

Aerobic Oxidation of Cumene to Cumene Hydroperoxide Catalyzed by Metalloporphyrins¹

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Abstract—A protocol for the aerobic oxidation of cumene to cumene hydroperoxide (CHP) catalyzed by metalloporphyrins is reported herein. Typically, the reaction was performed in an intermittent mode under an atmospheric pressure of air and below 130°C. Several important reaction parameters, such as the structure and concentration of metalloporphyrin, the air flow rate, and the temperature, were carefully studied. Analysis of the data obtained showed that the reaction was remarkably improved by the addition of metalloporphyrins, in terms of both the yield and formation rate of CHP while high selectivity was maintained. It was discovered that 4 or 5 h was the optimal reaction time when the reaction was catalyzed by monomanganeseporphyrin (*p*-Cl)TPPMnCl (7.20×10^{-5} mol/l) at 120°C with the air flow rate being 600 ml/min. From the results, we also found that higher concentration of (*p*-Cl)TPPMnCl, longer reaction time and higher reaction temperature were all detrimental to the production of CHP from cumene. Studies of the reaction kinetics revealed that the activation energy of the reaction (*E*) is around 38.9×10^4 kJ mol⁻¹. The low apparent activation energy of the reaction could explain why the rate of cumene oxidation to CHP in the presence of metalloporphyrins was much faster than that of the non-catalyzed oxidation.

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INTRODUCTION

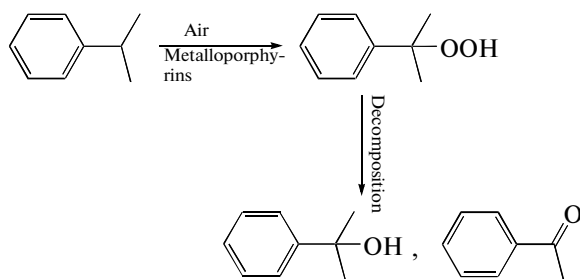
Liquid phase oxidation of cumene to cumene hydroperoxide (CHP) in the presence of oxygen or air is an important process in the industrial production of phenol and acetone [1], and more than 90% of the world's phenol production is currently based on the cumene hydroperoxide route [2]. In addition, CHP can be used as the initiator of chain auto-oxidation reaction and polymerization, the accelerant of rubber vulcanization and the oxidant in fine chemical and polymer synthesis.

Due to the reason that the C–H bond at the benzylic position in cumene can be easily activated, cumene can be oxidized to cumene hydroperoxide (CHP) in the presence of air/oxygen. The main industrial process for CHP production currently is carried out without any catalyst, which leads to the difficulty for the activation of the oxygen molecules [3–5]. Consequently, there are some limitations associated with current industrial processes, such as long induction period, low reaction speed and numerous side-reactions [6–9]. An efficient and potentially industrially applicable protocol for the aerobic oxidation of cumene to CHP is highly desirable.

Metalloporphyrins, which resemble the important enzyme cytochrome P450 structurally, are among the most heavily investigated enzyme-mimic systems. The researchers have found that iron [10–16], manganese

[17–22], chromium [23–25] and cobalt [26–29] porphyrin complexes can be used as model compounds for cytochrome P-450 monooxygenase to catalyze the transfer of an oxygen atom from oxidants (such as PhIO, H₂O₂, NaClO, etc.) to saturated hydrocarbons at ambient temperature and pressure, and put forward the high-valent oxo–metal radical cation intermediate and hydrogen radical abstraction mechanism for the hydrocarbon hydroxylation catalyzed by metalloporphyrins. These results are of importance in understanding the mechanism of the heme monooxygenase-catalyzed reaction in biological systems. In recent years, oxidation of hydrocarbons catalyzed with molecular oxygen by metalloporphyrins under mild conditions has attracted much interest because of their potential application and the environmentally friendly conditions [30–49]. A process, which is based on this catalytic, biomimetic oxidation, has been successfully developed in SINOPEC CORP to produce cyclohexanone [40]. As catalysts, metalloporphyrins can offer many distinctive advantages, such as the required amount of metalloporphyrins can be very small, and they can be used as not only in homogeneous catalysis but also in heterogeneous catalysis where they are immobilized on solid supports. Though previous works have shown that hydrocarbons can be oxidized to produce alcohols, ketones and acids in the presence of metalloporphyrins, producing hydroperoxides directly from hydrocarbons with metalloporphyrin catalysts is still rare.

