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Heterogeneous Catalytic Oxidation of Cumene (Isopropyl Benzene) in Liquid Phase

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The liquid-phase oxidation of cumene (isopropyl benzene) with molecular oxygen at 80°C was investigated. Cobalt$^{II, III}$ oxide, MnO_2, NiO and Cu_2O were used as heterogeneous catalysts.

Detailed studies of the effect of catalyst weight, hydrocarbon concentration, and initial hydroperoxide concentration on the rate of oxidation were conducted employing cobalt$^{II, III}$ oxide as the catalyst. The oxygen absorption rate was found to be proportional to the 0.4 power with respect to the catalyst weight, and to the 1.5 power with respect to the cumene concentration.

The concentrations of the main products of oxidation of cumene, cumene hydroperoxide, dimethyl phenyl carbinol and acetophenone were found to depend on the weight of catalyst.

Reaction mechanisms and rate expressions for the oxidation of cumene were proposed.

INTRODUCTION

The oxidation of cumene (isopropyl benzene) in the liquid phase has been studied in considerable detail (*1–7*). It is a typical example of the process of oxidation of alkyl aromatic hydrocarbons, whose most important feature is the high yield of hydroperoxide.

Studies of the liquid phase oxidation of tetralin (*8*) and paraxylene (*9*) have been carried out in this laboratory employing *p*-type semiconductors (oxides of cobalt, manganese, nickel, and copper). The present work was carried out to find (a) the effect of the oxides of cobalt, manganese, nickel and copper in the liquid-phase oxidation of cumene and (b) to study the similarities of the oxidation reactions of cumene with those of tetralin and *p*-xylene.

EXPERIMENTAL SECTION

Apparatus

The details of the apparatus and the operation have been described by Mukherjee and Graydon (*8*).

The oxidation experiments were conducted at constant pressure. The reactor was set in a shaker and was connected by a flexible hose to an oxygen buret. All experiments were done at shaking rates about 1000 oscillations/min. Mukherjee and Graydon (*8*) have shown that rates of oxidation were independent of shaking rate above this value. The reactor was immersed in a constant temperature oil bath, whose temperature could be maintained within ±0.2°C. The volume of oxygen consumed was directly measured by noting the upward movement of the Hg level in the oxygen buret.

The products of oxidation were analyzed with a Beckman Model IR-9 infrared spectrophotometer.

Catalyst

A major part of the present study was done using cobalt oxide as the catalyst, which was supplied by J. T. Baker Chemical Co. Its analysis was 71.5% Co with trace impurities at 0.01% level. Caloyannis (*10*) had analyzed and characterized this catalyst, which he used for his study of the liquid-phase oxidation of p-xylene. Some of the important aspects of the catalyst were as follows: specific surface area was found to be 2.4 m^2/g, employing the BET method. It showed absorption bands in the range of 550–600 cm^{-1} in the infrared spectrum using the potassium bromide pellet technique. In the X-ray diffraction studies *d*-values of 2.86, 2.44 and 1.43 were obtained. The above corresponded to a Co_3O_4 structure, by comparative studies.

Manganese dioxide (MnO_2) whose analysis was given as 99.5% MnO_2 was manufactured by Fisher Scientific Co. Nickel oxide (NiO), whose trace impurities were given as being less than 0.15% was also manufactured by Fisher Scientific Co. Cuprous oxide (Cu_2O) was a product of Matheson, Coleman and Bell. Assay as Cu_2O is given as not less than 95.0%.

Reagents

Cumene (isopropyl benzene). Cumene (reagent grade) obtained from Eastman Chemical Products was batch distilled in a vacuum, and the top and bottom fractions were discarded. The distillate was stored under a nitrogen atmosphere. An infrared analysis gave no evidence of the presence of any hydroperoxide in the distilled cumene.

