Selective oxidation of ethylbenzene with air catalyzed by simple μ-oxo dimeric metalloporphyrins under mild conditions in the absence of additives

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Abstract

The paper reported the catalysis of simple μ-oxo dimeric metalloporphyrins for the selective oxidation of ethylbenzene with air under mild conditions in the absence of additives. Two simple μ-oxo dimeric metalloporphyrins, μ-oxo-bis(tetraphenyl-porphinato)iron [TPPFe]$_2$O and μ-oxo-bis(tetraphenylporphinato)manganese [TPPMn]$_2$O were used as catalyst in the oxidation of ethylbenzene with air under mild condition. The results show that the products of ethylbenzene oxidation catalyzed by [TPPFe]$_2$O or [TPPMn]$_2$O with air are acetophenone and α-phenylethanol exclusively under $T > 60\,^\circ$C and atmospheric pressure and in absence of any additive. [TPPMn]$_2$O is an active catalyst with high selectivity and turnover number of 2134 for oxidation of ethylbenzene by air when temperature reacts at 70 $^\circ$C. The kinetic study shows that the ethylbenzene oxidation is zero-order for oxygen and first-order for ethylbenzene. The activation energy of the reaction is 72.7 kJ/mol. Comparing with the corresponding monometalloporphyrins TPPFeCl and TPPMnCl, [TPPFe]$_2$O and [TPPMn]$_2$O have the better catalytic activity for ethylbenzene oxidation with air without any additive under mild conditions.
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1. Introduction

In recent two decades, the catalysis of metalloporphyrins for alkene epoxidation and alkane hydroxylation under mild conditions has widely received considerable attention [1]. A new approach to oxidation of alkane and alkene by PhIO, NaClO, H$_2$O$_2$, etc. catalyzed by metalloporphyrins under mild condition have made great success [2–45]. Use of air as oxygen source in alkane and alkene oxidations catalyzed by metalloporphyrins has raised great prospect to the

oxidation of hydrocarbon compounds [46]. A number of reports have described that metalloporphyrins can catalyze the monooxygenation of alkane and alkene based on the complex oxygen donor system, such as O$_2$–zinc, O$_2$–ascorbic acid, O$_2$–NaBH$_4$, etc. [47–62]. Also there are many papers reporting that oxidation of alkane and alkene can be finished by novel metalloporphyrins, such as polyhalogen-metalloporphyrins with air apart from the reducer [63–81]. These observations have understandably simulated considerable interest in the applications for selective oxidation of hydrocarbon with air under mild conditions.

In alkane oxidations, work over the last several decades has indicated that μ-oxo dimeric iron porphyrins are either inactive or have very low activity.

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Recently, our work [82–85] showed that simple μ-oxo bisiron and bismanganese porphyrins could catalyze the hydroxylation of cyclohexane with PhIO, and that μ-oxo bismetalloporphyrins have higher activity than monometalloporphyrins. Some other work [46,63,86] testified that μ-oxo dimeric iron(III) porphyrins in the perhaloporphyrin series were active catalysts for alkane oxidation with air. The work of Ellis and Lyons showed that both iron(III) μ-oxo iron dimers and ferryl(III) species coexist for the catalytic oxidation of hydrocarbon with dioxygen by perhaloporphinatoiron series [46,63], and the work of Moore et al. declared that μ-oxo iron complexes of electron-deficient iron porphyrin complexes derived their activity for air oxidation of alkanes from conversion of the μ-oxo dimer to the corresponding iron hydroxo complex [86]. But the catalysis of simple μ-oxo dimers for the alkane oxidation with air has not been reported up to now. In order to gain an insight into the catalysis of simple μ-oxo dimeric iron and manganese porphyrins for the inert hydrocarbon bond oxidation with air under mild conditions and in absence of any additive, we synthesized two simple μ-oxo dimers, μ-oxo-bis (tetraphenylporphinato)iron [TPPFe]$_2$O and μ-oxo-bis (tetraphenylporphinato)manganese [TPPMn]$_2$O, and studied their catalysis for the oxidation of ethylbenzene with air without additives under mild conditions. The results indicate that simple μ-oxo dimeric iron and manganese porphyrins can catalyze air to oxidize ethylbenzene to acetophenone and α-phenylethanol with high regioselectivity under mild conditions under which no reaction occurs when no μ-oxo dimer catalyst is used. Comparing with monometalloporphyrins, μ-oxo dimeric metalloporphyrins have the better catalysis for the hydrocarbon oxidation again.

