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Heterogeneous Liquid-Base Oxidation of Cyclohexene with Manganese Dioxide as Catalyst

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The oxidation of cyclohexene and the decomposition of cyclohexenyl hydroperoxide have been studied in liquid phase using manganese dioxide as catalyst. The dependence of the initial rate on the catalyst amount has been studied both for the oxidation and the decomposition reactions.

It is postulated that a degenerate chain branching mechanism occurs. Hydroperoxide which is produced in the propagation step is decomposed on the solid, providing the free radicals necessary for the initiation of the chains. Cyclohexenol and cyclohexenone are produced in the initiation and termination steps.

Above a critical catalyst to hydrocarbon ratio, no oxidation reaction was observed. At that critical composition, the rate of hydroperoxide decomposition was equal to its rate of formation. The length of the chain decreased to a low value with increasing catalyst to hydrocarbon ratios.

INTRODUCTION

Previous studies have been made of the liquid-phase oxidation of hydrocarbons in the presence of insoluble catalysts mainly derived from transition metals. There are different opinions concerning the mechanism of these free radical reactions (*1*, *2*). A typical reaction studied is the liquid-phase oxidation of cyclohexene (*1*, *3*). The heterogeneous–homogeneous character of this reaction has been shown by Meyer *et al.* (*1*) using MnO_2 and CoO as catalysts. The initiation of free radicals occurs on the solid; whereas propagation and termination are homogeneous. However, their kinetic data are almost exclusively related to the initial rate of oxygen consumption; and no attempt was made to correlate the mechanism proposed with the presence of cyclohexenol and cyclohexenone observed in fairly large amounts, even in early stages of the oxidation. Therefore, it seemed worthwhile to extend this study by comparing the oxygen consumption with the hydroperoxide, alcohol, and ketone formation during the oxidation process.

These data permitted the proposal of a more general mechanism explaining the simultaneous formation and destruction of hydroperoxide. In order to emphasize the role played by the solid, a manganese dioxide of relatively high surface was used in a wide range of catalyst to hydrocarbon ratios.

EXPERIMENTAL METHODS

Catalysts and reagents. Special manganese dioxide (Fischer Scientific Co.) was used as catalyst. It proved to have a high surface (135 m^2/g) determined by BET nitrogen adsorption. Its structure, determined by X-ray, corresponded to pyrolusite (*4*). A fraction of particle size smaller than 200 mesh was employed in each case.

Cyclohexene (BDH Chemicals Ltd.), was agitated with ferrous sulfate to eliminate hydroperoxide. After washing and drying with sodium hydroxide, it was distilled in the presence of sodium in an inert atmosphere. The distilled fraction was kept under nitrogen in the cold.

Cyclohexenyl hydroperoxide solutions

were prepared by thermal autoxidation of cyclohexene up to a concentration of 0.410 mole/liter. Solutions of different concentrations of hydroperoxide in cyclohexene were prepared by dilution with pure cyclohexene.

Apparatus. All the reactions, both the cyclohexene oxidations and cyclohexenyl hydroperoxide decompositions, were performed in an insulated glass reactor provided with an internal heating coil. The reactor, large enough to contain 200 ml of reacting mixture, was provided with an oxygen line, a sample uptake line, and a thermometer scabbard. The reacting mixture was only in contact with glass and Teflon. Metallic surfaces were carefully avoided. The reactor was placed on a shaker so that the catalyst was uniformly suspended; and an appropriate heat transfer rate between coil and mixture was obtained. Oxygen was supplied to the reactor at a constant pressure of 4 psig through a Matheson 70-A model valve. A bottle of known volume, thermally isolated, was filled each time with oxygen up to a known pressure registered on a mercury manometer. This manometer was used to measure the rate of oxygen uptake. A vacuum pump provided vacuum over the mixture in the reactor when required. A recirculating thermostatic bath allowed control of the temperature in the reactor to within ±0.5°C.