Cumene hydroperoxide (α,α-dimethylbenzyl hydroperoxide). Cumene hydroperoxide (technical grade), used to calibrate the IR-9 spectrophotometer and as an additive to cumene for various reactions, was from Hercules Powder Co. According to Hercules Powder Co., the hydroperoxide content was 73.7% and the nonperoxide content was a complex mixture of cumene, and alcohol and ketone derivatives of cumene. The hydroperoxide content was found to be 6.33 g.mole/liter according to the iodometric titration, the technique employed by Wagner, Smith and Peters (*11*).

Dimethyl phenyl carbinol (α,α-Dimethylbenzyl alcohol) and acetophenone which were used for the calibration of IR-9 spectrophotometer, were obtained from Eastman Chemical Products and British Drug House, respectively. o-Dichlorobenzene used for diluting cumene for certain experiments was supplied by British Drug House.

RESULTS AND DISCUSSION

Initiation

The oxidation reaction of cumene was not initiated for a period of 90 min in the absence of the catalyst. Murthy and Graydon (*12*) have observed that the addition of both the catalyst and cumene hydroperoxide was necessary to initiate the oxidation of cumene. In the present study, however, the presence of the hydroperoxide was not found to be necessary to initiate the reaction.

About 2 or 3 min were required for the apparatus to attain steady state once the reactor with its contents was started to shake. It was therefore difficult to determine accurately the rates in the first 3 or 4 min. No initiation period was observed. If present at all, the initiation period was less than 1 or 2 min. The oxidation reaction always started within 4 min when 0.10 g or more of Co_3O_4/ml cumene was employed. With 0.05 and 0.01 g of Co_3O_4, visible oxygen absorption started around 5 and 7 min, respectively, indicating a short inhibition period at these low catalyst amounts.

Mukherjee and Graydon (*8*) and Caloyannis (*9*) did not find any lengthy induction periods in their studies on oxidation of tetralin and p-xylene, respectively, with certain heterogeneous catalysts. Meyer, Clement and Balaceanu (*13*) observed that to initiate the oxidation of cyclohexene in the presence of Cr_2O_3, the hydroperoxide had to be added to the initial reagents, whereas initiation was produced without the addition of hydroperoxide with CoO and MnO_2.

Since the oxidation reaction of cumene starts without an initiation period in the absence of the hydroperoxide, an initial direct reaction between the hydrocarbon and the catalyst seems probable. The contribution of such a reaction to the longer term oxidation in the presence of the peroxide product is a matter for speculation.

Comparison of Catalysts

Rates of oxidation were studied employing oxides of manganese, cobalt, copper and nickel. These catalysts were chosen for comparison with the earlier work done on liquid phase oxidation in this laboratory by Murthy and Graydon (*12*), Mukherjee and Graydon (*8*) and Caloyannis (*9*). Oxides of manganese, cobalt, copper and nickel were found to be very effective catalysts in the liquid phase oxidation of tetralin by Mukherjee and Graydon (*8*) and Co_3O_4 and MnO_2 in the liquid-phase oxidation of *p*-xylene by Caloyannis (*9*).

In this work the highest rate of oxidation was obtained with MnO_2 followed by Co_3O_4, NiO and Cu_2O in that order (Table 1). This corresponds with Murthy and Graydon's (*12*) findings. Only Cu_2O catalyzed oxidation had an induction period, a period of 46 min.

TABLE 1
COMPARISON OF CATALYSTS[a]

Run no.	Catalyst	Rate of oxidation (g.mole/sec)10^7
208	CO_3O_4	1.68
210	MnO_2	2.39
211	NiO	1.00
212	Cu_2O	0.58

[a] Reaction temp: 80°C; initial hydroperoxide concn: 0.162 g.mole/liter; amount of catalyst: 0.1 g; vol of cumene: 1 ml.

