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RESEARCH PAPER

EPR Study of Cumene Hydroperoxide Decomposition Catalyzed by *Tetra*-(*p*-chlorophenyl)porphinatomanganese Chloride

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Abstract: The decomposition of hydroperoxide in the presence of a metalloporphyrin is an important metalloporphyrin-catalyzed hydrocarbon aerobic oxidation reaction. This process affects the oxidation product selectivity, the formation rate of oxidation products, and also the life of the metalloporphyrin catalysts. The decomposition of cumene hydroperoxide (CHP) catalyzed by *tetra*-(*p*-chlorophenyl) porphyrinatomanganese chloride (T(*p*-Cl)PPMn^{III}Cl) was studied by EPR, and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was used as an EPR spin trap. Experiments revealed that only the cumoxyl radical adduct was present during the initial reaction time at 25 °C. Another kind of radical adduct, a rearrangement product of the cumylperoxyl radical spin adduct, was also detected by EPR when the concentration of CHP was increased. Results further show that CHP decomposition started by homolytic O–O bond cleavage because of the T(*p*-Cl)PPMn^{III}Cl catalyst generating cumoxyl radicals in the initial part of the reaction and this led to 2-phenyl-2-propanol. The cumylperoxyl radicals were formed from the subsequent reaction of cumoxyl radicals with CHP when the initial CHP concentration increased. A free radical route for this decomposition reaction was also proposed.

Key words: *tetra*-(*p*-chorophenyl)porphinatomanganese chloride; cumene hydroperoxide; alkoxyl radical; electron paramagnitic resonance; catalytic decomposition

Metalloporphyrins have been used as model compounds for cytochrome P450 monooxygenase to catalyze the hydroxylation of hydrocarbons under mild conditions [1–7]. Researchers have extended this biomimetic catalysis to the aerobic oxidation of hydrocarbons, which is of great importance to the petrochemical industry. For example, the aerobic oxidation of cyclohexane via metalloporphyrin catalysis to produce cyclohexanone has been recently industrialized by Sinopec Corp [8,9].

Hydroperoxides are very important intermediates in the metalloporphyrin catalyzed hydrocarbon oxidation with air. On one hand, the formed hydroperoxides can decompose to oxyl-radicals when continuously catalyzed by metalloporphyrins and thus the high concentration of free radicals is maintained and the oxidation reaction occurs in the system [10], which affects the reaction conversion, the production selectivity, and the product formation rate. On the other hand, the formation and accumulation of hydroperoxides in the system lead to the destruction and deactivation of the metalloporphyrin catalyst. Therefore, a decomposition study of hydroperoxide catalysis by metalloporphyrins is of great value to understand the exact nature of biomimetic catalysis by metalloporphyrins.

Although it is generally accepted that the metalloporphyrin catalyzed aerobic oxidation of hydrocarbons is a free radical reaction, there is little direct evidence for the interaction between the metalloporphyrins, hydroperoxides (intermediates formed in the reaction), and the free radicals in the reaction system. To understand the reaction mechanism between hydroperoxide and metalloporphyrins, cumene hydroperoxide (CHP) decomposition catalyzed by *tetra*-(*p*-chlorophenyl) porphyrinatomanganese (T(*p*-Cl)PPMn^{III}Cl) was studied by electron paramagnetic resonance (EPR) in this work. The free radicals generated in the reaction system were trapped by

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5,5-dimethyl-1-pyrroline *N*-oxide (DMPO).

1 Experimental

1.1 Decomposition of CHP

In a typical procedure a certain amount of metalloporphyrin (synthesized by a method similar to that used in the literature [11–13] and their structures were confirmed by IR, UV-Vis, MS, and ^{1}H NMR analysis) and cumene (AR grade) were put into a 50 ml three-neck flask. The flask was immersed in a thermostatic water bath equipped with a magnetic stirrer. A high concentration of CHP was added when all the metalloporphyrin dissolved and the reaction solution temperature reached the desired temperature. Samples were regularly taken out during the reaction and CHP was quantitatively analyzed by iodometric titration. The products were analyzed by GC (Shimadzu GC-2010 equipped with a 0.5 mm i.d. 30 m DB-5 capillary column and a flame ionization detector) and GC-MS (Shimadzu GC-MS QP2010). Unless specified otherwise all decomposition reactions were carried out under a nitrogen atmosphere and all the CHP was in cumene solution.

