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Cumene의 액상 촉매산화

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Catalytic Oxidation of Cumene in Liquid Phase

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요　약

공기 또는 산소를 산화제로 하여 Cumene을 액상산화시킬 때 유기금속촉매의 첨가에 따른 반응을 연구하였다. 본 실험에 사용된 촉매는 manganese naphthenate, cobalt naphthenate, molybdenyl naphthenate, copper phthalocyanine이었는데, 그중 cobal naphthenate가 가장 효과적이어서, 연쇄개시 시간을 단축시키고 또한 Cumene hydroperoxide의 생성을 촉진시켰다. 그러나 무촉매산화반응과 비교하여 볼때는 반응초기 부터 dimethyl phenyl carbinol의 생성을 촉진시키는 경향이 있다.

최적 cobalt naphthenate 촉매투입량은 약 5×10^{-8} mole/liter 이었으며, Cumene hydroperoxide의 농도는 45 %에 이르렀다.

Abstract

The oxidation of cumene in a liquid-phase by contacting it with oxygen or air through a porous filter plate was studied with and without an addition of a catalyst.

Various catalysts such as manganese naphthenate, cobalt naphthenate, molybdenyl naphthenate and copper phthalocyanine were used. Of the catalysts tested, cobalt naphthenate was found to be effective in shortening the induction period and accelerating the formation of cumene hydroperoxide and simultaneously decomposing the product into dimethyl phenyl carbinol from the very early stage of reaction, which was not the case when the catalyst had not been added. The most effective concentration of cobalt naphthenate was about 5×10^{-8} moles per liter of cumene and the maximum concentration of cumene hydroperoxide obtained was about 45%.

Introduction

The oxidation of cumene in the liquid phase proceeds through a chain reaction mechanism as the other hydrocarbons.

When cumene is oxidized by either air or oxygen without catalyst, cumene hydroperoxide is formed as the primary oxidation product(1,2,3a) and acetophenone, dimethyl phenyl carbinol and small amount of α-methyl styrene are, as by-products, produced by degenerate chain-branching reaction(2,4,5).

Various methods were investigated for the liquid phase oxidation of cumene. According to the reports, alkali organometal salts such as sodium stearate, sodium benzoate and sodium adipate(3b,6), bifunctional catalyst as Ba—Cd stearate(7), and transition metal salts of manganese, cobalt, chromium, lead, iron, and nickel(10,11) were effective in accelerating the oxidation rate and increasing the yield of cumene hydroperoxide.

Therefore, we selected the catalytic oxidation method and tried to investigate the most effective catalyst among molybdenyl naphthenate, manganese naphthenate, cobalt naphthenate and copper phthalocyanine, and the formation mechanisms of the oxidation products including cumene hydroperoxide.

Catalytic Oxidation Mechanism

In non-catalytic oxidation of cumene, cumene combines with oxygen dissolved in the liquid phase to produce cumyl free radicals as in reaction(1a).

(1a) $RH+O_2 \longrightarrow \dot{R}+\dot{O}OH$

and these radicals undergo reactions (2) and (3) producing cumene hydroperoxide.

(2) $\dot{R}+O_2 \longrightarrow R\dot{O}_2$

(3) $R\dot{O}_2+RH \longrightarrow ROOH+\dot{R}$

However, if the degenerate chain-branching reaction (4a) takes place at the same time

(4a) $ROOH \longrightarrow R\dot{O}+\dot{O}H,$

the cumyl-oxy free radicals react further with cumene producing dimethyl phenyl carbinol and cumyl radical as shown below:

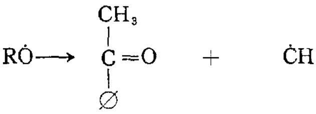
(5) $R\dot{O}+RH \longrightarrow ROH+\dot{R}.$

The termination reaction takes place by reaction (6) or (7):

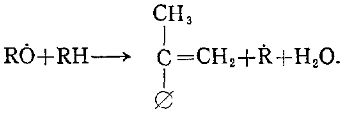
(6) $2R\dot{O}_2 \longrightarrow ROOR+O_2$

(7) $R\dot{O}_2 \longrightarrow$ Molecular product.