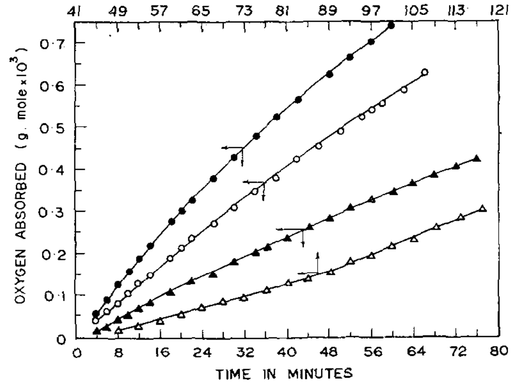

FIG. 1. Oxygen absorbtion curves for 1 ml cumene at 80°C, for different catalysts: (○) MnO_2; (●) Co_3O_4; (▲) NiO; (△) Cu_2O.

The rate of oxygen absorption was maximum, from the start of the run in the experiments catalyzed with Co_3O_4, MnO_2, and NiO (Fig. 1). In the experiment using Cu_2O, which had a long induction period and whose rate was the lowest, the rate did not reach the maximum until approximately 20 min after the start of the reaction. The cobalt oxide catalyst was chosen for a detailed study described in the following sections.

Catalyst Weight

The rate of oxidation increased with the increase in the weight of catalyst. This has been observed by many investigators (*3*, *8*, *9*, *12–14*) in their studies of liquid-phase oxidation of cumene and other hydrocarbons with heterogeneous catalysts. Changes in the volume of the solution which was varied from 0.8 to 3.0 ml did not affect the rate.

In the initial stages, the rate increased very rapidly with the increase in the catalyst weight, but later it fell off gradually and finally the reaction would not start at all at very high catalyst amounts (Fig. 2). Table 2 shows the data. The apparent order of the reaction with respect to the catalyst was found to be 0.4.

Caloyannis (*9*) obtained an apparent order of 0.5 ± 0.05, with Co_3O_4 catalyst, up to an amount of 200 mg/ml, in the liquid-phase oxidation of *p*-xylene.

The experiments were conducted with increasing weights of catalyst for the same amount of cumene. When the weight of catalyst was 1.90 g/ml, the reaction did not start. A number of experiments were conducted and it was observed that the oxidation of cumene never started above a catalyst weight of 1.85 g/ml. The catalyst weight above which the reaction did not start has been designated as "critical catalyst amount."

Investigations were done to find out whether such a phenomenon would be observed when cumene with an *initial cumene* hydroperoxide content was employed. Indeed, the same phenomenon was found when cumene with an initial hydroperoxide

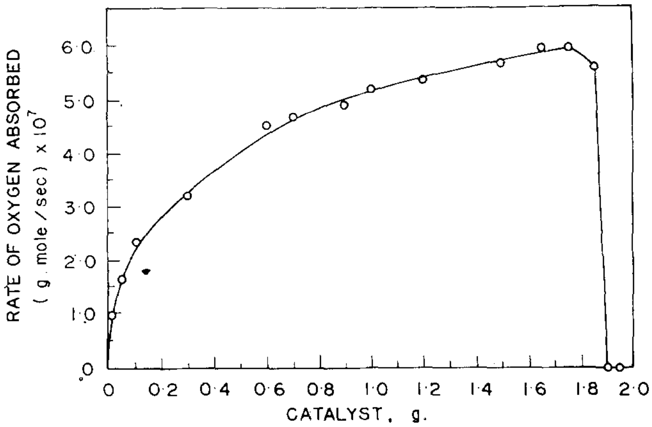

FIG. 2. The measured rates of oxygen absorption for 1 ml cumene at 80°C as a function of the weight of Co_3O_4.

content of 0.001 g.mole/liter was employed. The critical catalyst amount was 1.85 g/ml. However, when cumene with an initial hydroperoxide content of 0.162 g.mole/liter was used, the phenomenon was not observed even at a catalyst weight of 2.00 g/ml. Higher amounts of catalysts were not employed.

