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Heterogeneous Liquid-Phase Decomposition of Cyclohexenyl-Hydroperoxide in Cyclohexene with Manganese Dioxide as Catalyst

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The liquid-phase decomposition of cyclohexenyl hydroperoxide in cyclohexene has been studied using as catalysts three types of manganese dioxide with different specific surfaces. The influence of the initial hydroperoxide concentration, catalyst weight to liquid volume ratio and temperature was determined in each case. It is postulated that hydroperoxide forms an equilibrium complex with the catalyst which decomposes to yield free radicals. The initial activity of the oxides decreased with time during the reaction, and the observed decay in the rate of hydroperoxide decomposition has been attributed mainly to the deactivation of the catalyst surface.

Product distribution studies showed that the decomposition products were cyclohexenol, cyclohexenone, and water. The number of moles of alcohol formed was higher than the number of moles of ketone in each case.

A reaction mechanism is proposed and a rate equation consistent with the experimental results for hydroperoxide decomposition is presented.

INTRODUCTION

The decomposition of hydroperoxide plays an important role in the initiation of free radicals during autooxidation processes of hydrocarbons.

The thermal decomposition of cyclohexenyl hydroperoxide in hydrocarbon solvents has been studied in detail and a reaction mechanism which explained the kinetic and product distribution data has been proposed (*1, 2*). The catalytic decomposition of cyclohexenyl hydroperoxide using a soluble cobalt salt as catalyst in acetic media has been reported (*3*). Kinetic studies of the influence of hydroperoxide, solvents, catalyst, and reaction products were made in this instance.

Although some information is available about the thermal and homogeneously catalyzed decomposition of hydroperoxides other than cyclohexenyl hydroperoxide, heterogeneously catalyzed decompositions have not been extensively reported. In particular, very little work has been done with cyclohexenyl hydroperoxide in this area. Gould and Rado (*4*) have studied the activity and influence on product formation of insoluble oxides of transition metals as catalysts in this reaction and compared their effectiveness to that of the soluble acetyl acetonates of the same metals. They did not, however, give any kinetic data nor propose a reaction mechanism.

The present work was undertaken in an effort to establish a reaction mechanism which would describe adequately the decomposition of cyclohexenyl hydroperoxide in cyclohexene using manganese dioxide as catalyst. Studies were made using the manganese dioxide of highest specific surface as catalyst to determine whether the initial concentration of hydroperoxide, catalyst ratio, or temperature had any influence on product distribution.

EXPERIMENTAL

The reaction was performed in 10 ml tubes with Teflon-coated joints which fitted into a precision smooth-tapered joint provided with a Teflon stopcock. The same amount of catalyst was added to a series of reaction tubes, in each of which the reaction was allowed to proceed for different time intervals. A reactor tube containing the weighed catalyst was placed in an acetone–solid carbon dioxide mixture, and 2 ml of a previously prepared reactant solution were added slowly into the reactor to avoid suspension of the catalyst. The reactor was then joined to a vacuum system and the gas phase replaced with dry nitrogen. The Teflon stopcock was then closed to isolate the system. The reactor was attached to a wrist-action shaker to achieve vigorous agitation and plunged into a thermostat, the temperature of which could be controlled to within ±0.2°C. Time was recorded from the moment the tube was immersed in the oil bath. Once the desired reaction time interval had elapsed the tube was quickly put back into the acetone–solid carbon dioxide mixture to stop any further reaction, and the catalyst was allowed to settle. The clear liquid phase was then removed from the reactor for analysis.

Independent experiments showed that no detectable reaction took place before the reactor was placed in the thermostat, nor after it was taken out and dipped into the acetone-solid carbon dioxide mixture.