On the other hand, the cumyl-oxy radicals formed by reaction (4a) produce acetophenone through the fragmentation reaction (8), and α-methyl styrene by reacting with cumene as shown by reaction (9)

(8)


$$R\dot{O} \longrightarrow \overset{\displaystyle CH_3}{\underset{\displaystyle \varnothing}{C}}{=}O \quad + \quad \dot{C}H_3$$

(9)


$$R\dot{O}+RH \longrightarrow \overset{\displaystyle CH_3}{\underset{\displaystyle \varnothing}{C}}{=}CH_2+\dot{R}+H_2O.$$

According to the literatures(3c,12,13), when an organometallic salt is used as the catalyst, oxygen dissolved in the liquid phase is believed to form an unstable transition complex with the metallic ions and this complex reacts with the hydrocarbon molecules to produce free radicals as shown by reaction (1b)

(1b) $Me^{+n}+O_2 \longrightarrow (Me^{+(n+1)})\ldots(O-O)^-$

$(Me^{+(n+1)})\ldots(O-O)^- + RH \longrightarrow (Me^{+(n+1)})\ldots$
$(O-O)+\dot{R}$

$(Me^{+(n+1)})\ldots(O-O)^- \longrightarrow Me^{+n}+H\dot{O}_2$

$H\dot{O}_2+RH \longrightarrow H_2O+\dot{R}.$

This radical ($\dot{R}$) as well as the radicals produced by reaction (1a) reacts as in reactions (2) through (9). In this case, the hydroperoxide reacts with transition metal ions to form $R\dot{O}$ and $R\dot{O}_2$ radicals by reactions (4b) and (4c)(14,15)

(4b) $ROOH+Me^{+n} \longrightarrow R\dot{O}+Me^{+(n+1)}+\dot{O}H$

(4c) $ROOH+Me^{+(n+1)} \longrightarrow R\dot{O}_2+Me^{+n}+H^+.$

It is also reported(16) that the catalytic effect of cobalt salt is mainly due to the oxidation of cobalt from divalent to trivalent state, and that the cobalt of trivalent state reacts with oxidation products of cumene to form compounds which are inactive and less soluble in cumene solution. Therefore, when cobalt naphthenate is used as the catalyst, it is believed that reaction (4b) takes place rather than reaction (4c). On the whole, the mechanism of catalytic oxidation of cumene can be represented in table 1.

If the concentration of oxygen dissolved in the liquid phase is assumed to be sufficient for converting $\dot{R}$ into $R\dot{O}_2$, cumyl-peroxy radical can be regarded as the dominant radicals existing in the solution, and the chain termination will take place by reaction(7).

Table 1. Catalytic Mechanism of cumene in the Liquid-Phase

(1a) $RH+O_2\longrightarrow\dot{R}+\dot{O}OH$

(1b) $Co^{+2}+O_2\longrightarrow(Co^{+3})\cdots(O-O)^-$

$(Co^{+3})\cdots(O-O)^-+RH\longrightarrow Co^{+2}+\dot{R}+H_2O$

(2) $\dot{R}+O_2\longrightarrow R\dot{O}_2$

(3) $R\dot{O}_2+RH\longrightarrow ROOH+\dot{R}$

(4a) $ROOH\longrightarrow R\dot{O}+\dot{O}H$

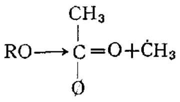
(4b) $ROOH+Co^{+2}\longrightarrow R\dot{O}+Co^{+3}+OH^-$

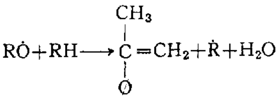
(4c)* $ROOH+Co^{+3}\longrightarrow R\dot{O}_2+Co^{+2}+H^+$

(5) $R\dot{O}+RH\longrightarrow ROH+\dot{R}$

(6)* $2R\dot{O}_2\longrightarrow ROOR+O_2$

(7) $R\dot{O}_2\longrightarrow$ molecular product

(8) 
$RO\longrightarrow\underset{\underset{O}{|}}{\overset{\overset{CH_3}{|}}{C}}=O+\dot{C}H_3$

