

# Study on oxidation mechanism of cumene based on GC-MS analysis

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## Abstract

Based on the gas chromatography (GC) and gas chromatography mass spectrometry (GC-MS) spectra, the analysis of the products of the catalytic oxidation and its mechanism can be elucidated. Here, the analysis of the aerobic oxidation products of cumene catalyzed by the polymer ferric complex through GC-MS has been performed. The main products are 2-phenyl-2-propanol (PP), 2-phenyl-2-*iso*-propyl hydroperoxide. From the analysis, the radical reaction mechanism was presumed. The relationship between the selectivity of cumene hydroperoxide and PP has been studied. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Catalytic mechanism; Cumene; Oxidation; GC-MS

## 1. Introduction

Molecular oxygen is very important for the life on earth, especially for the humankind. On the other hand, the development of efficient catalysts for the selective oxidation of hydrocarbons in the presence of molecular oxygen under mild condition has remained to be a difficult challenge to the catalytic science [1]. Much attention has been done on the construction of

the active center–quasi-porphyrin complex and its circumstance–polymer surroundings for mimicking the structure and properties of enzyme [2–7].

Gas chromatography mass spectrometry (GC-MS) technique integrates the excellent resolution ability of gas chromatography (GC) and the structural information of mass spectrometry (MS) [8]. Based on the GC and MS spectra for the analysis of the products, the reaction process and its mechanism can be elucidated. In this paper, the analysis of the aerobic oxidation products of cumene catalyzed by the polymer complex through GC-MS was performed. The main products are 2-phenyl-2-propanol (PP) and

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2-phenyl-2-propyl hydroperoxide (CHP). The radical reaction mechanism was studied.

## 2. Experimental

### 2.1. Materials and equipment

Cumene (C.P.) was purified by fractionating distillation just before use. The polymer-bound ferric complexes, which are *N,N,N,N*-type complexes (P-phenFephen), was prepared in our laboratory [9], and characterized by X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR) and inductively coupled plasma (ICP). All other reagents, such as ethyl alcohol and metal salts were of the highest grade commercially available and were used as received.

The metal contents were analyzed on a model ARL-3520 Inductively Coupled Plasmas Atomic Emission Spectrometry of USA. Small area XPS data were recorded with the PHI-5702 Multi-Technique System, Power Source by  $\text{MgK}_{\alpha}$  line and  $\text{Ag } 3d_{5/2}$   $\text{FWHM} \leq 0.48 \text{ eV}$ . IR spectra were recorded in KBr disks with an Alpha-centauri Fourier transform infrared spectroscopy (FT-IR) spectrophotometer.

### 2.2. Analysis of oxidation products by GC-MS technique

The reaction products of oxidation were determined and analyzed by using Shimadzu QP-1000A GC/MS system, GL-16A gas chromatograph with a  $5 \text{ m} \times 3 \text{ mm}$  OV-17 column,  $80\text{--}200^{\circ}\text{C}$  ( $10^{\circ}\text{C}/\text{min}$ ), Inj.  $220^{\circ}\text{C}$ , Dect.  $220^{\circ}\text{C}$ . The products were determined by comparing with the standard mass spectrometry of organic compounds, and fragmentation pattern.

### 2.3. Oxidation of cumene in the presence of molecular oxygen catalyzed by the polymer complexes

The oxidation of substrate was carried out in a glass reactor with a gas inlet tube and a gas

outlet tube. The gas inlet tube is connected to a measuring gauge glass and an oxygen storage bottle; the gas outlet tube could be opened to the air as necessary. In a typical oxidation reaction, the substrate and the catalyst (the polymer-bound complex) were added in the 5 ml of the special glass reactor. The oxygen was filled from the gauge glass and the atmosphere was discharged out of the glass reactor with the gas outlet tube. After closing the gas outlet tube and connecting the reactor with the measuring gauge glass, the reactor was put into a heat bath with a temperature of  $80^{\circ}\text{C}$ , and was stirred by the magnetic stirrer. The gauge glass measured the consumption of oxygen. After reacting for 8 h, the products were analyzed by gas chromatograph and GC-MS.