Reactants. Cyclohexene (BDH) was purified as described elsewhere (*5*) and stored under nitrogen in the dark cold. Cyclohexenyl hydroperoxide was prepared by oxidizing cyclohexene up to a concentration of about 0.5 mole/liter in an apparatus previously described (*6*). The thermal autoxidation of cyclohexene was initiated by adding traces of 2,2′-azodiisopropionitrile to the system, and the final solution, which proved to have less than 0.5 mole % cyclohexenone, cyclohexenol, and cyclohexene oxide as impurities, was stored under nitrogen in the dark cold. The desired reaction solutions were prepared by mixing appropriate amounts of the cyclohexenyl hydroperoxide solution and purified cyclohexene.

Analytical Procedures

The same method as described for an oxidized mixture of cyclohexane (*7*) was used in the present work. Part of the sample was titrated for hydroperoxide by the iodometric method (*8*), and the rest was treated with sufficient triphenyl phosphine for quantitative conversion of the hydroperoxide into cyclohexenol (*9*). 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 β MnO_2.

Catalyst B proved to be a nonporous γ MnO_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 (*10*).

Catalyst C was "Special Manganese Dioxide" (Fisher Scientific Co.). X-ray diffraction analysis showed a disordered structure. After pretreatment with oxygen at 400°C, β MnO_2 was identified. The specific surface as determined by BET nitrogen adsorption was 87.0 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 Initial Hydroperoxide Concentration

A series of peroxide decomposition experiments was performed starting with different initial concentrations of cyclohexenyl hydroperoxide at a constant temperature (60°C) and catalyst weight to liquid volume ratio. This set of runs was done for three different MnO_2 catalysts, and the results obtained for catalyst B are shown in Fig. 1.

The concentration of hydroperoxide decreased exponentially with time. This could lead to the conclusion that the rate of the

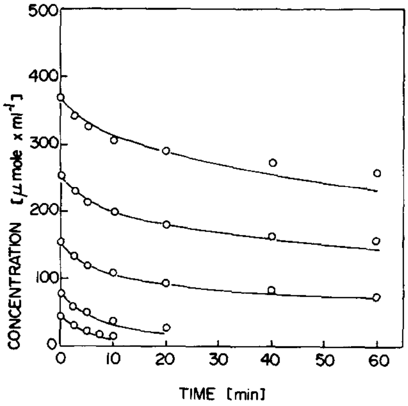

FIG. 1. Cyclohexenyl hydroperoxide decomposition in cyclohexene at 60°C, as a function of time, for different initial hydroperoxide concentrations. Catalyst ratio = 4 mg of catalyst B/ml. (○) Experimental points, (—) as predicted by Eq. (19).

decomposition is first order with respect to hydroperoxide concentration if it is assumed *a priori* that the activity of the catalyst is unchanged with time. However, it is apparent for all three catalysts that the initial rate of hydroperoxide decomposition increases with concentration for low peroxide concentrations, becoming practically constant at higher concentrations. These phenomena were also observed by Valendo *et al.* (*11*) when studying the decomposition of isopropylbenzene hydroperoxide in the presence of metal oxides. They concluded that, for sufficiently high hydroperoxide concentration, all active centers of the catalyst are bound in complexes with hydroperoxide and that the value of the initial rate of decomposition is determined solely by the rate of dissociation of the complex to radicals. In the present work a similar conclusion seems reasonable.

If the catalyst surface is saturated with hydroperoxide, an explanation must then be provided for the apparently exponential reduction of the decomposition rate with time. Min'kov *et al.* (*12*), when studying the mechanism of the oxidation of cumene on copper phthalocyanine, found that the activity of this catalyst changed during experiments on cumene hydroperoxide decomposition. The catalyst was carefully recovered after a certain reaction time had elapsed and was used again with fresh hydroperoxide solution. The initial rate of decomposition was smaller the longer the catalyst had been used previously until its activity reached a constant value. Furthermore, on the basis of inhibition experiments, they concluded that hydroxyl radicals produced from hydroperoxide decomposition were retained by the catalyst surface, contributing to the catalyst deactivation.

