

Selectively aerobic oxidation of C=C and allylic C–H bonds in α -pinene over simple metalloporphyrins

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Abstract

Simple metalloporphyrins (TPPMnCl, TPPCoCl, TPPFeCl, TPPNi, TPPCu or TPPZn) were employed as the catalysts for the aerobic oxidation of α -pinene in the absence of co-catalyst and solvents, and the catalytic selectivity of metalloporphyrins for aerobic oxidation of double bond and allylic C–H of α -pinene was investigated. The research results indicate that the reaction temperature, the metal nuclei, and peripheral substituents of the metalloporphyrins influence the catalytic selectivity of metalloporphyrins in the aerobic oxidation of α -pinene. Over TPPMnCl catalyst, the selectivity regarding the oxidation of C=C bond increased with decreasing temperature. Among various metalloporphyrins, TPPMnCl presented the largest selectivity regarding the oxidation of C=C bond and TPPFeCl the largest selectivity regarding the oxidation of allylic C–H bonds. With increasing the electron-donating abilities of the peripheral substituents in T(p-X)PPMnCl (X=Cl, CH₃, OCH₃, OH), the selectivities regarding the oxidation of C=C bond decreased. The results may provide an additional evidence for the stepwise mechanism through a radical intermediate.

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1. Introduction

In the past decades, selectively catalytic oxidation of alkenes to their oxo counterparts has attracted much attention [1,2]. Because of the poor selectivity in the alkene oxidation, people have been trying to discover better catalytic ways of alkene oxidation with air since 1960s [3]. However, the technology in which alkene was oxidized by air to produce oxo counterparts have not been improved very well till now. It was found that, when metalloporphyrins were used as catalysts, olefins could be oxidized by PhIO, NaClO, H₂O₂ [4–6] or molecular oxygen, in the presence of reductants or co-catalysts [7–11]. Recently, new progresses in this area were gotten by using multi-halogen metalloporphyrins or multi-substituent dioxoruthenium porphyrins as catalysts and by using directly air as an oxidant at ambient temperature and pressure [12–16].

In the previous papers, we reported the simple-metalloporphyrins-catalyzed oxidation of cyclohexane to cyclohexanol and cyclohexanone with air [17–19], in the absence of any co-catalyst or reductants, and excitingly, had put this process into industrial practice. In this paper, we reported the catalytic oxidation of α -pinene with air over some simple metalloporphyrins, in the absence of any co-catalyst or reductants under the mild conditions. Selectivities regarding the oxidation of C=C and allylic C–H bonds in α -pinene were investigated.

2. Experimental

2.1. Instruments and reagents

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

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Analysis of the products from the oxidation of α -pinene were performed on a Shimadzu GC-16A gas phase chromatography, using a OV-17 capillary column (0.5 mm i.d. \times 25 m) and a flame ionization detector (FID). A Perkin-Elmer 2400 elementary analyzer were also used.

All reagents and solvents used were analytical grade and obtained commercially. Pyrrole was redistilled before used. GC analysis showed that there was no impurity in α -pinene before use.

Metalloporphyrins were synthesized by a method similar to that reported in Refs. [20,21]. Their structures were identified by IR, UV-vis, MS, and elemental analysis.

2.2. Oxidation of α -pinene by molecular oxygen

A certain amount of metalloporphyrin and 70 ml of α -pinene were introduced together into a 100 ml three-neck flask equipped with a reflux condensation tube. The mixture was agitated and heated with an electromagnetic stirrer, keeping away from light. When the reaction temperature reached the preconcerted point, air was pumped continuously into the reaction system, with the flow rate of air being measured by a rotameter. Sampling was carried out every 30 min and the components of the reaction mixture were quantified by GC with internal standard method and identified by GC-MS.

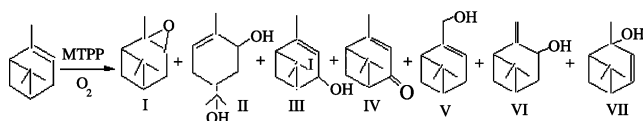
3. Results and discussion

3.1. Aerobic oxidation of α -pinene over simple metalloporphyrins

Scheme 1 shows the main products of the oxidation of α -pinene catalyzed by manganeseporphyrins.