Oxidation experiments. For each run the desired amount of MnO_2 was placed into the reactor with 200 ml of cyclohexene containing 5 ml of toluene. Separate experiments showed that toluene was inert in the reaction and maintained its concentration intact to within less than 0.5%. It was used as an internal standard for the analysis. Good agreement with the results when using chlorobenzene as internal standard were obtained. Once the mixture had reached the desired temperature, oxygen was supplied to the reactor. Liquid samples were taken from the reactor at various times and filtered to eliminate the catalyst. One milliliter was used to determine the total hydroperoxide content by the iodometric method described by Wagner *et al.* (*5*). The rest of the sample was treated with sufficient triphenylphosphine to convert the hydroperoxide into alcohol (*3*, *6*, *7*). The treated samples were kept at 0°C and analyzed by gas–liquid chromatography, using a column of polyethylene glycol 610 deposited on Chromosorb. Cyclohexenol, cyclohexenone, and cyclohexene oxide were separated. A typical product distribution diagram is shown in Fig. 1.

Catalytic decompositions of cyclohexenyl hydroperoxide. The cyclohexenyl hydroperoxide solution of known concentration was added, together with the desired amount of MnO_2 catalyst to the reactor, under nitrogen. As in the oxidation experiments, all the runs were performed at 60°C; and samples were taken for analysis at various times. The samples were analyzed as already described.

Occasionally when water analysis was required, the flame ionization detector was replaced by a thermal conductivity cell. The same chromatographic column was able to separate water.

RESULTS

The oxidation of cyclohexene. The data plotted in Fig. 2 represent the amount of

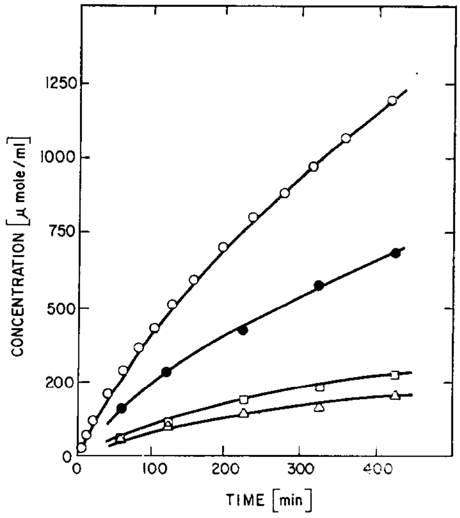

FIG. 1. Product distribution of the cyclohexene oxidation at 60°C, using 3.5 mg/ml of MnO_2 as catalyst: (○) oxygen consumed; (●) cyclohexenyl hydroperoxide; (□) cyclohexenol; (△) cyclohexenone.

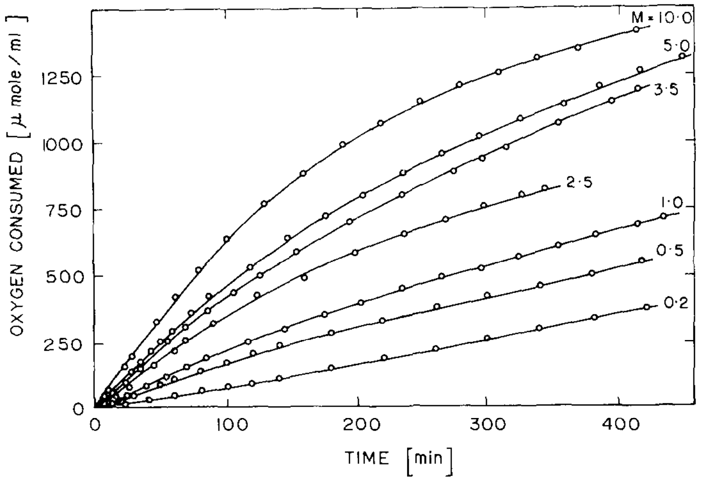

FIG. 2. Oxygen consumed, for the oxidation of cyclohexene at 60°C, as a function of time, for different MnO_2 catalyst to hydrocarbon ratios (M mg/ml); volume of hydrocarbon = 200 ml.

oxygen absorbed with time for various amounts of catalyst. In the absence of catalyst there was no observable oxygen consumption in 400 min. A sample of the supernatant reaction liquid after a reaction time of 50 min when placed in a fresh reactor without catalyst, showed a sharp decrease in the rate of oxidation to values corresponding to the uncatalyzed reaction, indicating that there was no homogeneous catalysis resulting from dissolved manganese. In addition, direct chemical analysis of the reaction liquid after 120 min of reaction by an atomic absorption procedure showed no manganese. The detection limit of the apparatus is of the order of 0.02 ppm.