In the present work, the decrease in rate with time could also be explained on the basis of a progressive deactivation of the catalyst surface. The present observations together with those of other authors will be considered later when proposing a reaction mechanism.

Effect of the Catalyst Weight to Liquid Volume Ratio

This effect was studied for the three oxides, and results obtained for catalyst B are illustrated in Fig. 2. In each case, the same initial hydroperoxide concentration was used at 60°C. The decrease in the decomposition rate with time was also observed in these experiments.

The calculated initial decomposition rates are plotted against the catalyst weight to liquid volume ratio for the 3 catalysts in Fig. 3. The slopes of the plots are indicative of the reaction order with respect to the

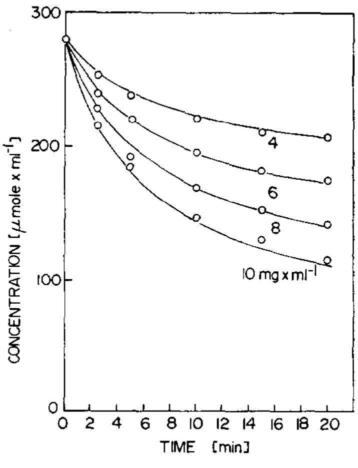

FIG. 2. Cyclohexenyl hydroperoxide decomposition in cyclohexene at 60°C, as a function of time, for different catalyst ratios of catalyst B. (○) Experimental points, (—) as predicted by Eq. (19).

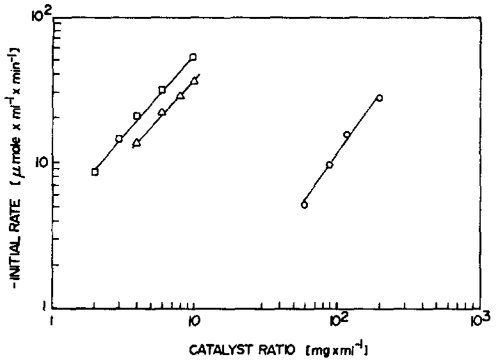

FIG. 3. Log of minus the initial rate of cyclohexenyl hydroperoxide decomposition in cyclohexene at 60°C as a function of the log of catalyst ratio, (○) catalyst A, (△) catalyst B, (□) catalyst C.

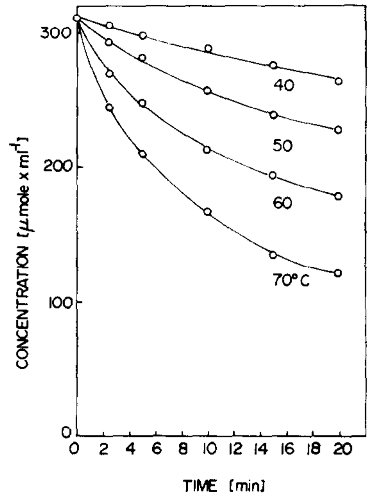

FIG. 4. Cyclohexenyl hydroperoxide decomposition in cyclohexene, as a function of time, for different reaction temperatures. Catalyst ratio = 4 mg of catalyst C/ml.

catalyst ratio, and the corresponding values are given in Table 1.

It is possible to conclude that the hydroperoxide decomposition rate has a first order dependency with respect to the catalyst.

Effect of Temperature

The decomposition of cyclohexenyl hydroperoxide in cyclohexene was studied in the temperature range of 40° to 70°C. In each case, experiments were started with the same initial hydroperoxide concentration and catalyst weight to liquid volume ratio. A set of experiments was performed for each of the three MnO_2 catalysts, and the results obtained for catalyst C are shown in Fig. 4.

The initial rates of hydroperoxide decomposition were determined and are presented on an Arrhenius plot for the three catalysts in Fig. 5. The corresponding activation energies were calculated and appear in Table 1.

