst does not affect the selectivity of cyclohexenol and cyclohexenone. However, working with the same reacting system (*7*), it was found that for long reaction periods (up to 450 min), the concentration of cyclohexenol becomes greater than the concentration of cyclohexenone, the lower the catalyst ratio employed. These results contrast with the alcohol to ketone concentration ratios obtained for the decomposition of cyclohexenyl hydroperoxide in cyclohexene (*9*), where alcohol is produced in considerably larger amounts than ketone. A big difference between the two systems is that during oxidation a considerable steady concentration of peroxy radicals is established at the very early stages of the reaction, yielding a high biradical termination rate which is known to produce equimolar amounts of alcohol and ketone for secondary peroxy radicals (*27,28*).

The rates of alcohol and ketone formation increased linearly with catalyst, as would be expected from the biradical termination reaction. On the other hand, the rate of hydroperoxide formation was only slightly affected by the catalyst ratio in the range studied. If the rate of hydroperoxide formation through the propagation reaction is proportional to the 0.5 order of the catalyst ratio and the rate of hydroperoxide decomposition is first order with respect to the catalyst (*9*), it can be anticipated that variations of catalyst ratios in the neighborhood of the maximum hydroperoxide rate will show little influence on this rate.

Effect of an Inert Solvent

The dilution effect on the MnO_2 catalyzed oxidation rate of cyclohexene was studied at 60°C, using chlorobenzene as an inert solvent. Catalysts A, B and C were employed.

On performing the study of the solvent effect on the oxidation rate some precautions must be taken if the oxidation proceeds via a chain branching mechanism. The rate of oxygen consumption may present different reaction orders with respect to the hydrocarbon concentration, depending on the conditions of the oxidation. If the oxidation proceeds under conditions where the limiting rate has not been attained, the reaction order will be 1; under limiting rate conditions it is expected to be 2. [This is illustrated by Eqs. (4) and (9).] Kamiya *et al.* (*29*) stated that at low hydrocarbon concentrations or comparatively high catalyst concentrations, an apparent order of 1.5 might be obtained. Such an order could lead to the incorrect conclusion that the hydrocarbon was involved in the rate controlling initiation reaction.

To determine the true influence of cyclohexene concentration on the oxidation rate, rates were measured in a region of catalyst ratios and hydrocarbon concentrations where the limiting rate of oxidation was not attained. This region was found by working with low catalyst ratios and high concentrations of cyclohexene. The experimental results are plotted in Fig. 2 for the three MnO_2 catalysts. Results of the reaction orders are presented in Table 1.

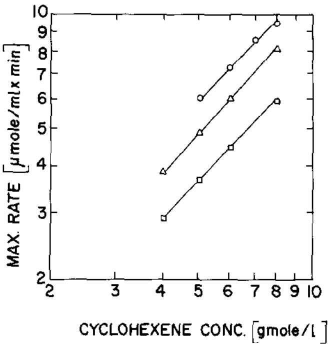


FIG. 2. Log of the maximum oxidation rate at 60°C as a function of the log of cyclohexene concentration. (□) catalyst A (30 mg/ml), (△) catalyst B (6 mg/ml), (○) catalyst C (5 mg/ml).

In general it can be said that the rate of oxygen consumption is first order with respect to the concentration of cyclohexene as expected by a rate law of the type indicated by Eq. (*4*). The same conclusion was reached by Meyer *et al.* (*5*) when studying the influence of solvents on the oxidation of cyclohexene with various metallic oxides.

The product distribution on the oxidation of cyclohexene for different concentrations in chlorobenzene was studied using catalyst C. A catalyst weight to liquid volume ratio of 5 mg/ml was used in each case, and the reaction temperature was maintained at 60°C. This study showed that although the rates of oxygen consumption and cyclohexenyl hydroperoxide formation showed a linear increase with the concentration of cyclohexene, the formation rate of final oxidized products (cyclohexenol and cyclohexenone) was practically independent of this parameter. This phenomenon gives support to a reaction mechanism where the rate equations for oxygen consumption and hydroperoxide formation are linearly dependent on hydrocarbon concentration, and the rates of cyclohexenol and cyclohexenone formation are independent of the hydrocarbon concentration.