¹ The article is published in the original.



Scheme 1. The catalytic oxidation of cumene with metalloporphyrins.

In this work, we attempted the oxidation of cumene to produce cumene hydroperoxide with air in the presence of metalloporphyrins at atmospheric pressure. We found that the metalloporphyrin catalysts were able to enhance the oxidation rate greatly, thus reducing the reaction time remarkably while maintaining good selectivities.

EXPERIMENTAL

Analytical Instruments and Reagents

Mass spectra were recorded on an Agilent 5973N mass spectrometer. UV-vis spectra were measured with a Perkin-Elmer L-17 UV-vis spectrophotometer. IR spectra were obtained with a Perkin-Elmer Model 783 IR spectrophotometer.

All reagents and solvents used were analytical grade and obtained commercially. GC analysis showed that there was no impurity in cumene before use.

Synthesis of Metalloporphyrins and the Experimentals

Various metalloporphyrins, such as (*p*-Cl)TPPMnCl, (*p*-Cl)TPPCo, TPPZn, [(*p*-Cl)TPPMn]₂O, and [TPPMn]₂O, were synthesized according to literature [50, 51] and purified via regular column chromatography. Their structures have been confirmed by elemental analysis, MS, UV-vis, and IR spectra [39–42].

The peroxidation of cumene was conducted in a 100 ml, four-necked Pyrex kettle equipped with a magnetic stirrer, a condenser, an oxygen inlet and a temperature controller with which the reaction temperature can be controlled to within ± 1 K. The flow rate of air was maintained at 300–800 ml/min. The stirring speed was kept at 600 rpm and the temperature was controlled at a certain point below 130°C. Metalloporphyrin catalyst was dissolved in cumene and the liquid was added to the reactor and heated to the desired temperature under the bubbling of nitrogen. Then the reaction was started by stirring and the bubbling gas was switched from nitrogen to air. At certain time intervals, parts of the reactant mixture was sampled and analyzed.

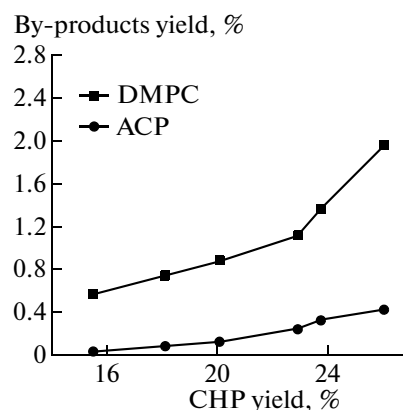


Fig. 1. Relationship between CHP and by-products Catalyst: (*p*-Cl)TPPMnCl (concentration, 7.2×10^{-5} mol/l), Reaction temperature: 120°C, Flow rate of air: 600 ml/min, Pressure: 1 atm.

The iodometric method was employed to analyzed the content of CHP [3, 52] in the reaction mixture, by-products were identified using GC–MS and were quantified by GC using benzene as the internal standard. Before being injected into GC, CHP in the reaction mixture samples was reduced to 2-phenyl-2-propanol.