The activation energies for the catalyzed decompositions of hydroperoxide are valuable data when studying the oxidation mechanism of cyclohexene with the same catalysts. If the activation energy of the overall oxidation process is determined, the activation energy of the catalyzed free radical initiation rate can ultimately be calculated and a comparison made between the processes of hydroperoxide decomposition and free radical initiation. However, as will be shown later, under the conditions at which the present initial rates were measured, the calculated activation energies corresponded to the decomposition of a hydroperoxide–catalyst complex.

By working with inhibitors, it has been established that hydroperoxides may decompose via simultaneous radical and nonradical mechanisms (*13*, *14*). On the other hand, as will be seen from the present mechanism, other reactions taking place on the catalyst surface may be an important source of free radicals. Therefore, the decomposition of a hydroperoxide–catalyst

TABLE 1

Catalyst	Type	BET specific surface (m^2/g)	Porosity characteristics	Catalyst order	E_a (kcal/mole)
A	βMnO_2	0.9	Nonporous	1.3 ± 0.4	10.5 ± 0.8
B	γMnO_2	32.0	Nonporous	1.1 ± 0.2	9.7 ± 1.8
C	βMnO_2	87.0	Porous	1.1 ± 0.1	16.1 ± 1.6

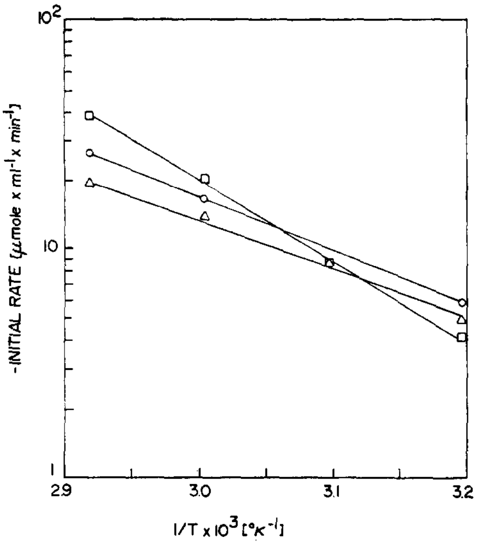

FIG. 5. Arrhenius plot for the decomposition of cyclohexenyl hydroperoxide in cyclohexene. (○) Catalyst A, (△) Catalyst B, (□) Catalyst C.

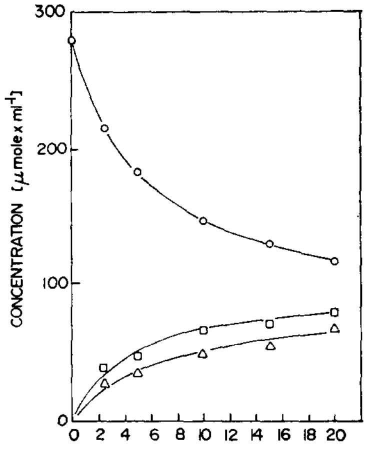

FIG. 7. Product distribution for the decomposition of cyclohexenyl hydroperoxide in cyclohexene at 60°C. Catalyst ratio = 10 mg of catalyst B/ml. (○) Cyclohexenyl hydroperoxide, (□) cyclohexenol, (△) cyclohexenone.

complex may not be the main source of free radicals for the propagation steps in the oxidation process.

Product Distribution

Cyclohexenol was found to be the major organic reaction product in the thermal decomposition of cyclohexenyl hydroperoxide in cyclohexene (*1*). However, in the catalyzed decompositions of cyclohexenyl hydroperoxide studied previously (*3*, *4*, *15*), water, cyclohexenol, cyclohexenone, and cyclohexene oxide were the reaction products detected. Detailed studies on product distributions were not reported.