For catalyst to hydrocarbon ratios smaller than 0.3 mg/ml the oxidation process seems to be slightly autocatalytic; whereas, from 0.5 mg/ml on, the rate of oxygen consumption is constant at the beginning, and no induction period is observed. The constancy of the rate during the first hour of reaction enables us to de-

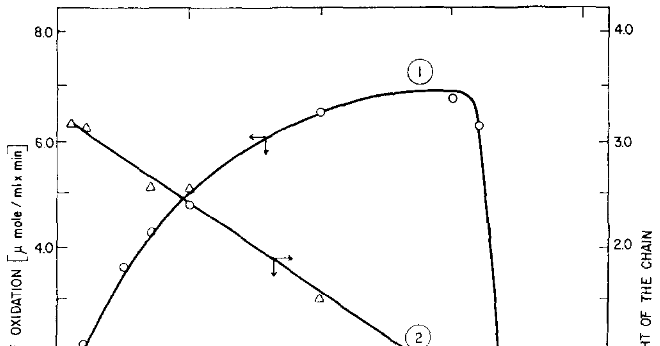

FIG. 3. Initial rate of oxidation of cyclohexene at 60°C as a function of MnO_2 catalyst to hydrocarbon ratio (curve 1); and the length of the chain as a function of MnO_2 catalyst to hydrocarbon ratio (curve 2).

termine with accuracy the influence of the amount of catalyst on the initial rate. Results shown on Fig. 3 (curve 1) fit a rate equation which is 0.5 order with respect to the catalyst/hydrocarbon ratio: this value is characteristic of an heterogeneous initiation and homogeneous propagation followed by a biradical termination, as postulated by Meyer *et al.* (*1*).

At small reaction times below about 60 min the reaction characteristics are very similar to those observed by Kamiya *et al.* (*8*). In particular the reaction rate shows an increase with catalyst amount, which reaches a maximum value at about 15 mg of catalyst/ml of substrate. This maximum was explained by Tobolsky (*9*) and Kamiya *et al.* (*8*) as a result of the attainment of steady state hydroperoxide concentration.

Further indication that the mechanism of Tobolsky (*9*), as adapted by Kamiya *et al.* (*8*), could be operative in the heterogeneous system, is given by the fact that, at low times, the oxygen consumption rate is 0.5 order, with respect to the catalyst ratio, when the hydroperoxide concentration is building up; and, at long times, this order is essentially zero where it might be thought that hydroperoxide has attained a

TABLE 1

Catalyst ratio M (mg/ml)	Time (min)	Conc. (μmoles/ml)			Cyclohexenyl hydroperoxide (μmoles/ml)	Oxygen consumed (μmoles/ml)	[Alcohol]/[ketone]
		Cyclohexene oxide	Cyclohexenone	Cyclohexenol			
0.5	60.0	—	19.0	16.0	104.0	107.3	
	120.0	—	30.0	26.0	170.0	201.0	
	220.0	1.7	47.5	63.0	291.0	329.0	
	320.0	4.1	55.6	78.0	351.0	438.0	
	420.0	5.6	70.0	111.0	434.0	538.0	1.43
1.0	151.0	4.5	40.8	62.0	226.0	310.0	
	261.0	8.2	71.0	105.0	357.0	482.0	
	380.0	11.1	88.0	110.0	456.0	640.0	
	490.0	15.2	108.0	147.0	594.0	764.0	1.42
3.5	60.0	2.1	58.5	60.0	154.0	262.0	
	120.0	3.3	95.6	118.0	286.0	482.0	
	220.0	4.8	142.0	197.0	423.0	761.0	
	320.0	6.8	162.0	233.0	572.0	988.0	
	420.0	7.5	202.0	279.0	681.0	1201.0	1.35
5.0	81.0	4.1	70.5	47.0	214.0	390.0	
	142.0	8.0	122.0	147.0	358.0	612.0	
	240.0	15.0	186.0	270.0	490.0	892.0	
	363.0	19.8	230.0	272.0	545.0	1152.0	
	490.0	30.2	275.0	420.0	725.0	1393.0	1.35
10.0	15.5	7.1	46.2	112.0	66.0	103.0	
	52.0	12.3	102.0	178.0	170.0	357.0	
	140.0	21.8	226.0	321.0	385.0	912.0	
	240.0	34.8	328.0	421.0	545.0	1118.0	
	370.0	44.0	486.0	543.0	629.0	1352.0	
	420.0	59.0	522.0	682.0	650.0	1420.0	1.27
16.0	40.0	—	182.0	199.0	99.0	251.0	
	80.0	7.5	225.0	272.5	162.5	456.0	
	120.0	12.6	306.0	303.0	236.0	611.0	
	180.0	17.2	432.0	492.0	314.0	780.0	
	240.0	28.4	500.0	564.0	368.0	910.0	1.10