A series of experiments were performed where solutions of cyclohexene in chlorobenzene of different concentrations were oxidized with increasing catalyst weight to liquid volume ratios. Catalyst C was employed and the reaction temperature was 60°C. The purpose of this set of experiments was to determine if, upon increase of the catalyst ratio, a limiting oxidation rate independent of catalyst would be obtained for each cyclohexene concentration.

The maximum oxidation rates of each run were plotted against the catalyst ratio in Fig. 3 for different concentrations of cyclohexene. The set of experiments was started with assumed hydroperoxide-free solutions. However, since the iodometric technique used to determine hydroperoxide quantitatively had a lower detection limit of about 3×10^{-3} g mole/liter, concentrations below this value could not be determined. Figure 3 shows that the maximum rate of oxidation increases with increasing catalyst ratios for each cyclohexene concentration, until, after a small increase in catalyst, a sharp complete inhibition takes place.

Inhibition phenomena have been frequently observed in catalyzed liquid-phase oxidations of hydrocarbons when employing soluble (*30,31*) and insoluble catalysts (*7,14,32*). It has been postulated that at the critical catalyst ratio the rate of hydroperoxide decomposition becomes equal to its rate of formation and that inhibition occurs with a slight increase in catalyst ratio due to the quantitative decomposition of hydroperoxide (*7*).

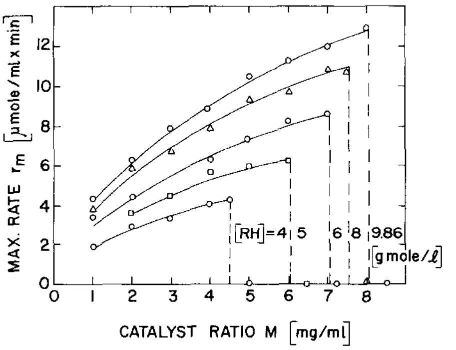


FIG. 3. Maximum oxidation rate of cyclohexene at 60°C as a function of catalyst ratio (catalyst C), for different concentrations of cyclohexene [RH].

The maximum rates of oxidation represented in Fig. 3 at the points of inhibition were plotted vs the corresponding concentrations of cyclohexene as shown in Fig. 4, curve 1. As shown, no straight line of slope 2 was obtained as would be expected from a limiting rate situation. Since the concentration of hydroperoxide was very small, it could have happened that for a sufficient amount of catalyst a quantitative adsorption of hydroperoxide onto the catalyst surface took place, producing inhibition before the limiting oxidation rate for the corresponding hydrocarbon concentrations could be attained.

In order to find out if the rate of oxidation would increase beyond the values found previously, a new group of experiments was performed with hydrocarbon concentrations of 4, 6 and 9.86 (pure cy-

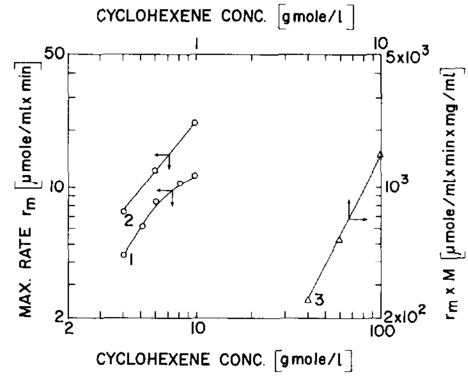


FIG. 4. Log of the maximum oxidation rate of cyclohexene at 60°C, at the critical catalyst ratio, as a function of the log of cyclohexene concentration. Initial hydroperoxide in trace amounts (1). Initial hydroperoxide concentration = 86 (μmole/ml) (2). Log of the maximum oxidation rate times the critical catalyst ratio as a function of the log of cyclohexene concentration. Initial hydroperoxide concentration = 86 (μmole/ml) (3).