Figures 6, 7, and 8 show typical product distribution curves for the decomposition of cyclohexenyl hydroperoxide at 60°C using the three MnO_2 catalysts. Cyclohexene oxide was not identified as a product of the

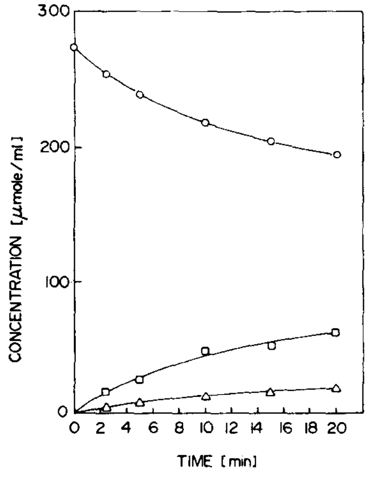

FIG. 6. Product distribution for the decomposition of cyclohexenyl hydroperoxide in cyclohexene at 60°C. Catalyst ratio = 90 mg of catalyst A/ml. (○) Cyclohexenyl hydroperoxide, (□) cyclohexenol, (△) cyclohexenone.

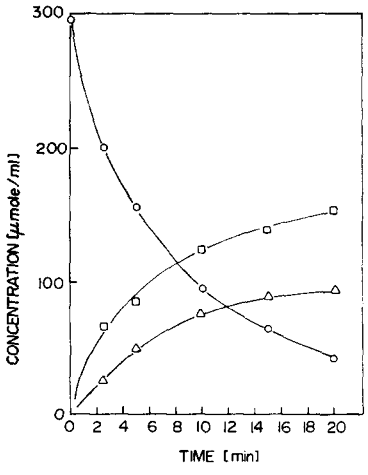

FIG. 8. Product distribution for the decomposition of cyclohexenyl hydroperoxide in cyclohexene at 60°C. Catalyst ratio = 10 mg of catalyst C/ml. (○) Cyclohexenyl hydroperoxide, (□) cyclohexenol, (△) cyclohexenone.

reaction and could have been formed only in trace amounts. No quantitative analysis for water was made but its presence was noted in the formation of a condensation film on the walls of the reactor.

It can be concluded from the figures that with all three catalysts a greater amount of cyclohexenol than cyclohexenone was formed. However, the ratios of the alcohol to ketone concentrations were quite different for each catalyst indicating that other factors besides the chemical nature of the oxide play a decisive role in the product distribution.

Using the manganese dioxide of highest specific surface as catalyst, product distributions were studied in some detail. The influence of the initial hydroperoxide concentration, catalyst ratio, and temperature was evaluated. Examination of the product distribution data revealed a decrease in the alcohol to ketone concentration ratio on increasing the initial hydroperoxide concentration, when the catalyst ratio and temperature were maintained constant. The same tendency was apparent when the catalyst ratio was increased keeping constant the initial hydroperoxide concentration and temperature. This phenomenon may be related to the formation of a catalyst–hydroperoxide complex in equilibrium with hydroperoxide and unoccupied sites on the catalyst surface. The higher the concentration of the complex in the system, the closer to unity is the alcohol to ketone concentration ratio. The decomposition of the complex through a radical path would produce alkoxy radicals which, upon interaction with cyclohexene, would give rise to cyclohexenol. A nonradical decomposition path could imply the disproportionation of two neighboring adsorbed hydroperoxide molecules which would yield one molecule of cyclohexenol and one of cyclohexenone.

Another important phenomenon is that the alcohol to ketone concentration ratio is not constant with time. With only a few exceptions, it is possible to say that at the early stages of the reaction, the rate of alcohol formation is greater than the rate of ketone formation, while at later stages of the reaction, the rates become more nearly the same. This could be related to the fact that additional amounts of ketone may be formed from termination reactions of peroxy radicals on the catalyst surface. Peroxy radicals are formed from regeneration steps of the catalyst (as will be seen in the next section), and therefore they have a larger concentration at later stages of the reaction. At the beginning, the reaction between alkoxy radicals and substrate to yield cyclohexenol is more important.

Finally it must be mentioned that in the experimental range studied, temperature does not appear to influence greatly the product ratio.

