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Kinetics of Liquid Phase Oxidation of Cumene with Cr_2O_3, MnO_2 and Fe_2O_3 Catalysts

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The liquid phase oxidation of cumene was investigated with Cr_2O_3, MnO_2 and Fe_2O_3 catalysts in the temperature range of 70–90°C. It was observed that a critical hydroperoxide to catalyst ratio existed, below which the reaction did not proceed.

Detailed studies of the concentrations of the main products of oxidation of cumene along with the effect of catalyst weight, and hydrocarbon concentration on the rate of oxidation were conducted employing these catalysts. The apparent activation energy for the overall oxidation was calculated to be 9.8 kcal/g mole.

A reaction mechanism has been proposed and a rate expression derived is in good agreement with the experimental data.

INTRODUCTION

Although the oxidation of cumene in the liquid phase has been studied in considerable detail, relatively little attention has been given to the insoluble catalysts and the heterogeneous reactions. Recently Varma and Graydon (*1*) studied the oxidation of cumene employing cobalt oxide as the catalyst. Among the various studies reported, there is wide disagreement in the reported data and the kinetics of the reaction are still not well understood (*1–7*).

In the present work, the oxides of chromium, manganese and iron were used to initiate the oxidation of cumene. The purpose here is to report the effect of a number of variables on the reaction rate in the presence of these catalysts and a reaction mechanism which might be used effectively to describe the kinetic data observed for some transition metal oxides.

EXPERIMENTAL METHODS

Materials

Cumene was factionally distilled, and the fraction boiling at 69–70°C at 41 mm was collected. This was treated with concentrated sulfuric acid followed by dilute alkali, and washed with distilled water. The dried cumene was stored in a nitrogen atmosphere.

Chlorobenzene was washed with concentrated sulfuric acid, washed with water and dried before storage and use. Cumene hydroperoxide solution was prepared by thermal oxidation of cumene at 60°C. The catalysts MnO_2, Fe_2O_3 and Cr_2O_3 of A.R. grade were obtained from manufacturers in the powdered form.

Oxidation Procedure

The apparatus was similar to that used by Bolland (*8*) in the thermal oxidation of ethyl linoleate. The desired temperature was maintained by a constant temperature water bath. The pressure in the system was kept constant during experiments by

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means of the relay and the gas generating cell. The absorption of oxygen was read from the gas burette. The stirrer speed was maintained constant through an adjustable steady speed motor.

Analysis of Products

Hydroperoxides. The hydroperoxide content in the product was estimated by the iodometric method (*9*).

Acetophenone. The yield of acetophenone was determined by infrared absorption, using a Perkin-Elmer, Model 521 ir spectrometer. A calibration curve was prepared by noting the absorption at 1694 cm^{-1} for several dilute concentrations of ketone in cumene and in mixtures of cumene and chlorobenzene.

Cumyl alcohol. The analysis of cumyl alcohol was made by comparing its absorption at 3600 cm^{-1} with those of standards prepared similarly as for acetophenone. The cumyl alcohol in the product was also estimated by the bromide-bromate method (*10*).

Dialkyl peroxide. This analysis was carried out by the method of Blanchard (*11*). Under the conditions of the experiment, no dialkyl peroxide could be detected.

RESULTS AND DISCUSSION

Initiation

When the oxidation of cumene was conducted in the absence of a catalyst or any free radical initiator, the reaction did not proceed even up to 120 min. In the case of MnO_2, where the detailed initiation study was performed, it was observed that the sample which refused to react immediately would start absorbing oxygen after standing for a long time. The cumene hydroperoxide which formed after prolonged standing caused the reaction to proceed. If cumene hydroperoxide was added, immediately the reaction proceeded. Therefore, it may be concluded that addition of both the catalyst and hydroperoxide was necessary to initiate the reaction.

Results of runs conducted for MnO_2 with various initial hydroperoxide concentrations indicated a limiting value (0.0043 g mole/liter) below which the rate of oxidation was negligible. Beyond this limiting value, there was no effect of increase in hydroperoxide concentration on the oxygen absorption rate (Table 1). It is believed that beyond a critical ratio, the same observation of effect of increase in hydroperoxide on the rate existed for Cr_2O_3 and Fe_2O_3 catalysts, but this effect was not determined with precision. However, a critical ratio of hydroperoxide concentration to catalyst amount of 2.3×10^{-4} g mole/g of catalyst was obtained for both catalysts. Further runs on cumene oxidation were conducted with a ratio of 2.3×10^{-4} g mole hydroperoxide/g of catalyst.