(9) 
$R\dot{O}+RH\longrightarrow\underset{\underset{O}{|}}{\overset{\overset{CH_3}{|}}{C}}=CH_2+\dot{R}+H_2O$

(10) $2R\dot{O}_2\xrightarrow{\qquad}2R\dot{O}+O_2$

(11) $C_6H_5C(CH_3)_2OOH\longrightarrow C_6H_5OH+CH_3COCH_3$

*Note; The reaction is negligible

The free radicals such as $\dot{R}$, $R\dot{O}$, $R\dot{O}_2$ and $\dot{C}H_3$ are so extremely active that stationary state concentrations of these radicals, at which the rates of formation and destruction of the radicals are equal, are rapidly established. At this stationary state, the rate of formation of $\dot{R}$, $R\dot{O}$, $R\dot{O}_2$ and $\dot{C}H_3$ are equal to zero, as in the following equation.

$$\frac{d(\dot{R})}{dt}=\frac{d(R\dot{O})}{dt}=\frac{d(R\dot{O}_2)}{dt}=\frac{d(\dot{C}H_3)}{dt}=0,$$

and using this equation, the following can be written:

$$K_{1a}(RH)(O_2)+K_{1b}(Co^{+2})(O_2)(RH)+K_{4a}(ROOH)$$
$$+K_{4b}(ROOH)(Co^{+2})-K_7(R\dot{O}_2)=0,$$

where R is $C_6H_5(CH_3)_2C$ and ( ) means concentration. From this equation,

$$(R\dot{O}_2)=K_7^{-1}\{K_{1a}(RH)(O_2)+K_{1b}(Co^{+2})(O_2)(RH)$$
$$+K_{4a}(ROOH)+K_{4b}(ROOH)(Co^{+2})\}.$$

From reactions (3), (4a) and (4b), the formation rate of cumene hydroperoxide becomes

$$\begin{aligned} d(CHP)/dt&=K_3(RH)(R\dot{O}_2)-K_{4a}(ROOH)\\ &\quad-K_{4b}(ROOH)(Co^{+2})\\ &=\Big\{K_3K_7^{-1}K_{1b}(O_2)(RH)+K_3K_7^{-1}K_{4b}(ROOH)\\ &\quad-K_{4b}(ROOH)\Big\}(Co^{+2})+K_3K_7^{-1}(ROOH)\\ &\quad+K_3K_7^{-1}K_{1a}(RH)(O_2)-K_{4a}(ROOH). \end{aligned} \qquad -(A)$$

Thus, if the above reaction mechanism is right, the plot of the left term of equation(A) against cobalt naphthenate concentration will yield a straight line.

Experiment

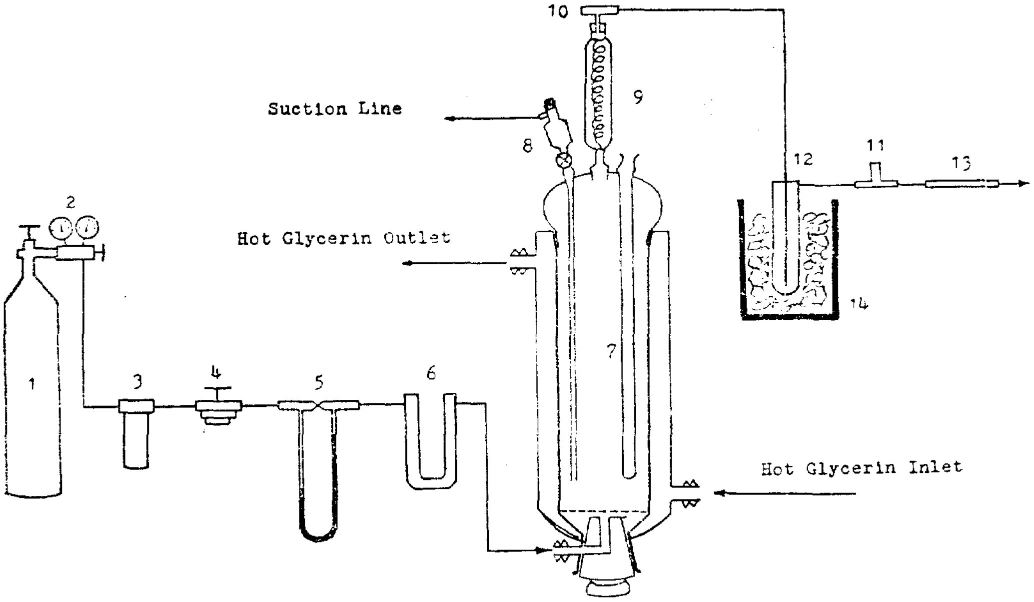
The schmatic diagram of the experimental apparatus is shown is Fig. 1. The major items are reactor, condenser, thermometer, oxygen supply unit and product sampling unit. The reactor was made of pyrex glass, and is maintained at constant temperature within ±0.1°C.