Reaction Mechanism

Before postulating a reaction mechanism, some conclusions reached from the experimental observations will be summarized as follows:

(a) The initial rate of cyclohexenyl hydroperoxide decomposition is practically independent of the initial peroxide concentration, except at low concentration levels where a proportionality of the rate and the concentration is observed. This behavior is associated with the formation of a catalyst–hydroperoxide complex.

(b) The hydroperoxide concentration decreases exponentially with time even when the decomposition rate is not influenced by the peroxide concentration. This is thought to be due to the deactivation of the catalyst surface.

(c) The amounts of hydroperoxide decomposed indicate that the catalyst could not be irreversibly deactivated *(6)*, therefore, a regeneration step of the active sites on the catalyst surface must be included in the reaction mechanism.

On the basis of the previous conclusions, the following set of reactions, which is equivalent to the Haber–Weiss mechanism *(16)*, will be considered as the main steps for the decomposition of cyclohexenyl hydroperoxide:

$$\mathrm{ROOH} + \mathrm{M}^{+n} \overset{K_1}{\rightleftharpoons} (\mathrm{ROOH}\,..\,\mathrm{M}^{+n}), \qquad (1)$$

$$(\mathrm{ROOH}\,..\,\mathrm{M}^{+n}) \xrightarrow{k_2} \mathrm{RO}^{\cdot} + \mathrm{M}^{+(n+1)}\underset{\cdots}{}\mathrm{OH}^{-}, \qquad (2)$$

$$\mathrm{ROOH} + \mathrm{M}^{+(n+1)}\underset{\cdots}{}\mathrm{OH}^{-} \xrightarrow{k_3} \mathrm{RO}_2^{\cdot} + \mathrm{H_2O} + \mathrm{M}^{+n}. \qquad (3)$$

Here: ROOH = cyclohexenyl hydroperoxide, M^{+n} = active transition metal site on the catalyst surface, $RO^{\cdot}$ = cyclohexenoxy radical, $RO_2^{\cdot}$ = cyclohexenyl hydroperoxy radical.

As indicated by Ingold (*17*), the alkoxy and peroxy radicals may react in the homogeneous phase according to:

$$RO^{\cdot} + ROOH \rightarrow ROH + RO_2^{\cdot}, \qquad (4)$$

$$RO_2^{\cdot} + ROOH \rightarrow RO^{\cdot} + ROH + O_2, \qquad (5)$$

$$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}, \qquad (6)$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}. \qquad (7)$$

In these steps: ROH = cyclohexenol, RH = cyclohexene, R = cyclohexenyl radical.

Free radical termination reactions could take place both homogeneously and on the catalyst surface:

$$2RO_2^{\cdot} \rightarrow \text{Inactive products} + O_2 \qquad (8)$$

$$2RO^{\cdot} \rightarrow \text{Inactive products}, \qquad (9)$$

$$2R^{\cdot} \rightarrow \text{Inactive products}, \qquad (10)$$

$$R^{\cdot} + M^{+m} \rightarrow \text{Inactive products}, \qquad (11)$$

$$RO^{\cdot} + M^{+n} \rightarrow \text{Inactive products}, \qquad (12)$$

$$RO_2^{\cdot} + M^{+n} \rightarrow \text{Inactive products}. \qquad (13)$$

In order to derive a rate expression for the consumption of hydroperoxide, the following assumptions will be made:

a. Homogeneous reactions for the decomposition and formation of hydroperoxide are unimportant when compared with the heterogeneous decompositions [Eqs. (1), (2), and (3)].

b. Involvement of the catalyst in free radical termination is assumed to be negligible.

c. Final reaction products (alcohol, ketone, and water), have no inhibiting effect on the catalyst.