RESULTS AND DISCUSSION

Aerobic Oxidation of Cumene Over Metalloporphyrins

The cumene oxidation process catalyzed by metalloporphyrins is shown as below (Scheme 1). A part of cumene hydroperoxide (CHP) can decompose under certain conditions. The decomposition of CHP was accelerated by prolonged reaction time, at higher temperature or through the accumulation of CHP, and the main by-products from CHP decomposition were 2-phenyl-2-propanol (DMPC) and hypnone (ACP) as well as trace amount of phenol and other acids. From Fig. 1, the amount of DMPC was 5–8 times of the amount of ACP. When the yield of CHP reached a certain level (22.9%, the selectivity of CHP being 94.4%), there was a sharp increase of the by-product DMPC formation, which was subsequently followed by noticeable decrease in terms of CHP selectivity, as shown in Fig. 1.

The Variation of the CHP Yield with Respect to the Temperature

Due to fact that the oxidation of cumene is relatively slow at low temperature and CHP tends to decompose at higher temperature, the reaction was carried out below 130°C in the presence of a small amount of metalloporphyrins ((*p*-Cl)TPPMnCl). When only minute amount of metalloporphyrin was added to the reaction, we found that more CHP can be produced at 120°C accompanied by few by-products

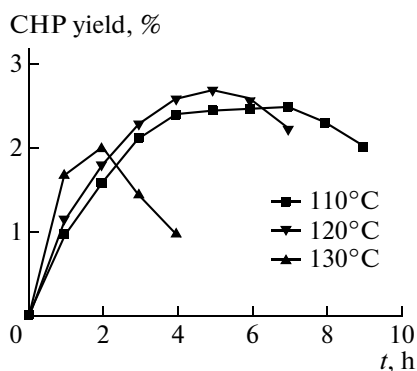


Fig. 2. Effect of the temperature on the cumene oxidation with metalloporphyrin Catalyst: (*p*-Cl)TPPMnCl (concentration, 7.2×10^{-5} mol/l), Flow rate of air: 600 ml/min. Pressure: 1 atm.

such as 2-phenyl-2-propanol and hypnone. Results from reactions with or without catalyst were shown in Figs. 2 and 3, respectively.

According to Figs. 2 and 3, between 110–130°C, the oxidation rate from cumene to CHP with catalyst was considerably faster than the one without catalyst. When the catalyst concentration was extremely low (7.20×10^{-5} mol/l), the yield of CHP production was still better than that of the oxidation with no catalyst by 3–10%. Furthermore, the reaction with catalyst had no induction period at 110°C, and 10% CHP can be obtained within 1 h. On the contrary, the reaction with no catalyst had a induction period around 2 h, and only 0.9% CHP was obtained after 1 h.

As Fig. 2 showed, the initial reaction rate was quite fast at 130°C, but the CHP formed decomposed quickly because of the high temperature, resulting in a rather low CHP yield. On the other hand, when the temperature was maintained at 120°C, yield of CHP reached 27.1% in 5 h in the presence of catalyst, while it took 8 h for the reaction with no catalyst to reach its peak of CHP yield (23.3%). So it seemed that tem-

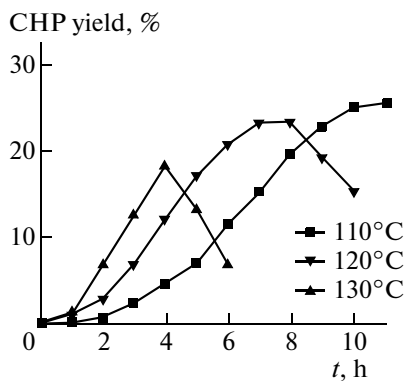


Fig. 3. Effect of the temperature on the cumene oxidation without catalyst Catalyst: none, Flow rate of air: 600 ml/min. Pressure: 1 atm.

perature being around 120°C and reaction time being 4–5 h were the optimal conditions for the best result when the reaction was catalyzed by (*p*-Cl)TPPMnCl (7.20×10^{-5} mol/l).