A small amount of C. P. grade cumene was washed with concentrated sulfuric acid and 10 % sodium hydroxide aqueous solution. After being repeatedly washed with distilled water and dehydrated with anhydrous sodium sulfate, it was distilled at the temperature range from 152° C to 153° C.

Fifty milliliters of purified cumene was introduced into the reactor and heated to the desired temperature by circulating the hot glycerin, whose temperature was controlled in a thermoregulated bath, to the reactor jacket. After the desired temperature was reached, the catalyst was added into cumene, and at the same time the bubbling of oxygen was started initiating the reaction.

The flow rate of oxygen is measured with the capillary-type flowmeter calibrated with a soap film flowmeter.

Most vapors of cumene and other products accompanying oxygen from the reactor are condensed and refulxed to the reactor, and the rest of the vapors is collected in the cold trap for its compositions to be analyzed. At suitable time intervals, parts of the reactant mixture were sampled and analyzed. The concentration of cumene hydroperoxide was determined by the iodometric titration method(17). Other products including cumene and dimethyl phenyl carbinol were analyzed by gas chromatography. The columns packed with SE-52 and carbowax 400 were used at 90°C. The details of operating conditions are listed in Table 2.



1. Oxygen Cylinder
2. Pressure Regulator
3. Filter
4. Flow Rate Controller
5. Capillary-type Flowmeter
6. NaOH-tube
7. Thermometer Well
8. Liquid Sampler
9. Reflux Condenser
10, 11. Vapor Sampler
12. Cold Trap
13. Capillary Tube
14. Cold Trap Jacket

Fig. 1. Experimental Apparatus for Cumene Oxidation

Table 2. Gas Chromatography Operating Conditions

Injection port temperature: 110°C

Column oven temperature: 90°C

Detector oven temperature: 110°C

	Column 1. (A-B in series)	Column 2.
Column	4 mmϕ×1.5 m(A) 4 mmϕ×1.5 m(B)	4 mmϕ×3 m
Packing material	(A):SE-52(5%) (B):Carbowax 400	SE-52(5%)
Sample	1 ml (gas)	2 μl (liquid)
Carrier gas(H_2)	45 ml/min.	30 ml/min.

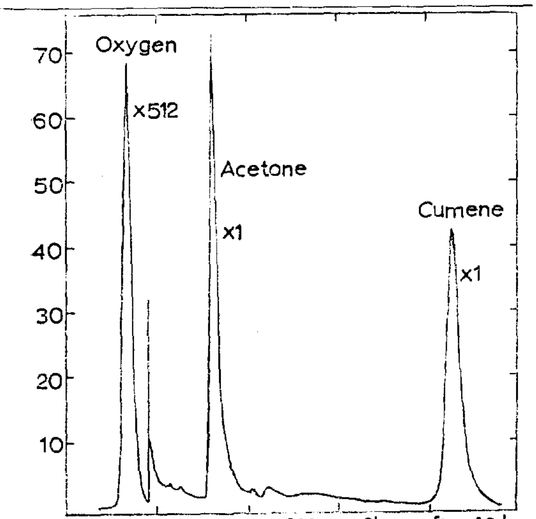


Fig. 7. Gas chromatogram of Vapor Phase after 19 hrs.