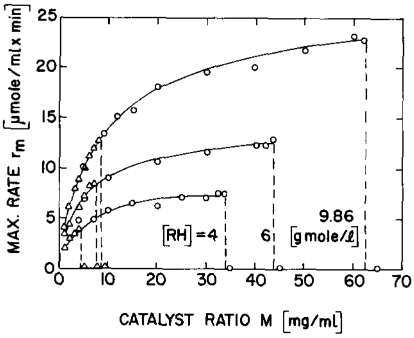


FIG. 5. Maximum oxidation rate of cyclohexene at 60°C as a function of catalyst ratio (catalyst C), for different concentrations of cyclohexene [RH]. (△) Experiments started with trace amounts of hydroperoxide, (○) initial hydroperoxide concentration = 86 (μmole/ml).

clohexene) g mole/liter. The runs were started with an initial cyclohexenyl hydroperoxide concentration of 82 μmole/ml. Results for the maximum oxidation rates vs the catalyst ratios are plotted in Fig. 5 together with the values obtained previously (low hydroperoxide concentration) for the corresponding concentrations of cyclohexene. Figure 5 shows that for all three concentrations of cyclohexene, the maximum rates of oxidation increased appreciably beyond the values where inhibition was effective when using solutions of low hydroperoxide content. This confirms that limiting rates of oxidation were not obtained previously, prior to the occurrence of inhibition.

In order to reach the break point where inhibition was effective, much higher catalyst ratios than those employed before had to be used. The points indicated as zero oxidation rates at 34, 45 and 65 mg/ml of MnO_2 cannot be considered strictly as such since oxygen consumption took place for about 1 min before complete inhibition occurred. In such a short time period, no measurements were possible for the determination of an oxidation rate and these points were plotted at zero rate to illustrate the advent of inhibition. After oxygen consumption had stopped, the system was left for about 30 min in the same reacting conditions to verify that the reaction would not commence. Analysis of the solution after this period indicated that hydroperoxide had decomposed quantitatively showing that the rate of hydroperoxide decomposition was larger than its rate of formation at complete inhibition.

It can be observed from Fig. 5 that occurrence of inhibition is not precisely related to a certain ratio of catalyst weight to hydroperoxide concentration (*14*). Although the same initial hydroperoxide concentration of 82 μmole/ml was provided for each cyclohexene dilution, inhibition was found at different catalyst ratios. This proves that the phenomenon is related to the fact that the rate of hydroperoxide formation is proportional to the first order of hydrocarbon concentration and its rate of decomposition is independent of this variable (9) as shown by Eq. (6).

The limiting rates were plotted against the three cyclohexene concentrations studied in Fig. 4, curve 2. It can be seen that, although the three points lie on a straight line, the slope of the curve is not 2 as expected for a second order dependency of the limiting oxidation rate upon hydrocarbon concentration. However, if the product of the limiting rate times critical catalyst ratio is plotted vs cyclohexene concentration (Fig. 4, curve 3), the points lie on a straight line of slope 2. It can therefore be concluded that the limiting rate of oxidation was proportional to the square of cyclohexene concentration, but inversely proportional to the first order of the critical catalyst ratio.

Effect of the Initial Cyclohexenyl Hydroperoxide Concentration

The influence of the initial hydroperoxide concentration on the maximum oxidation rate was studied starting the oxidation of cyclohexene at 60°C with a fixed catalyst ratio of 5 mg/ml of catalyst C, and

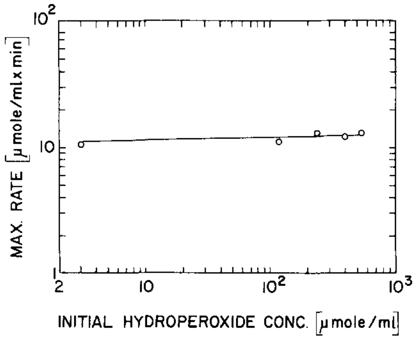


FIG. 6. Log of the maximum oxidation rate of cyclohexene at 60°C as a function of the log of initial hydroperoxide concentration. Catalyst C (5 mg/ml).

different initial concentrations of cyclohexenyl hydroperoxide.

Figure 6 shows that the maximum rate of oxidation is practically independent of the initial hydroperoxide concentration in the experimental range covered. The maximum rate of oxidation of the experiment performed with the supposedly hydroperoxide-free cyclohexene was plotted at the concentration corresponding to the detection limit of the analytical method since the real concentration was less than or equal to this value.