This phenomenon of over-catalysis was found by Mukherjee and Graydon (*8*) while investigating tetraline oxidation with Mn_2O_3 as catalyst. When the hydrocarbon was diluted, the break came at an even lower catalyst weight corresponding to a constant hydrocarbon to catalyst ratio. They also found that there exists a critical ratio of initial hydroperoxide concentration to catalyst weight, below which the reaction did not proceed. They have explained the phenomenon by postulating two distinct sites on the catalyst: active adsorption sites and inactive adsorption sites. The inactive sites preferentially absorb hydroperoxide but do not contribute to radical formation. They postulated that the active sites were responsible for hydroperoxide decomposition to give radicals RO• and •OH which propagate the reaction. The reaction takes place only if there is enough hydroperoxide to saturate the inactive sites and to adsorb on the active sites to produce a sufficient quantity of radicals for the reaction.

TABLE 2
EFFECT OF CATALYST WEIGHT ON THE RATE OF OXIDATION[a]

Run no.	Co_3O_4 catalyst (g)	Rate of oxidation (g.mole/sec)10^7
231	0.01	0.96
233	0.05	1.63
229	0.10	2.31
230	0.30	3.15
236	0.60	4.49
241	0.70	4.66
246	0.90	4.87
277	1.00	5.13
279	1.20	5.35
284	1.50	5.65
285	1.65	5.92
286	1.75	5.92
292	1.85	5.55
	1.90	(no reaction)
	2.00	

[a] Reaction temp: 80°C; initial hydroperoxide concn: 0; vol of cumene: 1 ml.

Meyer, Clement and Balaceanu (*13*) found that the oxidation of cyclohexene did not take place when a large quantity of chromic oxide catalyst was employed and then the reaction was initiated by adding a bit of hydroperoxide. They observed that there was a critical concentration of hydroperoxide below which the reaction did not take place and the critical concentration increased with the mass of the solids used.

In homogeneous catalysis, an interesting work by Betts and Uri (*15*) in the oxidation of 2,6,10,14-tetramethylpentadecane revealed very similar findings. With well-defined chelates which are soluble in hydrocarbons there are certain concentrations at which a transition from catalysis to inhibition occurs. According to them, as long as the concentration of the hydroperoxide is very low, a relatively inefficient initiation reaction involving molecular oxygen which is first order with regard to the catalyst competes with a termination reaction which is second order with regard to the catalyst. At a certain catalyst concentration, the inhibition is therefore bound to overtake initiation, but the situation would change abruptly if hydroperoxide were present, since initiation involving catalyst and hydroperoxide is much more efficient than the reaction involving catalyst and molecular oxygen.

There is a suggestion that the phenomenon of over-catalysis is closely connected to the rate of reaction. As described earlier, the rate of oxidation increases as the catalyst weight is increased. This continues until the rate reaches a maximum, whereupon with a further small increase in the catalyst weight, the oxidation does not start; the phenomenon of over-catalysis is exhibited. The rate does not fall off gradually. The same feature can be observed in Mukherjee and Graydon's (*8*) data.

The explanation given by Betts and Uri (*15*) fits their results well. They have proposed a second order dependency with regard to the catalyst in the termination reaction. Such a high value seems plausible for soluble catalysts, but extremely unlikely with insoluble ones. It is possible that the termination reaction is of only a slightly higher order than that of the initiation reaction with respect to the insoluble catalyst.

The phenomenon of over-catalysis or catalyst-inhibitor conversion has never been reported in the oxidation reactions of cumene unlike those with tetralin and cyclohexene. In the present investigation, this phenomenon was experienced with CO_3O_4 as catalyst; however it is possible that other insoluble catalysts might also produce the same result.

Initial Hydroperoxide Concentration

Experiments were conducted to determine the effect of the initial cumene hydro-

TABLE 3

RATE OF OXIDATION OF CUMENE WITH VARIOUS INITIAL HYDROPEROXIDE CONCENTRATIONS[a]