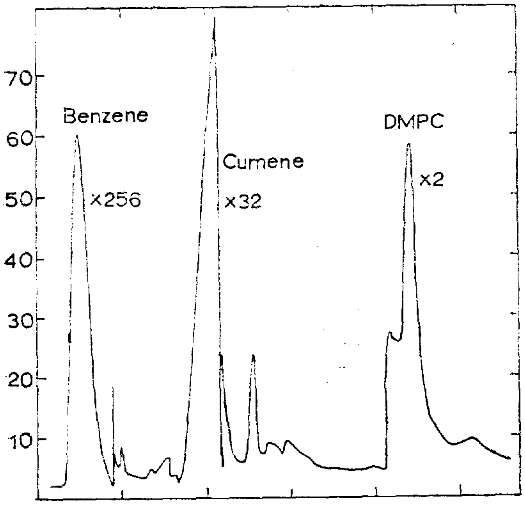


Fig. 8. Gas chromatogram of Liquid Phase after 19 hrs.

The illustrations of gas chromatograms are shown in Fig. 7 and Fig. 8.

For the calibration of gas chromatogram, the internal standard method(18) was employed, in which bezene was used as the internal standard material.

Results and Discussion

1. Non-catalytic Oxidation

Non-catalytic oxidations by air and oxygen as oxidants were conducted at 90°C and 120°C, respectively. In comparison with the case where air was used as the oxidant, the oxidation rate was 3 times faster when oxygen was used, The ratio of dimethyl phenyl carbinol to cumene hydroperoxide formed when oxygen was used as an oxident was 0.02 to 0.3 and when air was used, the ratio was approximately 0.15. Negligible amount of α-methyl styrene was detected in both cases.

2. Catalytic Oxidation-Molybdenyl Naphthenate

When 0.05-1 milliliters of molybdenyl naphthenate (Mo-metal content; 1%) was added into 100 milliliters of cumene and the reaction was carried out at 80 and 90°C, the amount of cumene converted was nearly negligible. Thus, it was found that molybdenyl naphthenate was not the proper catalyst for the reactions(1b), (4b) and (4c).

3. Catalytic Oxidation-Copper Phthalocyanine

Fig. 2 shows the results when 0.05 grams of copper phthalocyanine was mixed into 100 milliliters of cumene at 90°C, and the results of non-catalytic oxidation at 90°C. As shown in Fig. 2, when copper phthalocyanine was used, the oxidation rate of cumene was slightly faster than the non-catalytic oxidation rate. The ratio of dimethyl phenyl carbinol to cumene hydroperoxide formed was smaller than that in the case of the non-catalytic oxidation, and the attainable yield of cumene hydroperoxide was increased.