2. Experimental

2.1. Instruments and reagents

Gas chromatography was performed on a Shimadzu GC-16A spectrometer. ^{1}H NMR were recorded on AC-80 spectrometer. IR spectra were obtained on a PE-783 spectrometer. Visible spectra were recorded on a PE L-17 spectrometer. A PE-2400 elemental analysis meter was used. Mass spectra were measured on Class-5000 GC–MS spectrometer.

Pyrrole was redistilled before use. Ethylbenzene was purified by rectification before use. Other reagents all were analytical or commercial chemical grade. Organic solvents were purified by standard procedures.

2.2. Synthesis of metalloporphyrins

TPPH$_2$ was prepared according to the literature [87,88], purified with neutral Al$_2$O$_3$ column. TPPMnCl, [TPPMn]$_2$O, TPPFeCl, and [TPPFe]$_2$O were synthesized from the literature [89–91]. All the compounds were characterized by element analysis, IR and UV spectrometer. TPPFeCl: C$_{44}$H$_{28}$N$_4$FeCl, calcd. C, 75.06; H, 4.01; N, 7.92%; found: C, 75.10; H, 3.85; N, 7.90%; IR (KBr): $\nu_{Fe–Cl}$, 380 cm^{-1}; UV-Vis (benzene): 418.8, 507.2, 572.4, 652.8, 685.6 nm. TPPMnCl: C$_{44}$H$_{28}$N$_4$MnCl, calcd. C, 75.16; H, 4.01; N, 7.97%; found: C, 75.32; H, 3.95; N, 7.80; IR (KBr): $\nu_{Mn–Cl}$, 320 cm^{-1}; UV-Vis (benzene): 477.2, 533.6, 585.2, 620.4 nm. [TPPFe]$_2$O: C$_{88}$H$_{56}$N$_8$Fe$_2$O, calcd. C, 78.11; H, 4.17; N, 8.28%; found: C, 78.09; H, 4.23; N, 8.05%; IR (KBr): $\nu_{FeO–Fe}$, 870, 895 cm^{-1}; UV-Vis (benzene): 407.6, 570.0, 611.2 nm. [TPPMn]$_2$O: C$_{88}$H$_{56}$N$_8$Mn$_2$O, calcd. C, 78.21; H, 4.18; N, 8.29%; found: C, 77.81; H, 4.16; N, 8.45%; IR (KBr): $\nu_{Mn–O–Mn}$, 876, 849 cm^{-1}; UV-Vis (benzene): 418.2, 472.7, 578.3, 616.2 nm.

2.3. Oxidation of ethylbenzene catalyzed by metalloporphyrins

Ethylbenzene oxidations with air in this paper were carried out using the following procedures unless otherwise specified. To a mixture of ethylbenzene (30 ml) and metalloporphyrin (10 mg) in a 50 ml of capped three-necked flask equipped with condenser and temperature gauge was reacted with air (0.06 m^3/h) continuously.

The flask was incubated by warmed sulfuric acid. The temperature of sulfuric acid was controlled by a temperature controller. The change ranges of the temperatures of the mixtures were ±0.5 °C. The oxidation products were analyzed by GC–MS spectrometer and GC spectrometer for qualitative analysis and quantitative analysis, respectively. Yields were calculated based on the input moles of ethylbenzene. Samples for dynamics analyses were regularly collected from reactant system at intervals of 15 min

by micro-injector. Quantitative calculations used an internal standard method. The standard material was 1,4-dichlorobenzene.

3. Results and discussion

3.1. Oxidation of ethylbenzene with air catalyzed by μ-oxo bismetalloporphyrins

Oxidation of ethylbenzene with air catalyzed by μ-oxo dimeric metalloporphyrins [TPPMn]$_2$O or [TPPFe]$_2$O yields acetophenone and α-phenylethanol when $T > 60\,^\circ$C at the atmosphere pressure (Scheme 1). The reaction products are exclusively the α-oxidation products.