If these simplifications are not made, the simultaneous equations arising from considering all the reaction steps presented are practically intractable. On the other hand, if mainly peroxy radicals terminate on the surface of the catalyst as assumed in the previous section, it is expected that a simplified rate model could interpret adequately the observed phenomena, at least at early stages of the reaction.

The following types of sites will be distinguished on the catalyst surface:

1. Initial sites of fresh catalyst (S_0).
2. Sites free to absorb hydroperoxide (S_f), indicated as M^{+n} in the reaction mechanism.
3. Sites forming a catalyst–hydroperoxide complex (S_1), indicated as $(ROOH..M^{+n})$ in the mechanism.
4. Sites with adsorbed hydroxy groups (S_2), $M^{+(n+1)}\ldots\ldots OH^-$ in the mechanism.

Calling: $[ROOH] = C$ (hydroperoxide concentration) and $[S_i] = S_i$ (concentration of catalyst site i), it follows that

$$S_f = S_0 - S_1 - S_2. \qquad (14)$$

If the catalyst–hydroperoxide complex soon attains equilibrium,

$$S_1 = K_1 C S_f = \frac{K_1 C}{(1 + K_1 C)} (S_0 - S_2). \qquad (15)$$

The rate of formation of the sites with adsorbed hydroxyl radicals will be,

$$\frac{dS_2}{dt} = \frac{k_2 K_1 C}{(1 + K_1 C)} (S_0 - S_2) - k_3 C S_2. \qquad (16)$$

Considering that the variation of C with time is negligible compared with the change of S_2, and calling:

$$f(C) = \frac{k_2 K_1 C}{(1 + K_1 C)}, \qquad (17)$$

Eq. (16) yields upon integration,

$$S_2 = \frac{S_0 f(C)}{(f(C) + k_3 C)} (1 - \exp\{-[f(C) + k_3 C]t\}). \qquad (18)$$

After suitable substitutions, the rate of hydroperoxide decomposition will be:

$$\frac{dC}{dt} = \frac{f(C) S_0}{(f(C) + k_3 C)} (2k_3 C + [f(C) - k_3 C] \exp\{-[f(C) + k_3 C]t\}). \qquad (19)$$

The initial concentration of catalyst sites, S_0, is proportional to the initial catalyst weight to liquid volume ratio, such that:

$$S_0 = \beta M_0, \qquad (20)$$

where β is a constant characteristic for each oxide.

The constants of the rate Eq. (18) were determined numerically for each catalyst by making use of the experimental data. The equation was then integrated to reproduce the hydroperoxide concentration versus time data collected at 60°C.

The solid lines drawn on Figs. 1 and 2 represent the values as predicted by the rate model for catalyst B. Reproducibility of the experimental points is within ±5% for the three MnO_2 catalysts, except for low concentrations (less than 10 μmole/ml) where small differences between experimental points and models produce large percentual errors. It can be observed from Fig. 1 that the model does not follow accurately the experiments after about 20 min. This is attributed mainly to a departure from the simplifying assumptions made earlier that no radical termination on the catalyst surface will be of importance, and that reaction products like water *(18)* will not have an inhibiting effect on the catalyst.

For time zero, Eq. (19) reduces to:

$$-\left.\frac{dC}{dt}\right|_{t=0} = f(C)S_0 = \frac{k_2K_1C}{(1+K_1C)}S_0. \quad (21)$$

This equation explains the behavior of the initial rate of hydroperoxide decomposition for different initial peroxide concentrations. It also is consistent with the first-order dependency of the rate upon the initial catalyst ratio.

Under the conditions at which the initial rate was measured to determine the effect of the temperature for each catalyst, it can safely be said that this rate was independent of the initial hydroperoxide concentration, since the experiments were performed with initial concentrations greater than 250 μmole/ml. In this case Eq. (21) is further reduced to:

$$-\left.\frac{dC}{dt}\right|_{t=0} = k_2S_0, \quad (22)$$

which indicates that the activation energy of reaction (2) was determined.