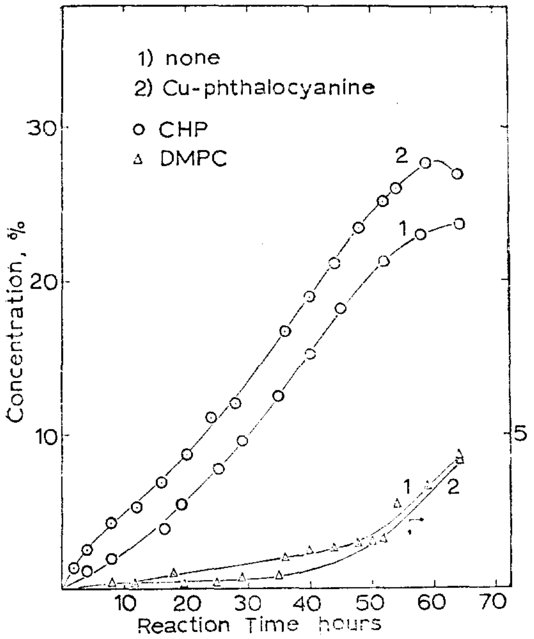


Fig. 2 Products Concentration vs. Reaction Time at 90°C

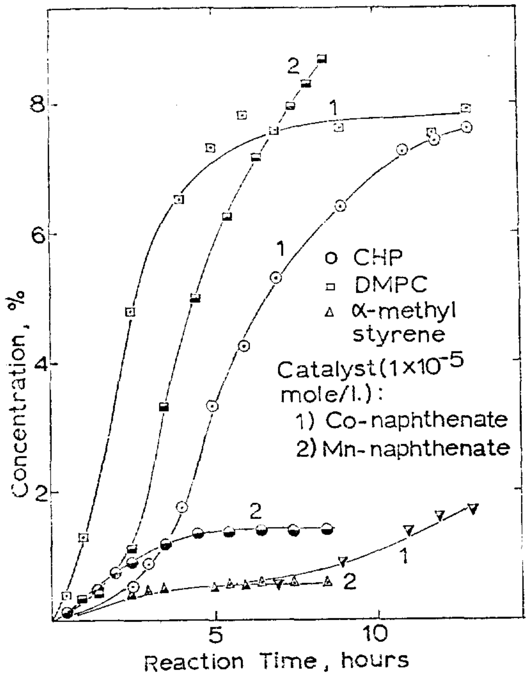


Fig. 3 Products Concentration vs. Reaction Time at 90°C

4. Comparison of the Catalysts used

Fig. 3 shows the experimental results when 1×10^{-5} moles/liter of cobalt naphthenate and manganese naphthenate as the catalyst were mixed into cumene at 90°C.

As shown in Fig. 3, when manganese naphthenate was used as the catalyst, the concentration of cumene hydroperoxide remained constant after 4 hours, while that of dimethyl phenyl carbinol increased continuously. Such phenomena may be explained as follows: cumene hydroperoxide decomposes as reaction(4b) producing cumyl-oxy radicals, and these radicals react with cumene to produce dimethy phenyl carbinols by reaction(5). After 4 hours have elapsed, the rates of formation of and decomposition of cumene hydroperoxide become equal.

As shown in Fig. 2 and Fig. 3, when cobalt naphthenate was used as the catalyst, the concentration of cumene hydroperoxide was higher than when manganese naphthenate or copper phthalocyanine was used.

5. Temperature Dependence of Cobalt Naphthenate

Fig. 4 shows the kinetic curves of cumene hydroperoxide and dimethyl phenyl carbinol when 5×10^{-8} moles per liter of cobalt naphthenate was mixed into cumene at the reaction temperatures of 100, 110 and

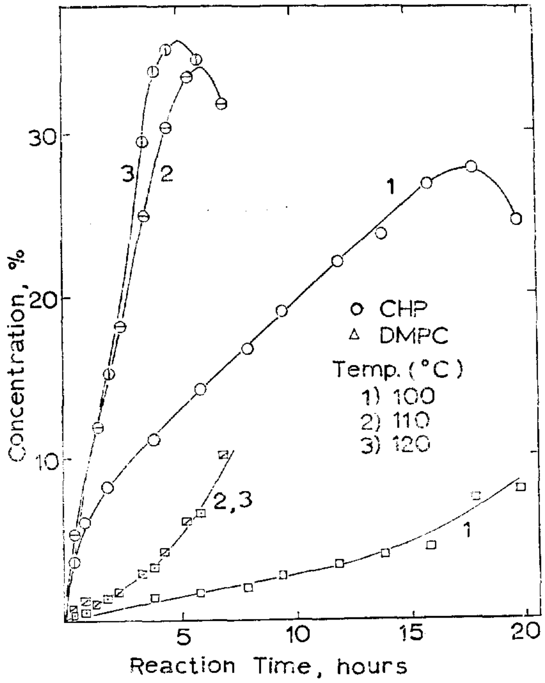


Fig. 4 Products Concentration vs. Reaction Time.
Cat. : Co-Naphthenate(5.08×10^{-8} mol/l.)