The Variation of the CHP Yield with the Flow Rate of Air

The effect of air flow rate on the CHP yield was also investigated when the stirring speed was maintained 600 rpm. The rate of cumene oxidation to produce CHP increased with the increase of the flow rate of air when the reaction was catalyzed by (*p*-Cl)TPPMnCl (7.20×10^{-5} mol/l) under atmospheric pressure at 120°C, as shown from Fig. 4. A huge increase of the CHP yield can be observed when the air flow rate was changed from 450 to 600 ml/min. When the flow rate of air was further increased to 800 ml/min, the CHP yield changed very little in the first 5 h, however, after that, the decomposition of CHP was much faster than that of the reaction run at 600 ml/min. This phenomenon can be explained as follows. Before reaching 600 ml/min, the oxygen dissolved in the liquid phase did not reach saturation level, thus the production of CHP increased with the increase of the flow rate of air. Beyond the saturation point (600 ml/min), the increase of oxygen flow no longer increased the reaction rate since it did not alter the concentration of oxygen in cumene. Additionally, the higher flow rate of air would accelerate the decomposition of CHP. Taking everything into consideration, it seemed, the flow rate of 600 ml/min was the optimal choice.

The Variation of the CHP Yield, with the Catalyst

Effect of various metalloporphyrins. In this work, several metalloporphyrins, such as (*p*-Cl)TPPCo, TPPZn, (*p*-Cl)TPPMnCl, [(*p*-Cl)TPPMn]₂O, and [TPPMn]₂O, were tested as catalyst for the cumene oxidation (7.20×10^{-5} mol/l, based on the content of metal ions). MnAc₂ · 4H₂O was also tested as the control catalyst with the same concentration. All reactions

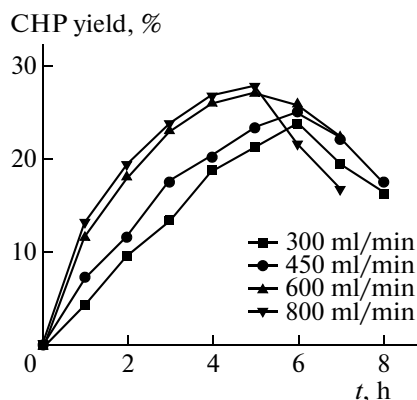


Fig. 4. Effect of the flow rate of air.

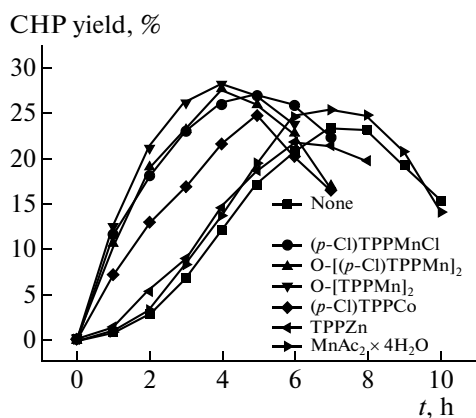


Fig. 5. Effect of different catalysts.

were carried out under atmospheric pressure at 120°C and the air flow rate was maintained at 600 ml/min. Except for TPPZn, both the CHP yield and the reaction rate of the cumene oxidation was improved by the addition of metalloporphyrin catalysts. The effects of manganese porphyrins, such as (*p*-Cl)TPPMnCl, [(*p*-Cl)TPPMn]₂O, and [TPPMn]₂O, were particularly better than the other metalloporphyrins and MnAc₂·4H₂O. And the peak yield of CHP could reach 28.30 or 27.7% using [(*p*-Cl)TPPMn]₂O and [TPPMn]₂O as catalyst, respectively, which were only slightly better than that of (*p*-Cl)TPPMnCl (Fig. 5).