Effect of the Porosity and Specific Surface of the Catalysts

Yurchak *et al.* *(19)* attempted to evaluate the effect of intraparticle diffusion when studying the liquid-phase oxidation of isobutane with a $CoO/MoO_3/Al_2O_3$ catalyst. By considering a simplified phenomenological reaction model, they were able to estimate the effectiveness factors of the peroxide and radical intraparticle diffusing species. On the basis of the calculated values, they concluded that the catalytic decomposition of hydroperoxide is virtually unaffected by diffusion, but the decomposition of radicals is strongly influenced by diffusion even with a particle radius of 10 μ. Radicals generated in the interior of the catalyst pores by hydroperoxide decomposition cannot efficiently propagate the chain before undergoing decomposition to products such as ketone.

Our main concern was the rate of hydroperoxide decomposition and the fate of the generated radicals was not considered of primary importance. The homogeneous hydroperoxide decomposition by interaction with free radicals was neglected relative to the heterogeneous reaction. Therefore, on the basis of the previous considerations, it was assumed that the catalytic decomposition of cyclohexenyl hydroperoxide was unaffected by intraparticle diffusion.

The problem of determining the fraction of catalyst surface active in liquid phase oxidation processes was considered by Pyatniskaya *et al.* *(20)* when studying the liquid-phase oxidation of cumene on cupric and manganese oxides of different grain size. They concluded that the process proceeds on the external surface or in a very thin surface layer in the case of a catalyst with a developed internal surface. A shortcoming of their study is that they considered the external specific surface of nonporous glass powder equal to the external specific surface of the catalyst particles of equivalent grain size.

In the present study, examination of the three catalysts under the electron scan microscope led to the conclusion that the use of an average particle diameter to determine the external surface was misleading because of clustering and surface roughness.

Since catalysts A and B were determined to be nonporous (21) it is possible to assume that the complete BET specific surface will be active in the process of the liquid phase decomposition of cyclohexenyl hydroperoxide.

Equation (21) for the initial rate of hydroperoxide decomposition can be rewritten as:

$$-\left.\frac{dc}{dt}\right|_{t=0} = \alpha S_p M_0 f(C) \qquad (23)$$

where S_p is the specific surface of the catalyst which effectively participates in the reaction, and α a constant dependent on the particular catalyst but independent of the specific surface.

It will be assumed that α is equal for the three MnO_2 catalysts and $f(C)$ was estimated as 0.204, 0.243, and 0.210 min^{-1} for catalysts A, B, and C, respectively, when considering the set of experiments represented on Fig. 3.

At a fixed catalyst weight to liquid volume ratio, the quotient of Eq. (23) applied to the two nonporous catalysts yields

$$\frac{S_{pB}}{S_{pA}} = \frac{r_{B_0} f(C)_A}{r_{A_0} f(C)_B} \qquad (24)$$

where r_{B_0} and r_{A_0} stand for the initial rates of decomposition when using catalysts B and A, respectively.

Values taken from Fig. 3 for r_{B_0} and r_{A_0}, and those calculated for $f(C)_A$ and $f(C)_B$, give, $S_{pB}/S_{pA} = 33.6$. This quantity is in good agreement with the value 35.6 for the ratio of the BET surfaces for the catalysts, giving support to the assumptions made previously.

Following the same calculation procedure for catalysts A and C, it was established that 57.8 m^2/g out of 87 m^2/g were active for catalyst C. On the basis of a pore distribution study it was found that about 20 m^2/g belonged to the external surface, leaving therefore about 38 m^2/g of the internal surface active for the liquid-phase process.

It can be concluded from this study that, when employing a porous catalyst, the liquid phase decomposition of cyclohexenyl hydroperoxide in cyclohexene took place not only on the external surface of the catalyst but also on a considerable portion of the internal area. However, it must be kept in mind that although the three catalysts are manganese dioxide, their type and previous history are different, making it necessary to interpret these conclusions cautiously.

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