This fact showed that air oxidation of ethylbenzene could be catalyzed by simple μ-oxo dimeric metalloporphyrins under mild conditions, and perhaloporphyrins and reducers were not necessary. GC–MS analysis showed that the by-products of above reaction were styrene and benzaldehyde. The by-products were so small that the selectivity of α-oxidation products were greater than 99% when the temperature was lower than 90 °C. But the by-products increased when the reaction temperature was higher than 90 °C. Perhaps this is due to the elimination of H$_2$O from α-phenylethanol and oxidation of styrene, respectively [92]. The comparative research indicates that ethylbenzene can't be oxidized by air under same conditions when μ-oxo dimeric metalloporphyrins or monometalloporphyrins were absent, and the reaction which is running will terminate immediately when a small amount of hydroquinone, a common radical inhibitor, was added to the reaction system. HPLC analyses for the reactants at 70 °C showed that there existed the dimeric metalloporphyrins when the oxidation carried out 2 h. These show that the ethylbenzene

oxidation with air is a radical chain oxidation catalyzed by simple μ-oxo dimeric metalloporphyrins.

3.2. Comparison of the catalytic power of μ-oxo bismetalloporphyrins with monometalloporphyrins

For the purpose of comparing the catalytic power of μ-oxo dimeric metalloporphyrins with monometalloporphyrins, we studied the catalysis of two μ-oxo dimeric metalloporphyrins [TPPFe]$_2$O and [TPPMn]$_2$O and two monometalloporphyrins TPPMnCl and TPPFeCl for ethylbenzene oxidation with air. Monometalloporphyrins TPPMnCl and TPPFeCl were found to have the same catalysis for the oxidation of ethylbenzene with air under same conditions as μ-oxo dimeric metalloporphyrins. But the different metalloporphyrins had the different catalytic power for ethylbenzene oxidation with air. The researches showed that the different metalloporphyrins needed the different temperatures at which metalloporphyrins catalyzed the ethylbenzene oxidation with air. If the reaction temperatures were lower than the necessary temperature, no products in ethylbenzene oxidation were formed even if the oxidation lasted 48 h. The necessary temperatures were 40, 45, 50 and 60 °C for [TPPFe]$_2$O, TPPFeCl, [TPPMn]$_2$O and TPPMnCl separately. Comparing with μ-oxo manganese porphyrin dimer, the oxidation catalyzed by μ-oxo iron porphyrin dimer needed the lower reaction temperature to run the reaction. The other catalytic properties of four kinds of metalloporphyrins in ethylbenzene oxidation at 85 °C were listed in Table 1.

One can see from Table 1 that the total yield of the oxidation by the dimeric iron porphyrin is higher than those by the dimeric manganese porphyrin when the reaction is run for about 2 h, and the time of reaching maximum yield for iron porphyrin dimer is much faster than the one for manganese porphyrin
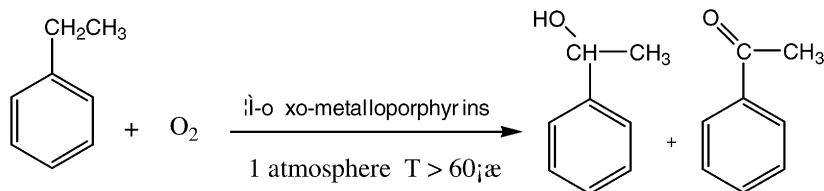
Scheme 1.

Table 1
Effects of metalloporphyrins on oxidation products

	[TPPMn]$_2$O	TPPMnCl	[TPPFe]$_2$O	TPPFeCl
Maximum yield time (h)	20	23	5	6
Ethylbenzene conversions	8.08	6.48	3.73	5.41
Maximum yield of acetophenone (%)	4.89	3.62	1.97	2.91
Maximum yield of α-phenylethanol (%)	3.19	2.86	1.76	2.50
Ketone/alcohol (mol/mol)	3.76	3.10	2.74	2.85
Total turnover number (mol/mol)	2024	783	878	642
Total yields at 2 h (mmol)	3.33	2.30	7.68	5.61

Reaction temperature is 85 °C. The flow rate of air is 0.06 m^3/h. Ethylbenzene is 30 ml. Catalysts are 10 mg.

dimer. This indicated that μ-oxo iron porphyrin dimer has higher activity than μ-oxo manganese porphyrin dimer. But the finally total yield of the reaction catalyzed by iron dimer is lower than manganese dimer. Comparing with the corresponding monometalloporphyrins, μ-oxo dimeric metalloporphyrins had the higher total yields and turnover numbers. These proved that μ-oxo metalloporphyrin dimers had higher activity than monometalloporphyrins for the ethylbenzene oxidation with air.