Run no.	IHC (g.mole/ liter)	Co_3O_4 Catalyst (g)	Rate (g.mole/ sec) × 10^7
209	0.162	0.01	(no reaction)
231	0	0.01	0.96
207	0.162	0.05	1.08
215	0.080	0.05	1.26
218	0.040	0.05	1.41
221	0.020	0.05	1.41
224	0.010	0.05	1.60
233	0	0.05	1.63
208	0.162	0.10	1.68
214	0.080	0.10	1.75
217	0.040	0.10	1.97
219	0.020	0.10	1.99
223	0.010	0.10	2.02
226	0.005	0.10	2.11
229	0	0.10	2.31
204	0.162	0.30	2.54
213	0.080	0.30	2.69
216	0.040	0.30	2.93
220	0.020	0.30	3.03
222	0.010	0.30	3.07
225	0.005	0.30	3.17
313	0.001	0.30	3.11
230	0	0.30	3.15
203	0.162	0.60	3.32
312	0.001	0.60	4.52
236	0	0.60	4.49
241	0	0.70	4.66
311	0.001	0.90	4.92
246	0	0.90	4.87
201	0.162	1.00	3.53
277	0	1.00	5.13
310	0.001	1.20	5.35
279	0	1.20	5.35
206	0.162	1.50	4.60
303	0.001	1.50	5.75
284	0	1.50	5.65
308	0.001	1.65	5.99
285	0	1.65	5.92
286	0	1.75	5.92
305	0.001	1.80	5.69
	0.001	1.85	(no reaction)
292	0	1.85	5.55
	0	1.90	(no reaction)
205	0.162	2.00	4.80

[a] Reaction temp: 80°C; vol of cumene: 1 ml.

peroxide concentrations on the rate of oxidation with various catalyst weights. Table 3 gives the detailed data. There is a gradual decrease in the rate with increases in the initial hydroperoxide concentration. However, the decrease in the rate is not very substantial.

Such a finding is not unusual in the oxidation of hydrocarbon with insoluble catalysts. Mukherjee and Graydon (*8*) had found that although the initial hydroperoxide (tetraline hydroperoxide) concentration helped considerably in shortening the induction period, it tended to decrease the rate of oxidation of tetralin to a very small extent.

Meyer, Clement and Balaceanu (*13*) found that the hydroperoxide (2-cyclohexene-1-yl-hydroperoxide) decreased the rate of oxidation reaction of cyclohexene when CoO and MnO_2 were used; however, for Cr_2O_3 the hydroperoxide increased the rate of reaction. Traylor and Russell (*7*) employing soluble catalysts, found that adding cumene hydroperoxide to cumene increased the rate of oxidation of cumene.

Hydrocarbon Concentration

To study the dependence of the rate of oxidation on the hydrocarbon concentration, with CO_3O_4 as catalyst, experiments were conducted using *o*-dichlorobenzene as diluent. The data obtained are summarized in Table 4. Figure 3 shows the oxidation rates at various hydrocarbon concentrations.

Log rate vs log hydrocarbon concentration was plotted, from which it was concluded that the rate of oxidation is of the order of 1.49 with respect to cumene concentration. Mukherjee and Graydon (*8*) obtained the orders 1.8, 1.4, 1.5 and 0.8 with respect to tetraline concentration employing Mn_2O_3, MnO_2, Cu_2O, and NiO, respectively. Caloyannis (*9*), using Co_3O_4 as the catalyst found two orders with respect to *p*-xylene concentration depending upon the diluent: 1.24 with *p*-dichlorobenzene and 0.98 with bromobenzene. Meyer, Clement and Balaceanu (*13*) found very similar results in the oxidation of cyclohexene. They obtained an order of one, when benzene was used as the solvent; but it was greater than one when cyclohexanone was used as the solvent. However for oxidation of cyclohexene with homogeneous catalysts Meyer, Clement and Balaceanu (*13*) obtained an order of one irrespective of the nature of solvents employed.

TABLE 4
Rates of Oxidation at Different Hydrocarbon Concentrations[a]

Run no.	Co_3O_4 catalyst (g)	concn (g.mole/liter)	Rate (g.mole/sec) × 10^7
276	0.6	6.81	3.80
264	0.6	6.45	3.50
260	0.6	5.38	2.72
272	0.6	4.66	2.29
273	0.6	4.30	1.90
274	0.6	3.94	1.67

[a] Reaction temp: 80°C; initial hydroperoxide concn: 0; vol of cumene: 1 ml.