## 3. Results and discussions

### 3.1. Analysis on spectrogram of products

The GS spectrum of the two main oxidation products has been shown in Fig. 1. Fig. 2 shows their mass spectra. The mass spectrum of PP is accorded with the standard mass spectrometry, and the structure of CHP is concluded with its fragmentation pattern. The fragmentation pattern of CHP was shown as in Scheme 1.

In the mass spectra of cumene [10,11], the  $\beta$ -fragmentation easily happens and it can be

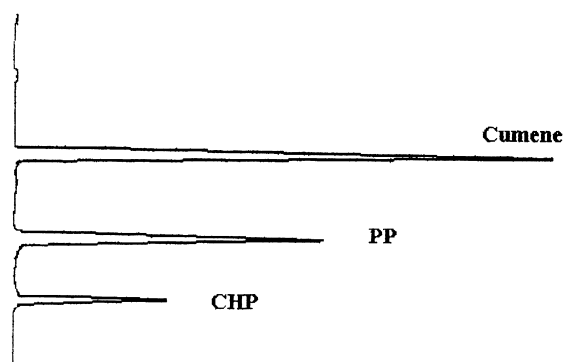


Fig. 1. The GC curve of cumene oxidation.

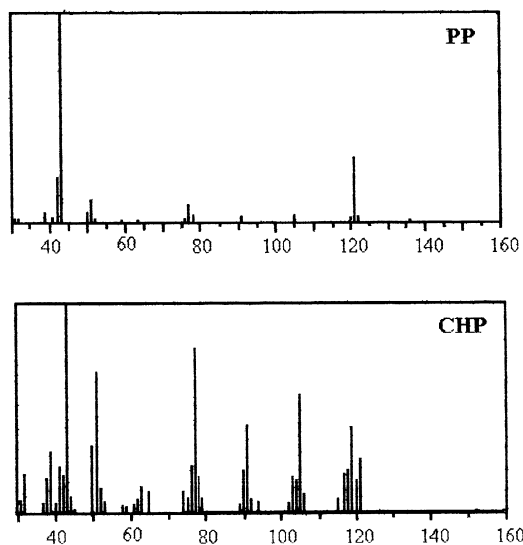


Fig. 2. The MS spectra of cumene oxidation.

rearranged to onium ion. In the mass spectra of CHP (Fig. 2), the base peak appears in  $m/e = 43$ , fragment peaks appear in  $m/e = 119, 105, 91, 77$ , but the molecular ion peak is too weak to be distinguished. The reason for it is that allyl hydroperoxide is not stable, and is easily fragmented.

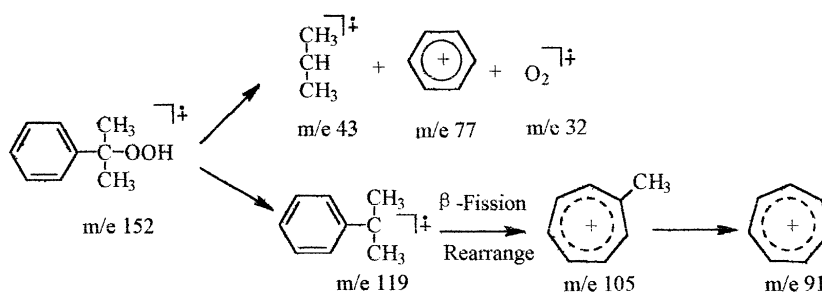
### 3.2. Mechanism of oxidation

In the catalytic oxidation in the presence of molecular oxygen, the appearance of hydroperoxide is an important sign for radical mecha-

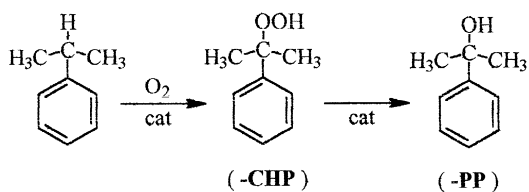
nism. The hydrocarbon hydroxylation is always accompanied with the consumption of a reductive agent [12,13], such as isobutyraldehyde, which was oxidized to organic acid. It was considered to be a radical mechanism and peroxy acid is an important intermediate. In the classical oxidation of cumene in the presence of molecular oxygen for preparing phenol [14], the selectivity for CHP reach 90–97% [15,16]. But in the system of PS-phenFephen without reductive agent, the selectivity for PP is more than 50%. The reaction equation is suggested as Scheme 2.