Mukherjee and Graydon (*12*) and Caloyannis and Graydon (*13*) reported a sim-

TABLE 1

CRITICAL HYDROPEROXIDE CONCENTRATION AND EFFECT OF CUMENE HYDROPEROXIDE CONCENTRATION ON THE REACTION RATE WITH MnO_2 AS CATALYST[a]

(ROOH) (g mole/liter)	Catalyst (g/liter)	ROOH/Catalyst (g mole/g)	Rate (g mole/s) $\times 10^7$
0.0043	25	0.00017	3.85
0.0043	50	0.00009	0
0.0085	50	0.00017	3.95
0.0506	50	0.00101	3.93
0.1548	50	0.00309	3.98

[a] Reaction temp, 80°C.

ilar behavior in their studies on oxidation of tetralin and *p*-xylene, respectively, with manganese and cobalt oxide catalysts. Meyer *et al.* (*14*) observed that to initiate the oxidation of cyclohexene in the presence of the catalyst Cr_2O_3, hydroperoxide had to be added to the initial reagents.

Kolmakov *et al.* (*6*) studied the influence of hydroperoxide on the rate of air oxidation of cumene, and found that the induction period was shortened considerably. However, Varma and Graydon (*1*) did not observe any induction period in their studies on oxidation of cumene with Co_3O_4 as a catalyst. Also, they reported that the presence of hydroperoxide was not necessary to initiate the reaction.

Comparison of Catalysts and Catalyst Weights

The three catalysts employed in the study of cumene oxidation were the oxides of manganese, iron and chromium. MnO_2 was chosen mainly for comparison with the earlier work done on liquid phase oxidation (*1,12–15*).

The amount of oxygen absorbed versus time of oxidation for all the three catalysts, is shown in Fig. 1. The data were obtained on the rate of oxygen absorption employing 0.01 g of catalysts/ml of cumene. Under these conditions, the highest rate of oxidation was 0.67×10^{-7} g mole/s for MnO_2.

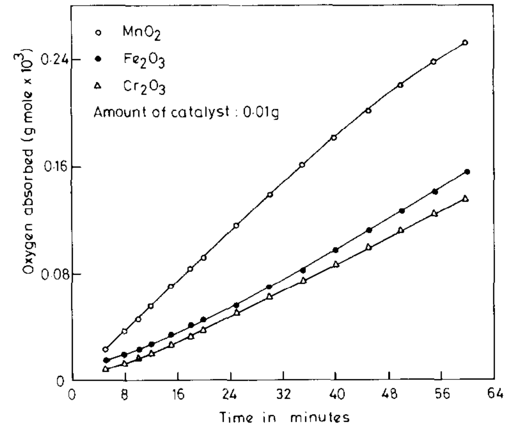

FIG. 1. Oxygen absorption curves for 1 ml cumene at 80°C for different catalysts.

Varma and Graydon (*1*) have made some preliminary rate studies on the cumene oxidation with MnO_2, Co_3O_4, NiO and Cu_2O catalysts. They have shown an oxygen absorption curve for MnO_2 employing 0.10 g of catalyst in 1 ml of cumene. The highest rate of absorption of oxygen was found to be 1.68×10^{-7} g mole/s. Under the above experimental conditions, we found that the rate of oxidation was negligible. A detailed study with varying catalyst amount was therefore made to study the "critical catalyst amount." The catalyst weight above which the reaction did not start is termed as "critical catalyst amount." Figure 2 shows that the increase in the catalyst amount beyond 0.07 g/ml of cumene resulted in rapid decrease of the oxidation rate, with complete stopping of the reaction beyond 0.1 g/ml of cumene. Investigations carried out in the present work at different temperatures showed that the critical catalyst amount was unaffected by variation in temperature (Fig. 2).

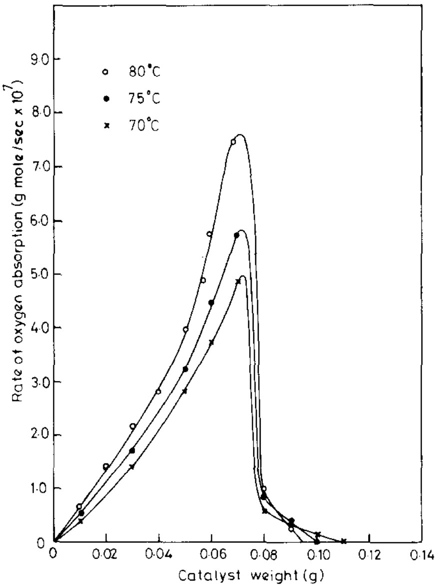

FIG. 2. Measured rates of oxygen absorption for 1 ml cumene at different temperatures as a function of the weight of MnO_2.