This type of behavior has been observed previously in catalytic liquid-phase oxidations of hydrocarbons. Several authors (*1,20,21,33*) working with soluble catalysts have attributed this phenomenon to the fact that the chain initiation reaction between catalyst and hydroperoxide is not a simple bimolecular reaction. Instead, the rate-controlling initiation step must involve the slow decomposition of a rapidly formed peroxide–catalyst complex.

In the case of heterogeneous catalysts, Gorokhovatsky (*32*) reported that the rate of radical initiation in the isopropylbenzene oxidation with NiO at 40°C was proportional to the hydroperoxide concentration over a range of 1.7×10^{-3} to 4.5×10^{-3} mole/liter. Increasing the concentration beyond 5×10^{-3} mole/liter gave no marked increase in the initiation rate, which remained practically constant. This indicated (as in the present work) that radical generation proceeds through the decomposition of hydroperoxide adsorbed on the catalyst surface.

For sufficiently long reaction chains the rate of oxidation is dependent upon the 0.5 order of the free radicals initiation rate, R_i. If, as assumed in Eq. (10), R_i is proportional to the rate of hydroperoxide decomposition, R_d, then the observed behavior of the rate with respect to the initial hydroperoxide concentration can be readily explained. It has been shown (*9*) that R_d depends on the initial hydroperoxide only for low concentrations and that it becomes independent of this variable at higher peroxide concentration levels. Any change in R_d because of variations in the initial hydroperoxide concentration will be less evident in the rate of oxidation due to the 0.5 order dependency upon R_i.

Evidence that hydroperoxide is partially decomposed via a nonradical path was found from direct hydroperoxide determinations. At early stages of the oxidation, a decay in hydroperoxide concentration was observed and after about 20 min of reaction the rates of hydroperoxide formation became equal for all the runs. The initial decay in hydroperoxide was more pronounced for the experiments started with higher initial peroxide concentrations. However, this difference had no influence on the corresponding rates of oxidation, as would have been expected from a quantitative conversion of the decomposed hydroperoxide into free radicals. Therefore a nonradical decomposition path is indicated.

Influence of the Initial Concentration of Cyclohexenol, Cyclohexenone and Cyclohexene Oxide

The oxidation of cyclohexene was studied at 60°C using a catalyst ratio of 4 mg/ml of catalyst C, and different initial concentrations of the oxidation products of cyclohexene.

Separate solutions with 500 μmole/ml of cyclohexeone and cyclohexenol in chlorobenzene were prepared and subjected to oxidating conditions at 60°C with a catalyst ratio of 5 mg/ml. While cyclohexenone did not show any conversion to further oxidized products after 210 min of reaction, about 0.65 mole% of cyclohexenol was converted into ketone after the same time.

The oxidation of secondary alcohols and ketones (*34*) has been reported as taking place through free radical mechanisms. While the oxidation products of alcohol are ketone and hydrogen peroxide (which decomposes rapidly into water and oxygen on solid surfaces), the oxidation products of ketone are acids and other compounds like lactones, none of which has been identified in the present work during the oxidation of cyclohexene.

The fact that pure cyclohexenol in chlorobenzene was converted into ketone to a negligible extent after a long time may be misleading since, during the oxidation of cyclohexene, peroxy radicals may produce a chain transfer by reacting with alcohol, yielding thus a higher conversion of ketone than the one observed in the preceding experiment.

It can be observed from Fig. 7 that cyclohexene oxide did not show any influence on the maximum rate of cyclohexene oxidation for increasing concentrations of oxide. In the case of oxidations with cyclohexenone initially present, an inhibiting effect can be observed which becomes independent of ketone concentration for values greater than 200 μmole/ml. However, for oxidations performed with solutions containing cyclohexenol, a rather strong and increasing inhibition effect took place. Oxidation did not begin with the solution of 400 μmole/ml.

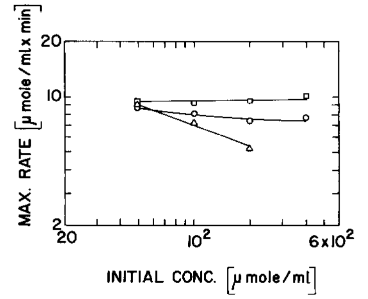


FIG. 7. Log of the maximum oxidation rate of cyclohexene at 60°C vs log of the initial concentration of: (△) cyclohexenol, (○) cyclohexenone, (□) cyclohexene oxide. Catalyst ratio = 30 (mg/ml) of catalyst A.