Based on the analysis of products and the results of Hsu [15,16], the radical reaction mechanism was presumed, which is shown in Fig. 3. In the initial steps, cumene may suffer from several different processes to become a cumyl radical. Firstly, cumene may dissociate its C–H bond photochemically or thermally for molecules with sufficiently high thermal energy. Secondly, impurities with available low energy pathway may dissociate into radicals, which then react with cumene to form cumyl radicals. Thirdly, the catalyst containing the metal complex may catalyze the reaction of cumene with oxygen to form cumyl radical and hydrogen peroxide.

In order to investigate the transformation from cumene hydroperoxide to PP, we monitored the component of reaction mixture every hour in the process of catalytic oxidation using GC. Accompanying the decrease of the cumene con-



Scheme 1. Fission of CHP.



Scheme 2.

tent, the contents of cumene hydroperoxide and PP increase, and the rate of producing PP is greater than that of cumene hydroperoxide. Fig. 4 shows the variation of the selectivity of cumene hydroperoxide and PP with the reaction time in the process reaction. The relative concentration of cumene hydroperoxide decreased from 72% to 40%, but the relative concentration of PP increased in the process of catalytic oxidation.

According to the above radical reaction mechanism, the change on the selectivity of cumene hydroperoxide and PP in the process of reaction can be explained as follows. In the beginning, the reaction was mainly the auto-oxidation of cumene, and the concentration of cumene hydroperoxide increased quickly. Then, cumene hydroperoxide was decomposed to cumene radicals, catalyzed by the polymer complex. On the other hand, the 2-phenyl-2-propyl oxygen radical reacts with cumene to form PP and 2-phenyl-2-propyl radical, of which the

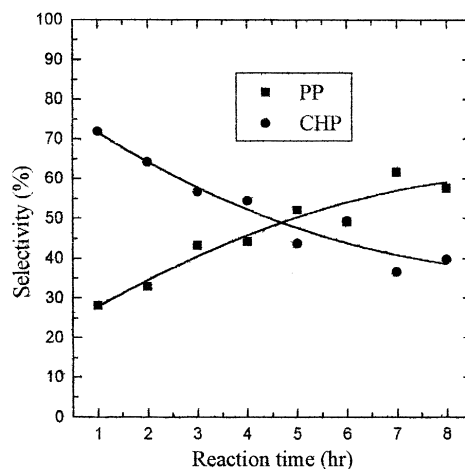


Fig. 4. Variation of the selectivity of PP and CHP in the oxidation system with the reaction time. Sub: cumene (3 ml); Cat: 3 mg; 100°C.

content of PP increased more quickly than that of CHP.

### Acknowledgements

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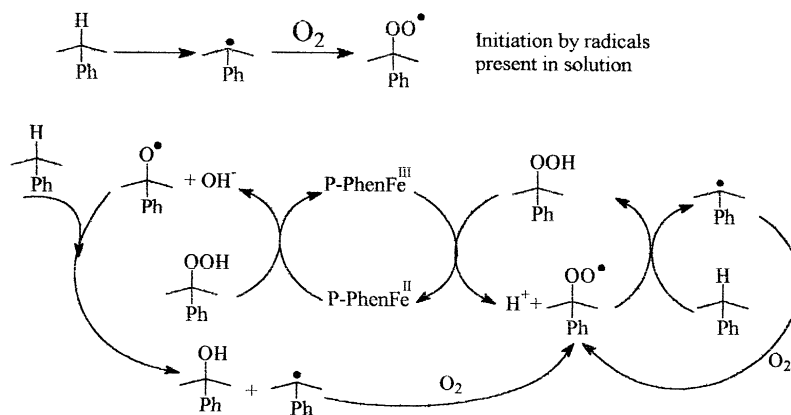


Fig. 3. The allyl peroxide decomposition mechanism for molecular oxygen reacts with cumene catalyzed by metal complexes.

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