GC analysis indicated that the product mixture was mainly composed of components resulting from the oxidation of C–C bond and allylic secondary C–H bond in α -pinene. Product I attributed to the oxidation of π -bond of α -pinene, and rearranged product II had also been proved to be from oxidation of π -bond [22]. Products III, IV and V belong to the oxidation products of allylic C–H bonds. No oxidation products of allylic tertiary C–H bond were detected. Trace amount of products VI, VII were also detected by GC-MS, which were failed to be identified by GC and could be neglected in the calculation of conversion and selectivity in this paper.

It had ever been suggested that the hydrogen of allylic tertiary C–H bond in α -pinene could be easily abstracted by active oxygen-containing radicals, assuming an allyl-resonance



Scheme 1.

stabilization, and forming the product II [22]. However, recent studies, basing on quantum chemical calculations and density functional theory, show that this hydrogen is difficult to be abstracted, due to its large C–H bond strength caused by the special strained ring structure of α -pinene, and it is the oxidation of π -bond that constitutes an important reaction channel to form product II [23–26]. The theoretical calculation indicated that abstraction of the hydrogen of allylic tertiary C–H bond in α -pinene does not yield a resonance-stabilized radical [24,25]. The radical orbital is pointing outward, and ring strain prevents it from attaining the required spacial attitude with respect to the double bond. Therefore, the unpaired electron remains localized on the allylic tertiary carbon, thereby somewhat increasing the four-membered ring strain. Forming a radical by removing hydrogen from the allylic tertiary carbon in α -pinene therefore requires more energy compared to the unstrained alkanes.

The experiments had been repeated for above three times, no any other oxidation products of allylic tertiary C–H bond except product II was detected by GC-MS on the mild conditions employed in this paper. Therefore, product II was considered as the product from C–C oxidation.

The yields of various products from the oxidation of α -pinene with and without a catalyst as a function of reaction time are illustrated in Figs. 1 and 2.

From Fig. 1, it can be seen that the yield of various products increased linearly with the reaction time within 5 h. As the reaction run for 5 h, the α -pinene conversion reached 16.22%, and the total selectivity to products from the oxidation of C–C bond up to 60.99%, with that to α -pinene epoxide being up to 32.56%. The selectivities to various products had an order I > II > III > IV > V.

The blank experiment results (Fig. 2) show that there were similar oxidation products in the reaction without catalyst, but only a 6.98% conversion of α -pinene and a 47.63% to products from C–C oxidation were obtained when the reaction was run for 5 h. In the same time, the selectivity to α -pinene epoxide dropped to 17.95%. The selectivities to the oxidation products had an order II > III > I > IV > V.

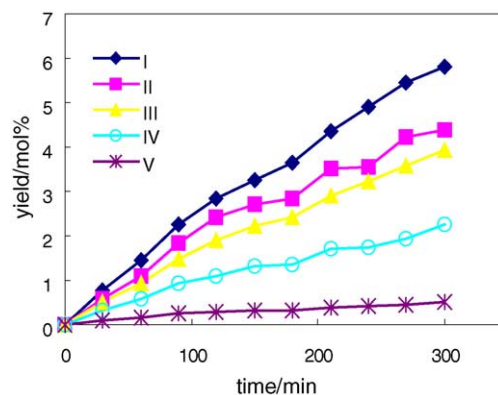


Fig. 1. The curves of reaction product distribution at 60 °C in the presence of TPPMnCl catalyst.

Table 1
Effect of temperature on the conversion of α -pinene and the selectivities to various oxidation products

Temperature ($^{\circ}\text{C}$)	Conversion (%)	Selectivity (%) ^a		
		Products I and II	Products III and IV	Product V
80	23.02	60.19	36.58	3.23
70	19.87	60.45	35.86	3.69
60	16.22	60.99	35.67	3.33
50	14.78	62.00	34.55	3.45
40	8.77	66.86	30.12	3.23

Conditions: the catalyst, TPPMnCl (concentration, 6×10^{-5} mol/L); the airflow rate, 16 L/h; ambient pressure; reaction time, 5 h.

^a Products I and II were considered as the products from C=C oxidation, products III and IV from allylic secondary C–H oxidation, and product V from allylic primary C–H oxidation.