It has been reported (*35*) that several alcohols produced different degrees of inhibition during the oxidation of tetralin. The decrease in activity was attributed to the interaction of alcohol with active radicals yielding less active radical species. On the other hand, Chalk and Smith (*1*) found that the metal catalyzed oxidation of cyclohexene is medium sensitive. The catalytic efficiency is influenced by molecules of varying coordinating power formed as by-products (alcohols, ketones, etc.) which can compete with hydroperoxide for coordination sites. Meyer *et al.* (*5*) found that the oxidation rate of cyclohexene using transition metal oxides as catalysts was considerably inhibited when working with solutions containing, initially, cyclohexenol and cyclohexenone. As in the present study, cyclohexenol appeared to be a stronger inhibitor than cyclohexenone.

On the basis of the experimental results, apparently cyclohexenone exhibits an inhibiting effect on the oxidation rate by competing for coordination sites on the catalyst with cyclohexenyl hydroperoxide. Cyclohexenol, on the other hand, appears to act as a free radical inhibitor in the homogeneous liquid phase. These effects were all too small to alter the initial oxidation rates reported.

Effect of Temperature

The influence of temperature on the rate of cyclohexene oxidation was determined for the three MnO_2 catalysts in the range of 40–70°C.

There are inherent dangers involved in assigning measured activation energies to specific elementary reactions (*30*), unless independent evidence is available that the measured rates are related to the same elementary reactions over the entire temperature range investigated. Two regions of oxidation can be distinguished. One is at low catalyst ratios where the oxidation rate is dependent upon the 0.5 order of the catalyst; for sufficiently long oxidation chains, the apparent activation energy of oxidation will be:

$$E_o = E_p + \tfrac{1}{2}E_i - \tfrac{1}{2}E_t, \qquad (13)$$

where E_p = activation energy of the propagation step, E_i = activation energy of the initiation, E_t = activation energy of the biradical termination of peroxy radicals.

In the other region where the oxidation rate is independent of catalyst, the activation energy of oxidation will be given by:

$$E_o = 2E_p - E_t. \qquad (14)$$

Since our purpose was to compare the activation energies of initiation (E_i) with those found for the MnO_2 catalyzed decomposition of cyclohexenyl hydroperoxide (*9*), sufficiently low catalyst ratios were used in order to make sure that in the temperature range studied the activation energy for the oxidation process is represented by Eq. (13).

The maximum oxidation rates were determined using 30 mg/ml of catalyst A, 5 mg/ml of catalyst B, and 4 mg/ml of catalyst C. They are represented on an Arrhenius plot as shown in Fig. 8. The corresponding activation energies were calculated and are represented in Table 1. The values of E_o obtained are in close agreement with those reported for the oxidation of cyclohexene with various oxides as catalysts (*5,6*).

In order to determine E_i from Eq. (13), the values of E_p and E_t must be known. In the case of cyclohexene, the determination of rate constants and activation energies of the propagation and termination reactions has been the concern of many investigators (*25,36–39*). However, the values reported in the literature are different for each reference, making uncertain the calculation of the activation energies of initiation (E_i) and their comparison with the activation energies found for the MnO_2 catalyzed decomposition of cyclohexenyl hydroperoxide (*9*). Therefore, it was not possible to decide whether the initiation of free radicals is due entirely to the decomposition of a catalyst–hydroperoxide complex.

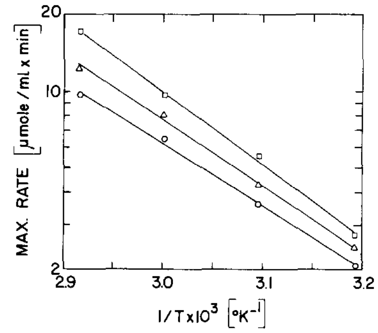


FIG. 8. Arrhenius plot for the oxidation of cyclohexene. (○) Catalyst A (30 mg/ml), (△) catalyst B (5 mg/ml), (□) catalyst C (4 mg/ml).

Product distribution studies made for the oxidation of cyclohexene in the range of 40–70°C employing catalyst C showed that temperature is not a variable which affects considerably the ratio of alcohol to ketone concentration. The rate of formation of cyclohexenol is only slightly favored with temperature compared with the rate of cyclohexenone formation.