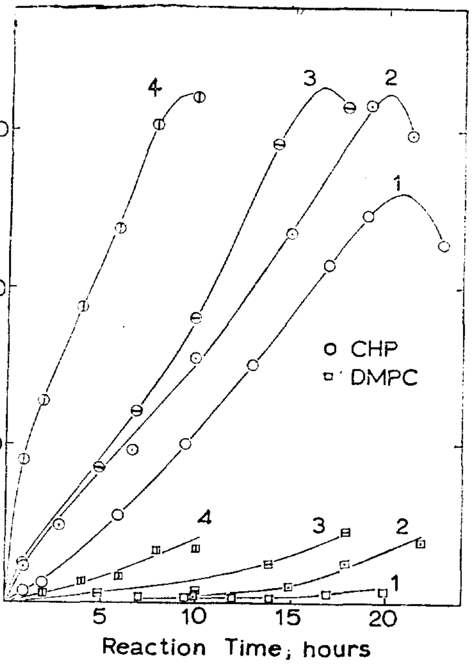


Fig. 5 Products Concentration vs. Reaction Time at 120°C Co-Naphthenate Concentration, $\times 10^8$ mole/l.: 1) 0 2) 1.52 3) 2.54 4) 4.06

120°C. As shown in Fig. 4, the higher the reaction temperature was maintained, the faster was the rate of oxidation, and the concentration of cumene hydroperoxide was nearly equal regardless of the reaction temperature.

6. Influence of the Concentration of Cobalt Naphthenate

Various amount of cobalt naphthenate was mixed into cumene at 120°C, and the results of the reactions were shown in Fig. 5. As shown in Fig. 5, as the amount of cobalt naphthenate was increased, the induction period was shortened and the concentration of cumene hydroperoxide was nearly equal regardless of the concentration of the catalyst, and the ratio of dimethyl phenyl carbinol to cumene hydroperoxide increased.

However, when 2.5×10^{-7} moles per liter of a catalyst concentration in cumene was reached, the concentration of dimethyl phenyl carbinol was inhibitably high even in the initial period of oxidation and the concentration of cumene hydroperoxide was lower than when smaller amounts of the catalysts were used. Such phenomena can be thought to arise due to the increase of the rate of reaction(4b) with the amount of the catalyst.

In Fig. 6, the formation rate of cumene hydroperoxide was plotted against the catalyst concentration in the propagation period. As shown in Fig. 6 a straight line was obtained. This means that the oxidation mechanism assumed is reasonable.

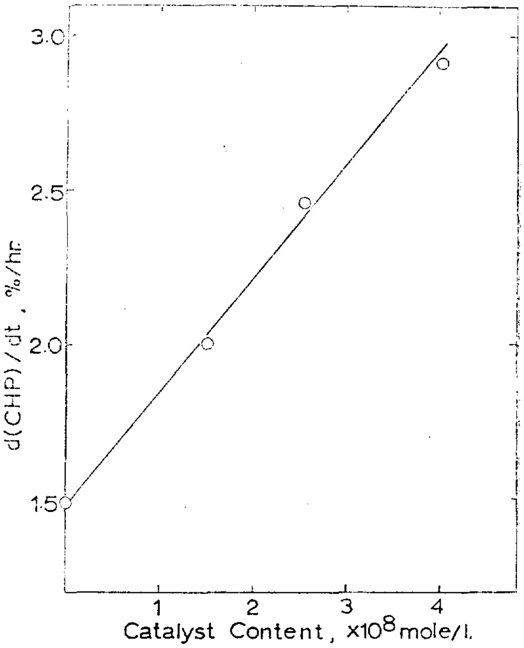


Fig. 6 Oxidation Rate vs. Catalyst Concentration in the Propagation Period

Conclusion

1. Cobalt naphthenate was found to be the most effective catalyst for the formation of cumene hydroperoxide among the catalysts used.
2. Within the range of reaction temperature from 100 to 120°C, the formation rate of cumene hydroperoxide increased with the increase of reaction temperature, and the maximum attainable concentration of cumene hydroperoxide was nearly the same regardless of reaction temperatures.
3. The most effective concentration of cobalt naphthenate, for the production of cumene hydroper-

oxide, in the oxidation of cumene was about 5×10^{-8} moles/liter, and the maximum concentration of cumene hydroperoxide obtained was about 45%.

4. When cobalt naphthenate was used as the catalyst, the catalytic oxidation mechanism of cumene in the liquid phase was believed to proceed through reactions (1a), (1b), (2), (3), (4b), (5) and (7).

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