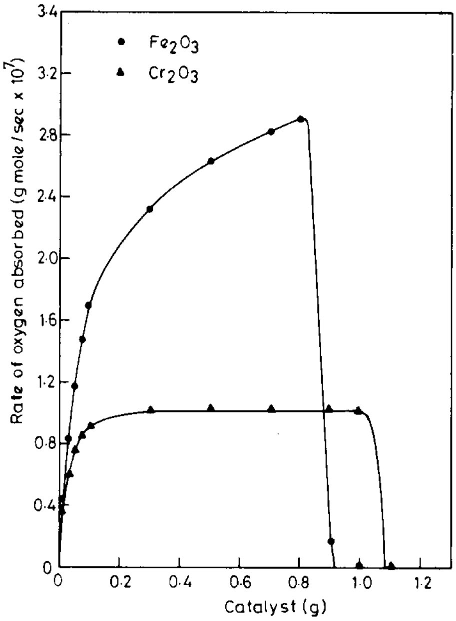

FIG. 3. Measured rates of oxygen absorption for 1 ml cumene at 80°C as a function of the weight of different catalysts.

Fe_2O_3 and Cr_2O_3 catalyzed oxidations showed a behavior similar to that of MnO_2. As shown in Fig. 3, the rate of oxygen absorption increased very rapidly up to a catalyst weight of 0.1 g/ml of cumene for both the catalysts. In the case of Fe_2O_3, at higher catalyst weights, the rate of oxygen absorption decreased gradually until 0.9 g/ml of cumene. At catalyst weights higher than this, the reaction would not start. Runs catalyzed with Cr_2O_3 showed that the rate of absorption of oxygen almost leveled off at catalyst weights higher than 0.3 g/ml of cumene, and the reaction completely stopped beyond a catalyst weight of 1.1 g/ml of cumene.

Kamiya and Ingold (*16*) observed that during the oxidation of tetralin in chlorobenzene, in the presence of various metal catalysts, e.g., cobalt stearate, the limiting oxidation rate increased with increasing catalyst concentration until a critical concentration was reached. Thereafter, further small increase in catalyst concentration caused a catastrophic decline in oxidation rate. Rouchard (*17*) also observed that when cumene was oxidized in the presence of the copper or zinc chelates, critical catalyst concentrations appeared. The inhibition observed after the critical catalyst concentration was attributed to interaction between radicals and metal catalyst.

The decrease in rate after the maximum was also observed by Neuberg *et al.* (*15*) while studying cyclohexene oxidation with MnO_2 as catalyst. They suggested that, beyond the critical ratio, the rate of hydroperoxide formation was smaller than the rate of decomposition. According to them, the oxygen consumption could occur only if there was some hydroperoxide left in the solution. The presence of hydroperoxide (a product) was a necessary condition for the progress of the free radical oxidation.

In Fig. 4 logarithmic rates of oxygen absorptions are plotted against catalyst weights for the catalysts MnO_2, Fe_2O_3 and Cr_2O_3. The apparent order of the reaction with respect to MnO_2, Fe_2O_3 and Cr_2O_3

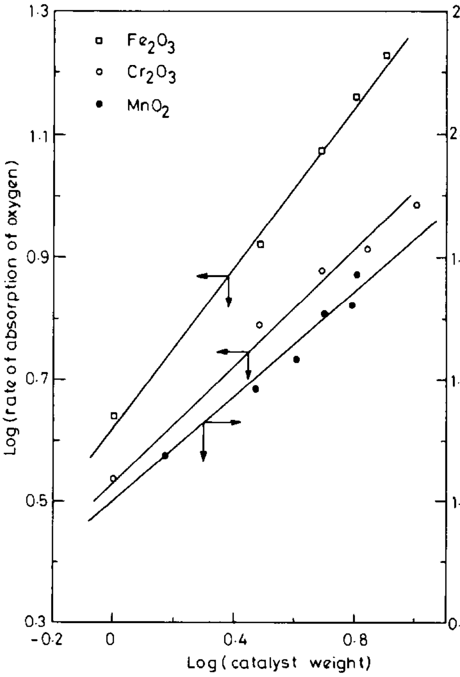

FIG. 4. Rate dependence with respect to catalyst weight for different catalysts at 80°C.

was found to be 0.80, 0.63 and 0.47, respectively.