steady concentration. However, a shortcoming of this mechanism is that the catalyst independent rates obtained for long reaction times are much lower than the catalyst dependent rates at short times. This decrease might result from a catalyst deactivation as a result of adsorption of products such as water. Small catalyst independent rates have been observed for homogeneous systems also (*10*, *11*).

An additional limitation to this mechanism is the observation from Table 1 that the hydroperoxide is by no means at steady state concentration after 50 min, nor even after 400 min of reaction. A similar limitation was observed for homogeneously catalyzed systems (*10*, *11*).

For catalyst to hydrocarbon ratios higher than 16 ± 1 mg/ml, the oxidation did not start at all. This rather surprising result is similar to results observed (*2*) during the oxidation of Tetralin using Mn_2O_3 as catalyst, and also similar to results observed in the homogeneous catalytic oxidation of Tetralin by Kamiya and Ingold (*12*). Further investigation of the critical phenomenon was undertaken.

A cyclohexene oxidation experiment was started with a catalyst concentration of 5.82 mg/ml, and the reaction continued for 60 min. A large amount of catalyst was added to the reactor (so that the final catalyst concentration was 50 mg/ml, far above the critical ratio), and the oxidation was allowed to proceed. As shown in Fig. 4, the hydroperoxide concentration decreased sharply. After 200 min, there was no hydroperoxide left in the solution; and the oxidation had ceased. This result suggests that, beyond the critical ratio, the rate of hydroperoxide formation is smaller than the rate of decomposition. The oxygen consumption can occur only if there is some hydroperoxide left in the solution. The presence of hydroperoxide (a product) is a necessary condition for the progress of the free radical oxidation.

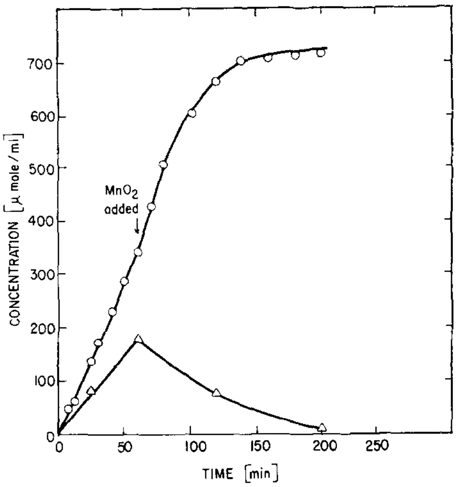

FIG. 4. Oxygen consumption (○), and cyclohexenyl hydroperoxide distribution (△), as a function of time; for the oxidation of cyclohexene at 60°C, with a MnO_2 catalyst to hydrocarbon ratio of 5.82 mg/ml up to 60 min, and 50 mg/ml from then on.

On the other hand, the possibility of a nonradical producing hydroperoxide decomposition reaction, perhaps with a rate depending on a higher order of the MnO_2 ratio, could be considered. Such a reaction may become important at a certain catalyst ratio, inhibiting the oxidation.

The rates of cyclohexene oxidation with MnO_2 obtained in the present work have a comparable order of magnitude to those reported by other authors for the same system (*1*, *3*), this is in spite of the differences in reacting volumes and catalyst qualities. Other heterogeneous catalysts were not studied; however, comparative studies using other metal catalysts for the oxidation of cyclohexene are available (*1*, *3*).