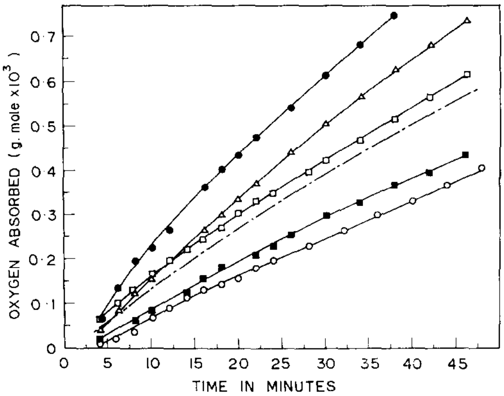

Fig. 3. Oxygen absorption curves for 1 ml of cumene at 80°C as a function of cumene concentration (g.mole/liter): (●) 6.81 (△) 6.45; (□) 5.38; (- -) 4.66; (■) 4.30; (○) 3.94.

Product Distribution

The main products of oxidation of cumene are reported by various investigators (*2–4, 16–18*) to be cumene hydroperoxide α,α-dimethyl phenyl carbinol and acetophenone. The main aim of this investigation was to find the effect of the catalyst weight on the distribution of the abovementioned products of oxidation. Cumene with varying initial hydroperoxide concentrations were also employed to find out

TABLE 5

DISTRIBUTION OF PRODUCTS OF CUMENE OXIDATION WITH Co_3O_4 CATALYSTS[a]

Run no.	IHC (g.mole/liter)	Co_3O_4 (g)	Hydroperoxide[b]		Alcohol		Acetophenone	
			a	b	a	b	a	b
213	0.08	0.30	7.31	34.03	8.66	45.27	3.96	20.70
214	0.08	0.10	5.54	49.70	4.80	50.30	—[c]	—[c]
215	0.08	0.05	4.55	60.00	2.50	40.00	—[c]	—[c]
216	0.04	0.30	5.47	35.26	7.03	48.89	2.28	15.85
217	0.04	0.10	4.00	46.15	4.20	53.85	—[c]	—[c]
220	0.02	0.30	5.68	35.17	7.33	47.05	2.77	17.79
219	0.02	0.10	4.56	47.20	4.55	47.10	0.075	7.76
221	0.02	0.05	5.16	60.70	3.63	39.30	—[c]	—[c]
222	0.01	0.30	6.63	34.73	8.24	43.82	4.03	21.43
223	0.01	0.10	5.00	47.30	5.10	49.27	0.35	3.43
224	0.01	0.05	4.92	57.04	3.63	42.96	—[c]	—[c]
225	0.05	0.30	6.76	34.43	8.43	43.25	4.35	22.32
226	0.05	0.10	4.62	49.42	4.73	50.58	—[c]	—[c]
230	0	0.30	6.72	34.74	8.06	41.63	4.575	23.63
229	0	0.10	6.75	45.76	6.76	45.83	1.24	8.41
233	0	0.05	5.40	55.96	4.25	44.04	—[c]	—[c]
231	0	0.01	4.74	74.76	1.60	25.24	—[c]	—[c]

[a] (a) (g.mole/liter) × 10^{-1}; (b) mole per cent of products; (IHC) initial hydroperoxide concentration; reaction temp: 80°C; vol of cumene: 1 ml.

[b] Amount of the initial hydroperoxide present is included in a.

[c] The acetophenone was detectable in the infrared spectra, but the intensity of absorption was too small for accurate measurements.

whether the hydroperoxide had any effect on the product distribution. The data are given in Table 5.

In the experiments, employing the lowest catalyst weights, the major product was the hydroperoxide and there was no measurable quantity of acetophenone present. (The acetophenone was detectable in the infrared spectra, although the intensity of its absorption was too small for accurate measurements.) The amount of hydroperoxide in the sample increased with the amount of catalyst; however, the yield of dimethyl phenyl carbinol and acetophenone, especially the former increased at a greater rate, surpassing that of the hydroperoxide. The mole percent of hydroperoxide of the total oxidized products decreased with the increase in the amount of catalyst. Murthy and Graydon (*12*) obtained similar data under similar conditions.