Neuberg *et al.* (*15*) and Meyer *et al.* (*14*) obtained apparent orders of 0.5 and 0.7 with MnO_2 catalyst, in the liquid phase oxidation of cyclohexene. Caloyannis and Graydon (*13*) and Varma and Graydon (*1*) obtained apparent orders of 0.5 and 0.4 with Co_3O_4 catalyst, in the liquid phase oxidation of *p*-xylene, and cumene, respectively. These orders of reaction may be compared with the results obtained from the present studies.

Cumene Concentration

The influence of hydrocarbon concentration on the rate of oxidation was studied with mixtures of cumene and monochlorobenzene, with MnO_2, Fe_2O_3 and Cr_2O_3 as catalysts. Runs were made at only one catalyst amount for all the catalysts. In Fig. 5 logarithmic rates of oxygen absorption are plotted against hydrocarbon concentrations. The orders with respect to hydrocarbon concentration were 1.01, 1.18 and 1.27 for MnO_2, Fe_2O_3 and Cr_2O_3, respectively.

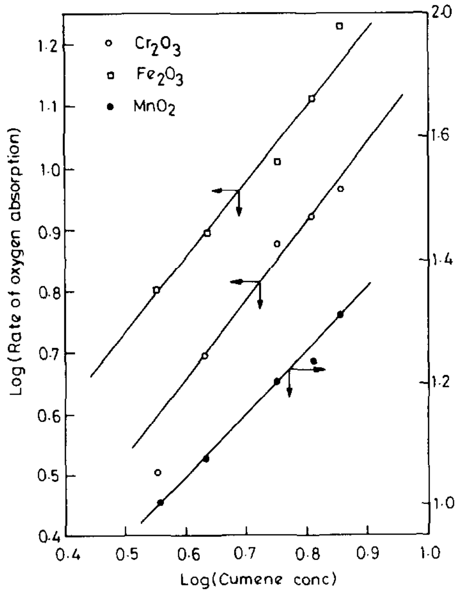

FIG. 5. Rate dependence with respect to cumene concentration for different catalysts at 80°C.

Kamiya *et al.* (*18*) have studied the oxidation of tetralin by cobalt salts. They have shown that for any substrate and solvent in which the rate of a metal-catalyzed oxidation is really first order with respect to the substrate the apparent order over a limited concentration range may lie above 1.0. In particular, at low hydrocarbon concentration or comparatively high catalyst concentration an apparent order of 1.5 might be obtained. This may explain our results of Cr_2O_3 catalyzed runs where a departure from first order dependence with respect to cumene concentration is obtained.

Leszczynski (*19*) obtained first order dependence with respect to cumene concentration with copper oxides. Caloyannis and Graydon (*13*), using Co_3O_4 as the catalyst found two orders with respect to *p*-xylene concentration depending upon the solvent: 1.24 with *p*-dichlorobenzene and 0.98 with bromobenzene. Meyer *et al.* (*14*) found very similar results in the oxidation of cyclohexene.

Product Distribution

Although the main products of oxidation of cumene have been reported by several workers (*1,3,20*), there is a wide disagreement in the quantitative results of the product distribution. The main products of the oxidation reaction are reported to be cumene hydroperoxide, dimethyl phenyl carbinol or cumyl alcohol acetophenone. The product distribution seems to depend upon the type of catalyst used and catalyst weights. The aim of this work was to find the effect of catalyst weight on the distribution of products in the cases of MnO_2, Cr_2O_3 and Fe_2O_3 catalysts. Table 2 shows the distribution of reaction products for the catalysts MnO_2, Cr_2O_3 and Fe_2O_3.

As the catalyst weight was increased, the yield of hydroperoxide increased but the mole percent hydroperoxide in the total oxidized products decreased.

Varma and Graydon (*1*) obtained similar

TABLE 2
DISTRIBUTION OF PRODUCTS OF CUMENE OXIDATION WITH MnO_2, Fe_2O_3 AND Cr_2O_3 CATALYSIS[a]

	MnO_2			Fe_2O_3			Cr_2O_3		
Catalyst wt (g)	Hydroperoxide	Alcohol	Ketone	Hydroperoxide	Alcohol	Ketone	Hydroperoxide	Alcohol	Ketone
0.01	70.00	30.00	—[b]	65.12	34.88	—[b]	62.56	37.44	—[b]
0.03	55.66	44.34	—[b]	56.69	43.31	—[b]	53.51	46.49	—[b]
0.05	50.04	49.96	—[b]	49.79	50.21	—[b]	47.31	52.69	—[b]
0.08	32.83	62.74	4.43	46.01	53.99	—[b]	43.20	56.74	0.06
0.10				44.33	54.92	0.75	41.00	57.92	1.08

[a] All the concentrations are reported in mole%. Amount of initial hydroperoxide is included in the hydroperoxide concentration. Reaction temp, 80°C; vol of cumene, 1 ml; reaction time, 45 min.