Effect of the concentration of metalloporphyrins

Metalloporphyrin (*p*-Cl)TPPMnCl was chosen for further study of the effect of metalloporphyrin concentration on CHP yield. The reactions were carried out with catalyst concentration ((*p*-Cl)TPPMnCl) at 7.20×10^{-5} , 1.44×10^{-4} , 3.00×10^{-4} , 4.32×10^{-4} , and 5.76×10^{-4} mol/l, respectively. Figure 6 showed that the yield of CHP was sharply enhanced with the increase of the catalyst concentration. When the concentration of (*p*-Cl)TPPMnCl was 7.20×10^{-5} mol/l, the yield of CHP was 27.1% after 5 h. However, when the concentration of the catalyst was doubled, the yield of CHP increased to 35%, and it ultimately reached 39% when the concentration of the catalyst was increased by 6 or 8 times. As shown in Fig. 5, increasing the concentration of (*p*-Cl)TPPMnCl may accelerate the reaction rate and enhance the CHP yield, on the other hand, increasing the concentration

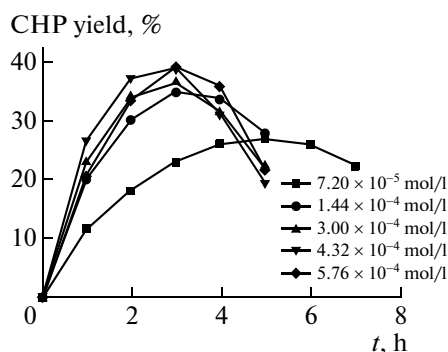


Fig. 6. Effect of the concentration of (*p*-Cl)TPPMnCl. Reaction temperature: 120°C. Flow rate of air: 600 ml/min. Pressure: 1 atm.

of (*p*-Cl)TPPMnCl may also accelerate the decomposition rate of CHP (Fig. 6) and decrease the selectivity of CHP (table).

Table showed the results of, selectivity of CHP with different catalyst concentrations. Under otherwise the same reaction condition, enhancing the catalyst concentration and prolonging reaction time led to decrease in the selectivity of CHP. Among the two, the effect of the catalyst concentration was more pronounced. We surmised that it was the by-products from the reaction such as trace of acids which may cause the decomposition of CHP, and metal ions from the self-oxidation of the metalloporphyrin catalyst in the reaction mixture may also accelerate the decomposition of CHP.

Reaction Rate Constant and Apparent Activation Energy

The study of reaction kinetics was carried out between 105–120°C and the reaction time was limited to the first 4 h because there seemed to be a linear relationship between the yield of CHP and reaction time during this period (Fig. 2) and only small amount of by-products was produced (Fig. 1). The reaction was run for 4 h with an air flow rate of 600 ml/min at 105–120°C using (*p*-Cl)TPPMnCl as the catalyst (7.20×10^{-5} mol/l) and the sample was analyzed every 30 min.

Figure 7 shows the changes of cumene concentration with reaction time at various temperatures. At all temperatures, a straight line can be fitted through the

Effect of (*p*-Cl)TPPMnCl concentration on the selectivity of CHP

(<i>p</i> -Cl)TPPMn concentration	CHP Selectivity, %				* CHP yield, %
	1 h	2 h	3 h	4 h	
7.20×10^{-5} mol/l	100.0	95.6	94.4	91.6	26.0
1.44×10^{-4} mol/l	98.2	93.1	91.8	87.6	33.7

* CHP yield after 4 h. Reaction temperature: 120°C. Flow rate of air: 600 ml/min. Pressure: 1 atm.

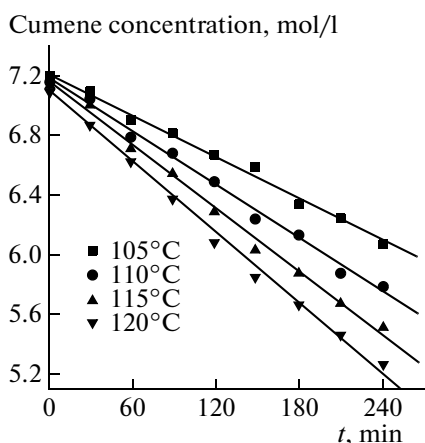


Fig. 7. Relationship between cumene concentration and reaction time.

collected data points, which strongly suggests zero-order kinetics in the first 4 h.