3.2. Effect of reaction temperature on selectivity

The conversion of α -pinene and the selectivities to the products from C–C and allylic C–H oxidation at temperatures ranging from 40 to 80 $^{\circ}\text{C}$ are listed in Table 1. With temperature increasing from 40 to 80 $^{\circ}\text{C}$, the α -pinene conversion increased from 8.77 to 23.02%, the selectivity to the products from C–C oxidation decreased from 66.86 to 60.19%, however, that to the products from allylic secondary C–H oxidation increased from 30.12 to 36.58%. The selectivity to the products from allylic primary C–H oxidation fluctuated slightly. The main oxidation product was α -pinene epoxide, to which the best selectivity was up to 32.56% at 80 $^{\circ}\text{C}$.

When the reaction temperature decreased, the selectivity to products I and II from C–C oxidation increased and those to products III and IV decreased. This is maybe come from the different bond energy between π -C–C bond and the allylic secondary C–H. The strength of allylic primary C–H bond is much higher than that of π -C–C bond and allylic secondary C–H bond, resulting in its lower oxidation selectivity to allylic primary C–H bond and slight fluctuation at the mild reaction temperature. The theoretical calculation indicated that the bond strength of allylic tertiary C–H in α -pinene is 427.6 kJ mol⁻¹, being 12.6 kJ mol⁻¹ higher than that of the normal primary C–H [24,25]. It is reasonable that the allylic tertiary C–H is hard to be oxidized under the given mild conditions, and in fact no any oxidation products of allylic

tertiary C–H bond were detected by GC–MS in our experiments when several duplicate runs done.

The bond energy of π -C–C bond is smaller than that of the allylic secondary C–H, so the oxidation rate is larger for the former than for the latter at the lower temperature. When the reaction temperature increased, the oxidation rate of the allylic secondary C–H increased faster than that of π -C–C bond, so the selectivity to products III and IV from the oxidation of allylic secondary C–H increased.

3.3. Effect of metalloporphyrins

In our experiments, it was found that the metalloporphyrins presented the very different catalytic activities, regarding the oxidation of α -pinene, dependent on the nature of the metal they contained. TPPNi, TPPCu and TPPZn showed almost no catalytic activity on the oxidation of α -pinene under the reaction conditions involved in this paper, with the conversions and the products distribution being similar to those of blank auto-oxidation. TPPMnCl, TPPCoCl and TPPFeCl, however, were found to be active in the catalytic oxidation of α -pinene, and their effect on the conversion of α -pinene and the selectivity to various oxidation products is shown in Table 2. It is indicated that the conversion of α -pinene over the metalloporphyrins investigated follow a sequence TPPMnCl > TPPCoCl > TPPFeCl > TPPNi–TPPCu–TPPZn. From Table 2, it also can be seen that the total selectivity to products I and II from C–C oxidation over the three metalloporphyrins have an order TPPMnCl > TPPCoCl > TPPFeCl, while those to products III, IV and V from allylic C–H oxidation are

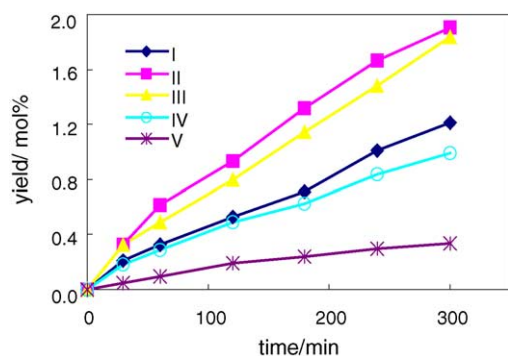


Fig. 2. The curves of reaction product distribution at 60 $^{\circ}\text{C}$ in the absence of the catalyst.

Table 2
Effect of metalloporphyrins catalysts on the conversion of α -pinene and the selectivity to various oxidation products

Catalysts	Conversion (%)	Selectivity (%)		
		Products I and II	Products III and IV	Product V
TPPMnCl	16.22	60.99	35.67	3.33
TPPCoCl	13.84	59.11	37.05	3.84
TPPFeCl	12.40	51.30	43.83	4.87

Conditions: the concentration of the catalyst, 6×10^{-5} mol/L; the temperature, 60 $^{\circ}\text{C}$; ambient pressure; the flow rate of air, 16 L/h; reaction time, 5 h.