[b] Acetophenone was detectable in infrared spectra, but the intensity of absorption was too small for accurate measurements.

data when the oxidation of cumene was carried out with Co_3O_4 catalyst. In their experiments, employing the lowest Co_3O_4 catalyst weights, the major products were the hydroperoxide and alcohol and there was no measurable quantity of acetophenone present. Twigg (*3*) did not report the complete product distribution, although he stated that acetophenone was also formed in considerable quantity.

Apparent Activation Energy

The logarithm of rate of absorption of oxygen was plotted with the inverse of absolute temperature for Fe_2O_3 catalyst at the temperatures of 70, 75, 80 and 90°C. The apparent activation energy for the overall oxidation was calculated to be 9.8 kcal/g mole.

Reaction Mechanism

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

a. There is a critical hydroperoxide to catalyst ratio with all the three catalysts MnO_2, Cr_2O_3 and Fe_2O_3, indicating that hydroperoxide saturates the catalyst surface, after which active sites are filled.

b. An excess of hydroperoxide does not affect the reaction rate, indicating that hydroperoxide is active only on the catalyst surface.

c. The apparent orders of the reaction with respect to catalyst weight and the hydrocarbon concentration are close to 0.5 and 1.0, respectively.

d. There is a critical weight of the catalysts above which the rate of oxidation drops catastrophically.

Although observation (d) is not easily subject to simple mechanistic explanations, coherent interpretations of the observations (a), (b) and (c) can be made. The oxidation of cumene has all the characteristics of an heterogeneous initiation and homogeneous propagation followed by a biradical termination. For the heterogeneous catalysis, it is assumed that the hydroperoxide absorbed on the catalyst, initially, is not active in the production of free radicals. Only the peroxide saturated catalyst produces free radicals. Such radicals may interact either with adsorbed hydrocarbon or hydrocarbon in solution. In either case the initiation step would be expected to follow.

Initiation:

$$\mathrm{ROOH...M} \xrightarrow{k_1} \mathrm{RO^{\cdot}...M} + \mathrm{{}^{\cdot}OH...M}, \tag{1}$$

$$\mathrm{RH} + \mathrm{RO^{\cdot}...M} \xrightarrow{k_2} \mathrm{ROH} + \mathrm{R^{\cdot}}, \tag{2}$$

$$\mathrm{RH} + \mathrm{{}^{\cdot}OH...M} \xrightarrow{k_3} \mathrm{H_2O} + \mathrm{R^{\cdot}}. \tag{3}$$

The propagation steps for oxidation are well understood and are believed to be operative in the liquid phase reactions in general. The scheme is as follows.

Propagation:

$$R^{\cdot} + O_2 \xrightarrow{k_4} ROO^{\cdot}, \qquad (4)$$

$$ROO^{\cdot} + RH \xrightarrow{k_5} ROOH + R^{\cdot}. \qquad (5)$$

The chain termination may take place by a molecular reaction between two $ROO^{\cdot}$ radicals.

Termination:

$$2ROO^{\cdot} \xrightarrow{k_6} \text{inactive products}. \qquad (6)$$

The following derivation is similar to one as described in Ref. (*12*). The concentration of ROOH. . .M is proportional to concentration of catalyst, i.e.,

$$k_1\,(\text{ROOH}\ldots\text{M}) = k(\text{M}). \qquad (7)$$

Assuming that steady-state concentration exist for $^{\cdot}$OH. . .M and $RO^{\cdot}$. . .M radicals, the following rate expression may be derived

$$\frac{-d(O_2)}{dt} = k_5\left(\frac{2k}{k_6}\right)^{1/2}(\text{M})^{1/2}\,(\text{RH}). \qquad (8)$$

As shown in Table 2, it may be observed that the appearance of alcohol in the product is proportional to the concentration of catalyst. The formation of alcohol being found to increase with decrease in the formation of hydroperoxide. This suggests that the alcohol is indeed formed through Eqs. (1), (2) and (3). The experimental orders thus obtained agree well with the derived rate expression.

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