Product distribution. Meyer *et al.* (*1*), studied the rate of oxygen consumption under such experimental conditions that the hydroperoxide was the main reaction product (more than 90% of the products). in a recent work, Gould and Rado (*3*), studying the oxidation of cyclohexene in the presence of soluble and insoluble catalysts, identified more completely the oxidation products: they observed with each catalyst the presence of cyclohexenyl hydroperoxide, cyclohexenol, cyclohexenone, cyclohexene oxide, and dimeric hydroperoxide in various amounts. The same compounds were observed previously by Van Sickle *et al.* (*6*) with homogeneous catalysts. In our experiments, we found

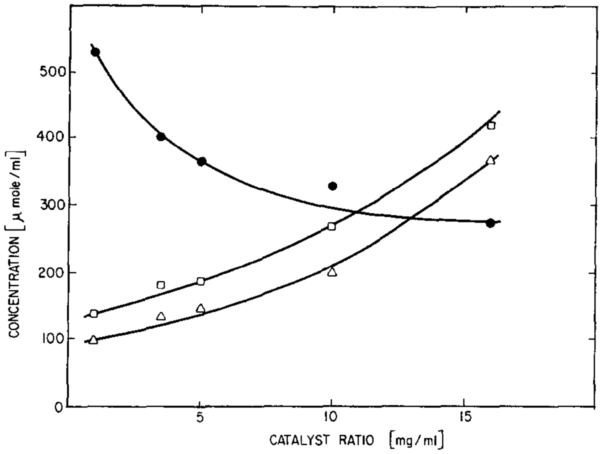

FIG. 5. Cyclohexenyl hydroperoxide (●), cyclohexenol (□), and cyclohexenone (△) concentrations, as functions of MnO_2 catalyst to hydrocarbon ratio, for 700 μmoles/ml of oxygen consumed, in each run of cyclohexene oxidation at 60°C.

essentially the same compounds as Gould and Rado (that is, hydroperoxide, alcohol, ketone, and epoxide). However, no attempt was made to separate monomeric from dimeric hydroperoxide, since the experimental procedure commonly used to separate these compounds may transform the monomeric hydroperoxide into the dimeric one. Besides these compounds, we also detected the presence of water, and benzene in very small amounts.

In Table 1, the product distributions at various times and for various amounts of catalyst are presented. It may be noticed (Fig. 5) that, for a given amount of oxygen consumed, the yield of alcohol and ketone increases with the amount of catalyst; whereas the hydroperoxide decreases. It is assumed that hydroperoxide, which is formed in the first oxidation step, is decomposed on the catalyst, producing free radicals which increases the rate of production of final oxidized products for increasing catalyst ratios.

It also follows from Table 1 that the ratio of alcohol to ketone concentrations decreases from 1.5 to 1.0 for increasing catalyst to hydrocarbon ratios.

A mole balance calculation for oxygen indicated that the oxygen consumed at any time is less than that accounted for as products by an amount equivalent to the amount of ketone produced. Therefore we assume the reaction:

$$ROOH \rightarrow R'{=}O + H_2O. \qquad (1)$$

Considering that alcohol is formed from the rest of the decomposed hydroperoxide,

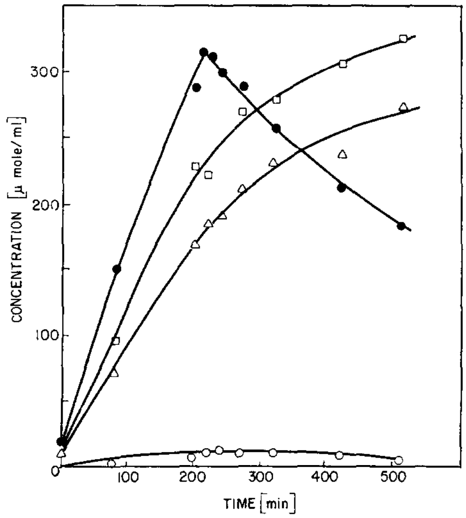

FIG. 6. Cyclohexenyl hydroperoxide (●), cyclohexenol (□), cyclohexenone (△), and cyclohexene oxide (○) concentrations, as functions of time for the cyclohexene oxidation at 60°C up to 200 min, and hydroperoxide decomposition from 200 min on under nitrogen atmosphere, using 2 g of MnO_2 as catalyst.

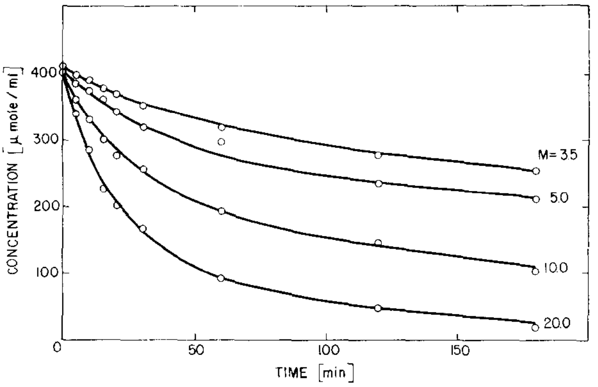

FIG. 7. Cyclohexenyl hydroperoxide concentration for its decomposition at 60°C as a function of time, for various MnO_2 catalyst to hydrocarbon ratios (M mg/ml).

an additional mole of substrate is required. So we postulate the reaction:

$$\mathrm{ROOH} + \mathrm{RH} \rightarrow 2\mathrm{ROH}. \qquad (2)$$

Here $R = C_6H_9$ and $R' = O = C_6H_8O$ (cyclohexenone).