1.2 Measurement of metalloporphyrin concentration

A series of different standard concentrations of T(*p*-Cl)PPMn^{III}Cl in cumene were prepared. The Soret band absorbency of T(*p*-Cl)PPMn^{III}Cl was measured by UV-Vis spectroscopy. A standard working curve was obtained by plotting the absorbance vs. the corresponding concentration of T(*p*-Cl)PPMn^{III}Cl. The concentration of T(*p*-Cl)PPMn^{III}Cl in the reaction system could thus be obtained using this standard curve.

1.3 EPR spin-trapping experiments

EPR is the main method used to study free radicals. Free oxyl-radicals, which are generated during the catalytic decomposition of organic hydroperoxides by metalloporphyrins, are difficult to detect by EPR because of their very short lifetimes. Therefore, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, Aldrich, ≥ 99%) was employed as a spin trap for the generated free radicals. The free radical adducts were identified by EPR spectra. Hydrocarbon oxidation reactions and organic hydroperoxide decompositions are typically carried out at higher than 100 °C in industry but it is difficult to trap the free radicals generated in these systems because of the instability of DMPO and its radical adducts at high temperatures. Hardly any suitable spin trapping agents can currently be used at high temperature and we carried out the spin trapping experiment at room temperature for this work.

The deoxygenated cumene solution containing metalloporphyrin was added to a glass reactor at 25 °C under nitrogen. The reaction was initiated by the addition of CHP while DMPO was added after 8 s. The reaction sample (50 μl) was then introduced to the flat cell after 5 min and scanned using EPR spectroscopy. The EPR parameters were: center field, 3 512 G; microwave power, 20 mW; modulation amplitude, 0.5 G; scan time, 167.77 s; scan range, 80 G.

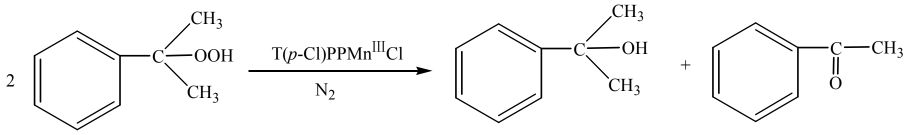
DMPO adduct EPR spectra were simulated using the EPR Winsim program [14]. The hyperfine coupling constants of the free radical adducts were analyzed by comparing computer simulation spectra with experimental spectra.

2 Results and discussion

2.1 Metalloporphyrin catalyzed decomposition of highly concentrated CHP

To obtain a suitable CHP concentration for the EPR experiment, highly concentrated CHP was decomposed in the presence of T(*p*-Cl)PPMn^{III}Cl. The CHP decomposition products, catalyzed by T(*p*-Cl)PPMn^{III}Cl, consisted mainly of 2-phenyl-2-propanol and acetophenone, as shown in Scheme 1.

The decomposition was carried out with a CHP concentration of 1.25 mol/L and a T(*p*-Cl)PPMn^{III}Cl concentration of 2.85×10^{-4} mol/L at 70 °C for 3 h. A qualitative analysis of the products was performed by GC-MS. Changes of CHP, 2-phenyl-2-propanol, and acetophenone concentrations with reaction time are shown in Fig. 1. 2-phenyl-2-propanol and acetophenone are the decomposition products of 1.25 mol/L CHP in cumene. The concentration of CHP decreased sharply in the first 5 min. After 5 min, the CHP decomposition slowed down considerably because of the low concentration of T(*p*-Cl)PPMn^{III}Cl and the inhibition of the catalyst by the high concentration of 2-phenyl-2-propanol that accumulates in the inital 5 min. Therefore, the amount of T(*p*-Cl)PPMn^{III}Cl did not change much afterwards. As shown in Fig. 1, the CHP decomposition rate is very low because of the presence of 2-phenyl-2-propanol in the solution.



Scheme 1. Decomposition of cumene hydroperoxide (CHP) catalyzed by metalloporphyrin.