Table 3
Effect of peripheral substituents on the conversion of α -pinene and the selectivities to various oxidation products

Catalyst	Conversion (%)	Selectivity (%)		
		Products I and II	Products III and IV	Product V
T(p-Cl)PPMnCl	18.68	62.21	34.41	3.38
TPPMnCl	16.22	60.99	35.68	3.33
T(p-CH ₃)PPMnCl	13.87	58.47	38.15	3.38
T(p-OCH ₃)PPMnCl	11.42	57.40	39.13	3.47
T(p-OH)PPMnCl	9.03	56.41	40.02	3.57

Conditions: same as Table 2.

in the inverse order. The catalytic activity and selectivity of different metalloporphyrins are influenced by the stability of different valences of metal atoms and the quantity of electric potential [27].

3.4. Effect of peripheral substituents

Peripheral substituents of the manganese porphyrins play an important role on the catalytic activity and selectivity, as shown in Table 3. With increasing the electron-donating abilities of the substituents of various metalloporphyrins, from the top to the bottom of Table 3, the conversion of α -pinene decreased from 18.68 to 9.03%, the selectivities to the products I and II from C–C oxidation decreased from 62.21 to 56.41% and those to the products III and IV from allylic secondary C–H oxidation increased from 34.41 to 40.02%. No obvious difference in the selectivity to product V from allylic primary C–H was observed over various metalloporphyrins catalysts. The yield of the product I (α -pinene epoxide) was found to reduce from 33.84 to 25.22% over the metalloporphyrins listed from the top to the bottom in Table 3. It appears that T(p-Cl)PPMnCl, among all the catalysts, possesses the best catalytic performance, with the largest conversion of α -pinene, the largest selectivities to the products from the oxidation of C–C bond (products I and II) and the smallest selectivity to the products from the oxidation of allylic secondary C–H bond (products III and IV); whereas T(p-OH)PPMnCl is quite the contrary.

The electron-withdrawing substituents at a meso position had been found to increase the catalytic activation of metalloporphyrins and retard the decomposition of catalysts [28]. The electron-donating substituents decreased the catalytic efficiency due to the dimerization of metalloporphyrins, being oxidized readily in solution [29]. In the present paper, the electron-donating substituents were found to reduce the selectivity to the products from the oxidation of C–C bond, suggesting that a lower electron density on the ring or metal is favorable to elevate the selectivities to the products from oxidation of C–C and allylic C–H bonds.

3.5. Preliminary consideration on the aerobic oxidation of α -pinene

In order to investigate the possible pathways for the formation of main products from α -pinene aerobic oxidation

over metalloporphyrins, the change in the concentration of manganese porphyrin (TPPMnCl) with reaction time at 60 °C was tracked by UV–vis spectra. As seen in Fig. 3, the concentration (the intensity of the absorption peaks) of TPPMnCl remains almost unchanged within the first 3 h of reaction, however, dropped rapidly after the reaction proceeding beyond 3 h. A complete destruction of the manganese porphyrin was observed at 5 h from the UV–vis spectra. In another experiment, after tenfold benzoyl peroxide [(C₆H₅CO)₂O₂] relative to the quantity of TPPMnCl were added in the reaction system, the absorption peak disappeared at 3 h, suggesting strongly that the porphyrin macrocycle may probably be destructed by the increased alkyl peroxide in the reaction system. We have also found that 2,6-di-*tert*-butyl-*p*-cresol could quench substantially the oxidation reaction. Therefore, it is reasonable to deduce that the oxidation of α -pinene catalyzed by metalloporphyrins is expected to proceed via a radical pathway. The theoretical study by Gunter and Turne [30] proved that the active intermediate in alkene oxidation over Fe(III)- or Mn(III)-porphyrin was a high-valence metal-oxygen positive radical M(IV)O⁺ (M = Fe, Mn, Co), which played an important role in the epoxidation and hydroxylation of alkenes [31]. In the present work, it was found that the selectivity to the products from C–C oxidation decreased and that to the products from allylic C–H oxidation increased, with increasing the electron density on the ring or metal of the metalloporphyrins (see Tables 2 and 3). The main pathways of the reaction between α -pinene and the active intermediate consisted of the oxidation of C–C bond and the