In order to confirm more directly the simultaneous formation and decomposition of hydroperoxide, the following experiment was performed: A standard MnO_2 catalyzed oxidation run of cyclohexene was performed during 200 min using 2 g of catalyst (Fig. 6). At this time, oxygen was eliminated under vacuum; and nitrogen was supplied to the reactor. The reaction was then allowed to progress in the absence of oxygen during 200 min more. The hydroperoxide concentration decreased almost as soon as the oxygen was evacuated. At the same time no significant break in the rate of alcohol or ketone formation was observed, leading to the conclusion that alcohol and ketone are formed only by hydroperoxide decomposition.

Decomposition of hydroperoxide in the absence of oxygen. Figure 7 represents the hydroperoxide decomposition runs for various amounts of catalyst and one initial hydroperoxide concentration. The initial rate method applied to these data shows a first order dependency with respect to the catalyst. Similar experiments were performed with various initial concentrations of hydroperoxide and a single catalyst to hydrocarbon ratio, showing first order dependency of the initial decomposition rate with respect to the hydroperoxide.

The kinetic law could be represented by the equation:

$$(-d[\mathrm{ROOH}]/dt)_{t=0} = k[\mathrm{ROOH}][\mathrm{MnO_2}]^*, \qquad (3)$$

the decomposition products observed were cyclohexenol, cyclohexenone, and water.

DISCUSSION

The purpose of this work was to consider a mechanism which would be consistent with the following inferences drawn from the experimental data:

1. The 0.5 order of the initial oxidation rate, with respect to the catalyst, is consistent with an initiation on the catalyst surface, and a biradical termination in the homogeneous phase (*1*). However, for catalyst to hydrocarbon ratios close to the breakpoint, the 0.5 order was no longer observed; for this region, termination must be both homogeneous and on the catalyst surface.

2. The hydroperoxide decomposition is very likely to have a free radical character, since the cyclohexene oxidation has been found to progress as long as some hydroperoxide is present in the solution (Fig. 4).

3. The first order of the hydroperoxide decomposition rate, with respect to the catalyst, is evidence that this reaction occurs on the catalyst.

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* $[MnO_2]$ = milligrams of MnO_2 per milliliter of hydrocarbon.

4. It follows from the former assumptions that the decomposition of hydroperoxide must be involved in the initiation reaction, so that the general mechanism of the free radical oxidation is a degenerately branched chain reaction.

5. The initiation and termination reactions should be consistent with the assumed stoichiometry of the hydroperoxide decomposition equations [Eqs. (*1*) and (*2*)] which are in agreement with the mass balance of the products. The decrease of the alcohol/ketone ratio for increasing catalyst concentrations must also be considered.

6. Following Kamiya *et al.* (*8*), we assume that the catalyst surface soon attains a redox steady state and that the decomposition of each hydroperoxide molecule produces two free radicals in the homogeneous phase.

7. The characteristics of these heterogeneously catalyzed oxidations are very similar to the characteristics of hydrocarbon oxidations homogeneously catalyzed by transition metal salts, so that a consideration of the postulated mechanism for these latter processes seems reasonable (*8*).

The following mechanism is an adaptation of that suggested by Kamiya *et al.* (*8*) with the addition of termination step 10, which they suggested but did not include in the derivation of their rate equations:

Initiation

$$ROOH + M \rightarrow RO^{\cdot} + M..HO^{\cdot} \qquad V_4 \qquad (4)$$

$$RH + M..HO^{\cdot} \rightarrow R^{\cdot} + M + H_2O \qquad V_5 \qquad (5)$$

$$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot} \qquad V_6 \qquad (6)$$

Propagation

$$R^{\cdot} + O_2 \rightarrow RO^{\cdot}_2 \qquad V_7 \qquad (7)$$

$$RO^{\cdot}_2 + RH \rightarrow ROOH + R^{\cdot} \qquad V_8 \qquad (8)$$

Homogeneous termination

$$RO^{\cdot}_2 + RO^{\cdot}_2 \rightarrow R'{=}O + ROH + O_2 \qquad V_9 \qquad (9)$$

$$RO^{\cdot} + RO^{\cdot} \rightarrow R'{=}O + ROH \qquad V_{10} \qquad (10)$$

where M is an active site of the catalyst surface.