Since the reaction kinetics can be considered as a zero-order kinetics, the reaction rate constant k can be expressed as Eq. (1) and its value can be obtained by calculating the slopes of the straight lines in Fig. 7:

$$-\frac{dC_{\text{cumene}}}{dt} = k,$$

$$k_{105} = 4.63 \times 10^{-3} \text{ mol l}^{-1} \text{ min}^{-1} = 7.72 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1},$$

$$k_{110} = 6.03 \times 10^{-3} \text{ mol l}^{-1} \text{ min}^{-1} = 1.01 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1},$$

$$k_{115} = 7.16 \times 10^{-3} \text{ mol l}^{-1} \text{ min}^{-1} = 1.19 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1},$$

$$k_{120} = 8.30 \times 10^{-3} \text{ mol l}^{-1} \text{ min}^{-1} = 1.38 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}.$$
(1)

The relationship of temperature (T , K) and rate constant (k) can be expressed as the Arrhenius equation:

$$\ln k = \ln k_0 - \frac{E}{RT}. \quad (2)$$

In Eq. (2), k_0 is the pre-exponential factor, and E represents the apparent activation energy of the reaction.

Figure 8 shows the $\ln k$ versus $1/T$ plot. According to the slope and intercept of the straight line in Fig. 8, the numerical value of E and k_0 can be obtained: $E = 38.9 \times 10^4 \text{ kJ mol}^{-1}$, $k_0 = 20.4 \text{ mol l}^{-1} \text{ s}^{-1}$. Compared with the non-catalyzed results from the previous works [53, 54] ($E = 71.2 \times 10^4 \text{ kJ mol}^{-1}$ in [53] and $E = 10.7 \times 10^5 \text{ kJ mol}^{-1}$ in [54]), we can see that metalloporphyrin catalysts can greatly decrease the apparent activation energy of the cumene oxidation to CHP, and that is

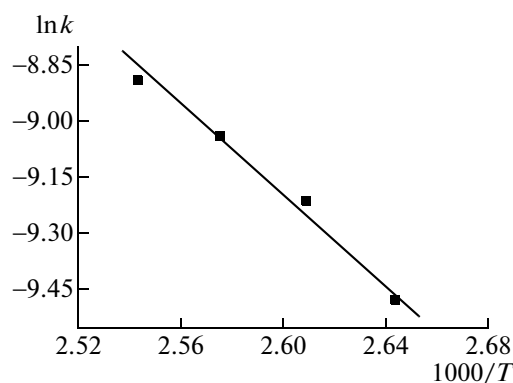


Fig. 8. Plot of $\ln k$ vs. $1/T$.

exactly why metalloporphyrins can accelerate the reaction remarkably.

CONCLUSIONS

In summary, an efficient protocol for the oxidation of cumene to cumene hydroperoxide (CHP) was developed using metalloporphyrins as catalysts with an atmospheric pressure of air. The effects of different catalysts, catalyst concentration, the flow rate of air and temperature on the reaction were examined. From the results, we can conclude that the reaction performed the best with single-metallomanganeseporphyrin and $[\mu]$ -oxo-bismanganeseporphyrin below 130°C . Under optimal conditions, yield as high as 33.7% and the selectivity of 87.6% can be achieved in as little as 4 h. Yet higher concentration of (*p*-Cl)TPP-MnCl, longer reaction time and higher reaction temperature were all detrimental to the production of CHP from cumene. Some plausible mechanisms of the reaction were proposed and kinetics of this reaction at its initial stages was also studied. The apparent activation energy of the reaction E was determined to be $38.9 \times 10^4 \text{ kJ mol}^{-1}$ and the pre-exponential factor k_0 was $20.4 \text{ mol l}^{-1} \text{ s}^{-1}$. The low apparent activation energy of the reaction could explain why the rate of cumene oxidation to CHP in the presence of metalloporphyrins was much faster than that of the non-catalyzed oxidation.

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