The decomposition of the hydroperoxide due to the metal ion could be the reason why the rate of accumulation of hydroperoxide diminishes at a higher catalyst weight. Such a conclusion is reported by Hock and Kropf (*3*) when the oxidation of cumene is carried out employing Cu_2Cl_2, $HgCl_2$, PbO_2, MnO_2, V_2O_5 and MoO_2, as well as by Kolmakov *et al.* (*4*) employing CuO and Cr_2O_3. Similar observations have also been made using soluble catalysts. With an increase in the concentration of the catalyst, the rate of decomposition of the hydroperoxide rose considerably under the action of manganese ions, when manganese resinate (*4*) and manganese butyrate (*19*, *20*) were used.

According to Blanchard (*2*) the yield of hydroperoxide is a function of the kinetic chain length, the higher the kinetic chain length the higher the yield. This concept applies qualitatively to the present investigation.

The initial hydroperoxide concentration in the range of 0.005 to 0.080 g·mole/liter did not have any significant effect on the product distribution.

Reaction Mechanism

The principal characteristics of cumene oxidation in liquid phase at 80°C could be summarized as follows:

1. Co_3O_4 does initiate the reaction and there is no induction period.
2. The reaction is initiated without the presence of cumene hydroperoxide or any other radical initiator.
3. The apparent orders of the reaction with respect to catalyst weight and the hydrocarbon concentration are 0.4 and 1.49, respectively.
4. There is a critical weight of the Co_3O_4 catalyst above which the reaction does not start.
5. The addition of the hydroperoxide slightly reduces the rate of oxidation of cumene.

Although observations 4 and 5 are not easily subject to simple mechanistic explanations, coherent interpretations of the observations 1, 2 and 3 can be made. The oxidation of cumene has all the characteristics of a free radical reaction. The first step is the initiation of the chain. Cumene (RH) is absorbed in the catalyst surface and through a surface redox cycle similar to that postulated for the cobalt salt catalyzed oxidations, hydrogen abstraction takes place and free radicals are formed.

$$Co^{3+} + RH \rightarrow R^{\cdot} + Co^{2+} + H^+, \qquad (1)$$

$$2Co^{2+} + 1/2O_2 \rightarrow 2Co^{3+} + O^{2-}, \qquad (2)$$

$$2H^+ + O^{2-} \rightarrow H_2O. \qquad (3)$$

Water is formed as a result of the interaction between hydrogen and oxygen, which may be held at different sites on the catalyst surface. The initiation is of the first order with respect to the catalyst.

In the second step, which is the chain propagation, the radical $R^{\bullet}$ adds a molecule of oxygen and is converted into the peroxy radical $ROO^{\bullet}$, which reacts with the substrate resulting in the formation of the hydroperoxide and a free radical which continues the chain.

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

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

The last stage is the chain termination (the destruction of the free radicals) which may take place by a bimolecular reaction between two $ROO^{\bullet}$ radicals.

$$ROO^{\cdot} + ROO^{\cdot} \rightarrow \text{inactive products.} \qquad (6)$$

The reaction mechanism of the Co_3O_4(M) catalyzed oxidation of cumene (RH) can be summed up in the following manner:

Initiation

$$RH + M \xrightarrow{k_1} R^{\cdot}. \qquad (7)$$

Propagation

$$R^{\cdot} + O_2 \xrightarrow{k_2} ROO^{\cdot}, \qquad (4)$$

$$ROO^{\cdot} + RH \xrightarrow{k_3} ROOH + R^{\cdot}. \qquad (5)$$

Termination

$$ROO^{\cdot} + ROO^{\cdot} \xrightarrow{k_4} \text{inactive products.} \qquad (6)$$