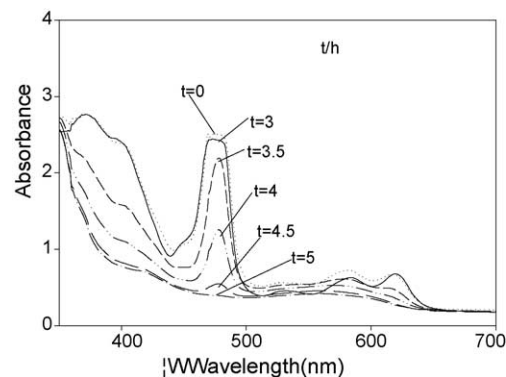
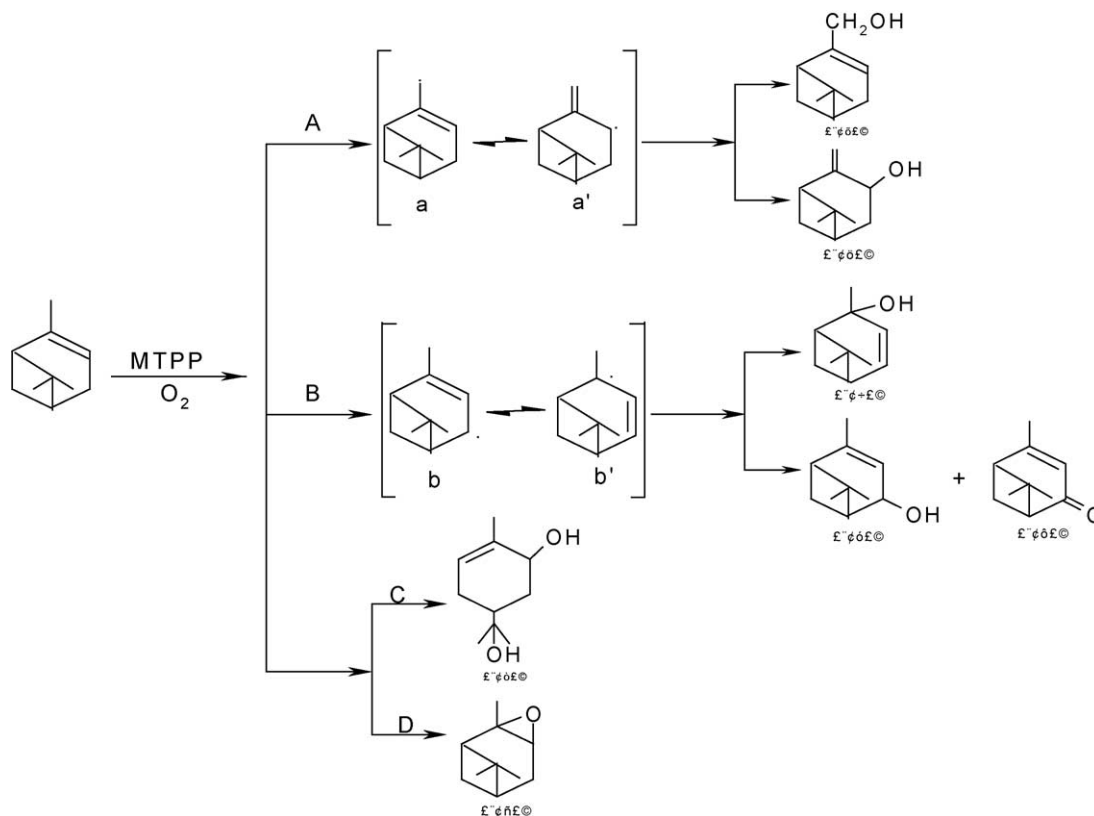


Fig. 3. Time-dependent electronic absorption spectra of TPPMnCl in the aerobic oxidation of α -pinene at 60 °C.



Scheme 2. Possible pathways for the formation of main products from α -pinene aerobic oxidation.

dehydrogenation from allylic carbon [32]. The abstraction of hydrogen atom would result in the formation of α -pinenyl radicals, which can be stabilized by allyl resonance (species a, a', b and b' in Scheme 2). Trace amount of Products VI and VII, formed from a' and b', respectively, were detected by GC–MS but failed to be by GC. The interaction of the active intermediate with the C–C bond would lead to the formation of products I and II, respectively. It is still argued, however, to the exact nature of the oxygen atom transfer. One of the viewpoints considered a stepwise transfer of oxygen proceeding through a radical intermediate [33,34], while a mechanism was concerted the oxygen insertion into the alkene double [35,36]. We are inclined to the stepwise mechanism, considering the fact that the oxidation products I and II were both detected in our experiments. A detailed mechanistic study on the aerobic oxidation of α -pinene catalyzed by simply metalloporphyrins is still in proceeding in our laboratory.

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