If it is supposed that the rates V_4 and V_5 are equal (catalyst at steady state composition), then it can be observed that the overall stoichiometry of the initiation and termination reactions is in agreement with reactions (1) and (2). Although termination reaction (10) is unlikely due to the high reactivity of the alkoxy radicals, it has been included, together with reaction (6), to explain the experimental fact that the ratio of alcohol to ketone concentration decreases to a value of 1 for high catalyst ratios.

If the proposed mechanism is valid, it should explain the presence of the break point observed for a catalyst to hydrocarbon ratio around 16 mg/ml. At the break point the rate of oxygen consumption is null, and the rate of hydroperoxide formation is equal to the rate of hydroperoxide decomposition (that is $d[\mathrm{ROOH}]/dt = 0$).

According to the proposed mechanism, the decomposition of an hydroperoxide produces two free radicals, and the formation of an hydroperoxide requires only one free radical. If we define the average "length of chain" as:

$$\text{length of chain} = \nu = \frac{\text{oxygen consumption rate}}{\text{free radicals initiation rate}}, \qquad (11)$$

we should have, at the break point, that ν approaches the value of 0.5.

The length of the chain could be evaluated from the experimental data, according to the proposed mechanism. The rate of ketone formation is representative of the termination rate. If we suppose steady concentration of free radicals, it also represents the rate of free radicals formation.

$$d[\mathrm{R'{=}O}]/dt = \tfrac{1}{2}(\text{rate of free radicals formation}). \qquad (12)$$

In Fig. 3 (curve 2) the length of the chain calculated in this way is plotted for various amounts of catalyst. It is interesting to point out that the extrapolated value of 0.5 for the chain length occurs for a catalyst ratio of 16.5 mg/ml, where the break point has been observed.

According to our degenerate chain branching mechanism, an autocatalytic process might be expected, since hydroperoxide produced during the propagation plays the role of initiator. However, except at very small amounts of catalyst, no autocatalytic process was observed (Fig. 2). A steady concentration of free radicals seems to be attained in a very short period of time. These free radicals could be produced by the fast decomposition of hydroperoxide always initially present in very small amounts in cyclohexene, or by direct reaction between the catalyst and the substrate.

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REFERENCES

1. MEYER, C., CLEMENT, G., AND BALACEANU, J. C., *Proc. Int. Congr. Catal., 3rd, 1964* **1,** 184 (1965).
2. MUKHERJEE, A., AND GRAYDON, W. F., *J. Phys. Chem.* **71,** 4232 (1967).
3. GOULD, E. S., AND RADO, M., *J. Catal.* **13,** 238 (1969).
4. SOREM, R. K., AND CAMERON, E. N. *Econ. Geol.* **55,** 228 (1960).
5. WAGNER, C. D., SMITH, R. H., AND PETERS, E. D., *Anal. Chem.* **19,** 976 (1947).
6. VAN SICKLE, D. E., MAYO, F. R., AND ARLUCK, R. M., *J. Amer. Chem. Soc.* **87,** 4824 (1965).
7. HORNER, L., AND JURGLEIT, W., *Justus Liebigs Ann. Chem.* **591,** 138 (1955).
8. KAMIYA, Y., BEATON, S., LAFORTUNE, A., AND INGOLD, K. U., *Can. J. Chem.* **41,** 2020 (1963).
9. TOBOLSKY, A. V., *India Rubber World* **118,** 363 (1948).
10. KAMIYA, Y., BEATON, S., LAFORTUNE, A., AND INGOLD, K. U., *Can. J. Chem.* **41,** 2034 (1963).
11. KAMIYA, Y., AND INGOLD, K. U., *Can. J. Chem.* **42,** 1027 (1964).
12. KAMIYA, Y., AND INGOLD, K. U., *Can. J. Chem.* **42,** 2424 (1964).