The above mechanism is postulated for the case when there is no hydroperoxide present in the cumene. In the oxidation reactions of cumene with an initial hydroperoxide content, the above mechanism will be altered. In the pure cumene, though no hydroperoxide was detectable using infrared, the presence of hydroperoxide in extremely low concentration is a possibility. If the hydroperoxide were present given the fragility of RO–OH bond, it would certainly contribute to some degree in the formation of free radicals. The effect of the hydroperoxide would then be felt in the initiation reaction and a possible mechanism is as follows:

$$ROOH\ldots M \underset{k_5}{\overset{k'_5}{\rightleftarrows}} RO^{\cdot}\ldots M + {}^{\cdot}OH\ldots M, \qquad (7)$$

$$RO^{\cdot}\ldots M + RH \xrightarrow{k_6} ROH + R^{\cdot}, \qquad (8)$$

$${}^{\cdot}OH\ldots M + RH \xrightarrow{k_7} H_2O + R^{\cdot}. \qquad (9)$$

The radical pair ($RO^{\bullet}$ and ${}^{\bullet}OH$) formed by the decomposition of ROOH molecule absorbed on the catalyst starts the oxidation by reacting with two cumene (RH) molecules to form two cumyl radicals ($R^{\bullet}$). Such a decomposition reaction is also possible to occur as soon as cumene hydroperoxide, which is a product of the propagation reaction, is formed.

In the proposed reaction mechanism, the reactions 4 and 5 are widely accepted as the propagation steps in the liquid-phase oxidation of hydrocarbons. As far as the initiation is concerned, it is very much dependent on various factors such as the type of hydrocarbon, the catalyst employed and the experimental conditions. In other words, it is extremely specific.

Derivation of a Kinetic Expression

First, an expression is derived for the mechanism wherein the initiation takes place between the hydrocarbon (RH) and the catalyst (M) in the absence of the hydroperoxide (ROOH).

$$\mathrm{R_i} = k_1 \quad (\mathrm{M})(\mathrm{RH}), \tag{13}$$

$$R_t = k_4 \quad (\mathrm{ROO^{\cdot}})^2, \tag{14}$$

$$\frac{-d(\mathrm{O_2})}{dt} = k_3(\mathrm{RH})(\mathrm{ROO^{\cdot}}), \tag{15}$$

or

$$\frac{-d(\mathrm{O_2})}{dt} = k_3\left[\frac{k_1}{k_4}\right]^{1/2}(\mathrm{RH})^{3/2}(\mathrm{M})^{1/2}. \tag{16}$$

A second rate expression can be derived in the case of the reaction initiated by the hydroperoxide. The derivation is similar to the one proposed by Mukherjee and Graydon (*8*) for the liquid-phase oxidation of tetralin employing $\mathrm{MnO_2}$ as the catalyst.

There will be an equilibrium between absorbed ROOH on the catalyst surface and $\mathrm{RO^{\bullet}}$ and $\mathrm{^{\bullet}OH}$ radicals formed. In other words a steady state concentration of $\mathrm{^{\bullet}OHM}$ and $\mathrm{RO^{\bullet}M}$ radicals is attained. Then

$$[\mathrm{^{\cdot}OHM}] = k_5\mathrm{M} = [\mathrm{RO^{\cdot}M}].$$

The final expression is

$$\frac{-d(\mathrm{O_2})}{dt} = k_3\left[\frac{(k_6+k_7)k_5}{k_4}\right]^{1/2}(\mathrm{RH})^{3/2}(\mathrm{M})^{1/2}. \tag{17}$$

The order of the reaction with respect to the catalyst weight is 0.5 and with respect to the hydrocarbon concentration is 1.5 in the kinetic expressions 16 and 17. In other words the order of the reaction does not change whether the reaction is initiated with or without hydroperoxide. Only the rate constants vary in the above case. In the present investigation an apparent order of 0.4 with respect to the catalyst and an order of 1.49 with respect to the hydrocarbon concentration were obtained, which agree well with the derived rate expressions.

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