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THE AUTOXIDATION OF α-METHYLSTYRENE CATALYZED BY COPPER PHTHALOCYANINE

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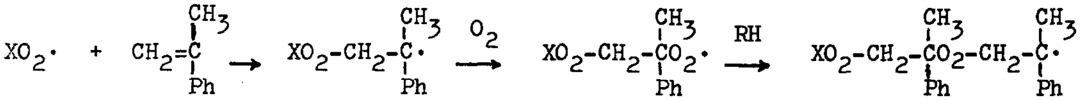
Although Kropf(1) suggested that copper phthalocyanine initiates the autoxidation of cumene by the hydrogen abstraction mechanism, copper phthalocyanine also decomposes cumyl hydroperoxide(2) to form peroxy or alkoxy radicals for undergoing the autoxidation. Recently, it was confirmed that various metal complexes(3) can be oxygenated with molecular oxygen, but there is still no definite evidence of such a reaction as the oxidation of hydrocarbon with oxygenated metal complex.

It must be most important to distinguish the two kinds of catalytic effects owing to copper phthalocyanine in the autoxidation of hydrocarbons. It is known that the autoxidation of α-methylstyrene(4,5) proceeds not by the hydrogen abstraction but by the additional mechanism as follows;



$$XO_2\cdot + CH_2{=}\underset{Ph}{\overset{CH_3}{C}} \longrightarrow XO_2{-}CH_2{-}\underset{Ph}{\overset{CH_3}{C}}\cdot \xrightarrow{O_2} XO_2{-}CH_2{-}\underset{Ph}{\overset{CH_3}{C}}O_2\cdot \xrightarrow{RH} XO_2{-}CH_2{-}\underset{Ph}{\overset{CH_3}{C}}O_2{-}CH_2{-}\underset{Ph}{\overset{CH_3}{C}}\cdot$$

Copper phthalocyanine(Cu-Pc) used is meta-stable ß-form. Oxygenated copper phthalocyanine(Cu-Pc-O) was prepared by the oxidation of Cu-Pc with 45% nitric acid at -5 to 0^oC as reported by Bansho(6). The analysis of oxidized Cu-Pc has given the formula of $(Cu\text{-}Pc\text{-}O)_2$, which was easily reduced to copper phthalocyanine.

The rate of oxidation of α-methylstyrene in the presence of Cu-Pc, Cu-Pc-O or copper decanoate($CuDe_2$) is shown in Tables I and II. The rate of oxidation initiated by azobisisobutyronitrile increases in the presence of Cu-Pc or Cu-Pc-O, and Cu-Pc-O initiates the autoxidation most effectively.

Although the autoxidation of α-methylstyrene proceeds entirely by the additional mechanism, very small amount of hydroperoxide yielded is expected to be decomposed by metal catalysts and initiates the oxidation as in the ordinary case of autoxidation. Copper decanoate is more powerful catalyst than Cu-Pc for the decomposition of cumyl hydroperoxide. However, as seen in Table II, copper decanoate gives the lowest rate of oxidation and Cu-Pc-O the highest.

Table I

The rate of oxidation of α-methylstyrene in the presence of 0.03 mole/l. azobisisobutyronitrile at 60°C

Catalyst	(mole/l.)	$-dO_2/dt \times 10^4$(mole/l.sec.)
None		1.26
Cu-Pc	0.01	1.40
Cu-Pc-O	0.01	1.65
$CuDe_2$	0.01	0.29

The oxygen absorption curve of α-methylstyrene catalyzed by Cu-Pc or Cu-Pc-O presents a very good straight line after short induction period. These results indicate that Cu-Pc-O and Cu-Pc initiate the autoxidation remarkably by the additional mechanism. The effective form of catalyst may not be Cu-Pc-O but probably $\text{Cu-Pc}\cdots O_2$, since Cu-Pc will not be oxidized to Cu-Pc-O at the reaction conditions employed.

Table II

The autoxidation of α-methylstyrene in the presence of Catalyst at 60°C

Catalyst	(mole/l.)	$-dO_2/dt \times 10^5$(mole/l.sec.)
Cu-Pc-O	0.01	8.5
Cu-Pc-O	0.004	5.2
Cu-Pc	0.01	5.4
Cu-Pc	0.004	3.8
$CuDe_2$	0.01	0.5
$CuDe_2$	0.004	0.35

The autoxidation of cumene catalyzed by Cu-Pc or Cu-Pc-O presents an interesting result showing that Cu-Pc-O is rather an inactive catalyst for the hydrogen abstraction mechanism, i.e., for the decomposition of hydroperoxide.

Because the induction period by Cu-Pc-O was longer than that by Cu-Pc and the rate of oxidation by Cu-Pc-O was lower than that by Cu-Pc.

The induction period of autoxidation of α-methylstyrene in the presence of inhibitor and initiator clearly shows that the catalytic effect of Cu-Pc is due to not hydrogen abstraction but to additional mechanism.

Table III

The induction period of the autoxidation of α-methylstyrene in the presence of 0.03 mole/l. AIBN and 0.005 mole/l. 2,6-di-tert-butyl-p-cresol

Catalyst	(mole/l.)	Induction period (min.)
None		220
Cu-Pc	0.01	190
Cu-Pc-O	0.01	165

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