Reaction Mechanism

The most important experimental observations made during the study of the MnO_2 catalyzed oxidation of cyclohexene may be summarized as follows:

a. The rate of oxidation is proportional to an order close to 0.5 with respect to catalyst for low catalyst ratios. For higher ratios, the order decreases from this value in the case of a high specific surface, porous MnO_2 (Catalyst C), until complete inhibition takes over. In the case of a low specific surface, nonporous MnO_2 (catalyst A), the rate of oxidation is independent of the amount of catalyst for high catalyst ratios.

b. For low catalyst weight to liquid volume ratios, the rate of oxidation is first order with respect to hydrocarbon concentration for the three oxides. In the case of catalyst C, complete inhibition of the oxidation is observed for certain catalyst ratios at different cyclohexene concentrations. At the point immediately prior to complete inhibition, the product of the oxidation rate and catalyst ratio is proportional to the square of the hydrocarbon concentration.

c. In the short oxidation period studied (up to 60 min), the concentration ratio of the oxidation products cyclohexenol and cyclohexenone is close to 1 and practically independent of catalyst ratio, hydrocarbon concentration and temperature.

d. For a fixed catalyst ratio and increasing hydrocarbon concentration, the rate of hydroperoxide formation increases linearly with the concentration of cyclohexene, while the rates of alcohol and ketone formation remain practically constant.

e. For a fixed cyclohexene concentration and increasing catalyst ratios, the rates of cyclohexenol and cyclohexenone formation increase linearly with catalyst, while the rate of cyclohexenyl hydroperoxide formation seems to increase slightly, pass through a maximum and then decrease slightly with catalyst.

f. The rate of oxidation is virtually independent of the initial concentration of cyclohexenyl hydroperoxide in the peroxide concentration range studied.

g. Cyclohexenol and cyclohexenone have no visible effect on the oxidation rate when they are present up to a concentration of 50 μmole/ml. For higher concentrations, they show an inhibiting influence.

The simplest reaction mechanism which accounts for many of the observed phenomena is presented as follows:

$$\text{Initiation}\left\{\begin{array}{llr}
\mathrm{ROOH} + \mathrm{M}^{+n} & \overset{k_1}{\rightleftharpoons} (\mathrm{ROOH}\ .\ .\ .\ \mathrm{M}^{+n}) & (15)\\
(\mathrm{ROOH})\ .\ .\ .\ \mathrm{M}^{+n} & \xrightarrow{k_2} \mathrm{RO}^{\cdot} + \mathrm{M}^{+(n+1)}\ .\ .\ .\ \mathrm{OH}^{-} & (16)\\
\mathrm{ROOH} + \mathrm{M}^{+(n+1)}\ .\ .\ .\ \mathrm{OH}^{-} & \xrightarrow{k_3} \mathrm{RO}_2^{\cdot} + \mathrm{H_2O} + \mathrm{M}^{+n} & (17)\\
\mathrm{RO}^{\cdot} + \mathrm{RH} & \xrightarrow{k_4} \mathrm{ROH} + \mathrm{R}^{\cdot} & (18)
\end{array}\right.$$

$$\text{Propagation}\left\{\begin{array}{llr}
\mathrm{R}^{\cdot} + \mathrm{O_2} & \xrightarrow{k_0} \mathrm{RO}_2^{\cdot} & (1)\\
\mathrm{RO}_2^{\cdot} + \mathrm{RH} & \xrightarrow{k_p} \mathrm{ROOH} + \mathrm{R}^{\cdot} & (2)
\end{array}\right.$$

$$\text{Termination}\left\{\begin{array}{llr}
\mathrm{RO}_2^{\cdot} + \mathrm{RO}_2^{\cdot} & \xrightarrow{k_t} \text{inactive prods.} + \mathrm{O_2} & (3)\\
\mathrm{RO}_2^{\cdot} + \mathrm{M}^{+n} & \overset{k_8}{\rightleftharpoons} (\mathrm{RO_2}\ .\ .\ .\ \mathrm{M}^{+n}) & (19)\\
\mathrm{RO}_2^{\cdot} + (\mathrm{RO_2}\ .\ .\ .\ \mathrm{M}^{+n}) & \xrightarrow{k_t'} \text{inactive prods.} & (20)
\end{array}\right.$$

Using the steady state approximation for the alkyl and alkyl peroxy radicals, the rate of oxygen consumption will be given by:

$$-\frac{d[\mathrm{O_2}]}{dt} = k_p\left(\frac{R_i}{2k_t + K_8k_t'\,[\mathrm{M}^{+n}]}\right)^{1/2}[\mathrm{RH}] + R_i\left(1 - \frac{k_t}{2k_t + K_8k_t'\,[\mathrm{M}^{+n}]}\right). \quad (21)$$

For sufficiently long reaction chains, when it is possible to assume that

$-d[O_2]/dt = -d[RH]/dt$, Eq. (21) is reduced to:

$$-\frac{d[O_2]}{dt} = k_p\left(\frac{R_i}{2k_t + K_8k_t'\,[M^{+n}]}\right)^{1/2}[RH]. \tag{22}$$

If the termination reaction of peroxy radicals on the catalyst surface, indicated by reactions (19) and (20), is negligible compared to the biradical termination (3), Eq. (4) is obtained.

When the limiting rate of oxidation is reached, it is assumed that the rate of formation of hydroperoxide through reaction (2) becomes equal to its rate of decomposition on the catalyst surface R_d. In these circumstances the total rate of hydroperoxide formation will be:

$$\frac{d[ROOH]}{dt} = k_p\left(\frac{R_i}{2k_t + K_8k_t'\,[M^{+n}]}\right)^{1/2} \times [RH] - R_d \equiv 0. \tag{23}$$

If R_i and R_d are related through Eq. (10), then:

$$R_i = \frac{\alpha^2\,k_p{}^2[RH]^2}{2k_t + K_8k_t'\,[M^{+n}]} \tag{24}$$

and the limiting rate of oxidation is:

$$-\left(\frac{d[O_2]}{dt}\right)_\infty = \frac{\alpha\,k_p{}^2[RH]^2}{2k_t + K_8k_t'\,[M^{+n}]} \left\{1 + \alpha\left(1 - \frac{k_t}{2k_t + K_8k_t'\,[M^{+n}]}\right)\right\}. \tag{25}$$

For a small enough value of α, Eq. (25) reduces to:

$$-\left(\frac{d[O_2]}{dt}\right)_\infty = \frac{\alpha\,k_p{}^2[RH]^2}{2k_t + K_8k_t'\,[M^{+n}]}. \tag{26}$$

It can be seen from Eq. (26) that for high catalyst ratios a point must be reached where $K_8k_t'\,[M^{+n}] \gg 2k_t$ and inhibition will start to be effective. In this situation, the product of the limiting oxidation rate and the critical catalyst ratio will be proportional to the square of the hydrocarbon concentration.

The influence of the catalyst ratio on the oxidation rate will depend on the expression for R_i. If R_i is proportional to the catalyst ratio and $2k_t \gg K_8k_t'[M^{+n}]$, then the rate of oxidation will be of 0.5 order with respect to the catalyst. When the rate of termination of peroxy radicals on the catalyst surface becomes competitive with the biradical termination, the reaction order with respect to the catalyst will become lower than 0.5, as predicted by Eq. (22). This behavior was observed for catalyst C.

If the termination rate of peroxy radicals on the catalyst surface is negligible compared with the biradical termination rate, then the rate of oxidation will be given by Eq. (4) for low catalyst ratios and by Eq. (11) from the moment the rates of formation and decomposition of hydroperoxide in the solution become equal. Therefore, a rapid transition from 0.5 to 0 order with respect to the catalyst ratio will take place, as observed for catalyst A.

Equations (4) and (22) predict first order of the oxidation rate with respect to hydrocarbon concentration for long oxidation chains in the region where the limiting rate has not been reached. This dependence was observed for the three catalysts (Fig. 2).

The dependence of the oxidation rate on the initial hydroperoxide concentration will depend on how R_i is related to R_d, and if Eq. (10) holds true, it is expected that the oxidation rate will depend on $[ROOH]_0$ for very low values of this concentration and become independent for higher values, as shown in Fig. 6.

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