Whether μ-oxo dimeric metalloporphyrins or monometalloporphyrins, the conversions of the oxidation catalyzed by manganese porphyrins were greater than those by iron porphyrins. Probably, it came from the fact that the self-oxidation of iron porphyrins is faster than manganese porphyrins during the catalysis process [93]. This was further proved by the monitor of reactants with UV-Vis. We found from the analyses for the reactants with UV-Vis that the absorbance of iron porphyrins in the ethylbenzene oxidation system disappeared faster than one of manganese porphyrins.

3.3. Effects of the flow rate of air

The flow rate of air influences the yields (see Table 2). The best flow rate of air is about 0.05 m^3/h. When the flow rate is below 0.05 m^3/h, the total yields are increasing with the increasing of the flow rate of air. But when the flow rate is higher than 0.05 m^3/h, the total yields are increasing with the length of time and have no relationship with the flow rate of air. This showed that the air oxidation of ethylbenzene was influenced by the diffusion rate of air when the flow rate of air is small than 0.05 m^3/h, and that the oxidation reaction was controlled by the kinetic factors.

3.4. Effects of the partial pressure of oxygen

The yields of dioxygen oxidation of the ethylbenzene for the different partial pressure of oxygen are listed in Table 3. One can see that the partial pressure of oxygen has no effect on the reaction rate when the partial pressure of oxygen is larger than 0.21. This shows that the ethylbenzene oxidation is zero-order

Table 2
Effects of air flow rate on ethylbenzene oxidation[a]

Air flow rate (m^3/h)	Total acetophenone and α-phenylethanol (mmol)							
	15 min	30 min	5 min	60 min	75 min	90 min	105 min	120 min
0.02	0.59	1.18	1.76	2.36	2.95	3.53	4.11	4.70
0.03	0.74	1.48	2.21	2.96	3.69	4.43	5.17	5.90
0.04	0.82	1.64	2.44	3.29	4.09	4.92	5.73	6.54
0.05	0.85	1.70	2.53	3.38	4.22	5.08	5.92	6.76
0.06	0.85	1.69	2.54	3.38	4.29	5.04	5.87	6.68
0.08	0.84	1.68	2.53	3.36	4.20	5.03	5.88	6.72

[a] Reaction temperature is 85 °C. Ethylbenzene is 30 ml. Catalyst is 10 mg.

Table 3
Effects of partial pressure of oxygen[a]

p.p.o.[b] (atm)	Total acetophenone (mmol)							
	15 min	30 min	45 min	60 min	75 min	90 min	105 min	120 min
1.00	0.43	0.86	1.28	1.68	2.09	2.50	2.85	3.25
0.80	0.45	0.87	1.28	1.71	2.11	2.51	2.89	3.30
0.60	0.43	0.85	1.27	1.68	2.09	2.49	2.88	3.25
0.40	0.44	0.87	1.29	1.71	2.09	2.50	2.88	3.28
0.21	0.43	0.88	1.29	1.71	2.12	2.55	2.89	3.32

[a] Reaction temperature is 85 °C. The flow rate of air is 0.06 m^3/h. Ethylbenzene is 30 ml. Catalysts are 10 mg.
[b] p.p.o.: partial pressure of oxygen.

reaction for the partial pressure of oxygen when air is used as the oxidant, and means that air is the suitable oxidant for ethylbenzene oxidation catalyzed by μ-oxo dimers.

3.5. Relationship between oxidation rates and the concentration of ethylbenzene

A number of different concentration sample of ethylbenzene in biphenyl were used to study the influences of the concentration of ethylbenzene on the oxidation reaction. The changes of the yields of the ethylbenzene oxidation with the time at the different concentration of ethylbenzene are indicated in Fig. 1.

Studies showed that no oxidation product was formed in initial 30 min when the concentration of ethylbenzene was 6.4 M. If the concentration of ethyl-

benzene was 6.0 M, there was no product when the reaction was run for 2 h.

Suppose that the concentration of ethylbenzene is a constant during the reaction due to its low conversion. Therefore, the amount of products (n_B) has direct proportion to reaction time (t) this is:

$$n_B = rt$$

Processing the experiment data in Fig. 1 with least square means gets the relationship between the concentration of ethylbenzene and the reaction rates as in Fig. 2. From the following kinetic relationship:

$$r = kC_A^n \quad \text{and} \quad \ln r - n \ln C_A = \ln k$$

we can get $n = 1.017$. So, the kinetic equation is $r = kC_A$. The ethylbenzene oxidation is first-order reaction for the concentration of ethylbenzene.
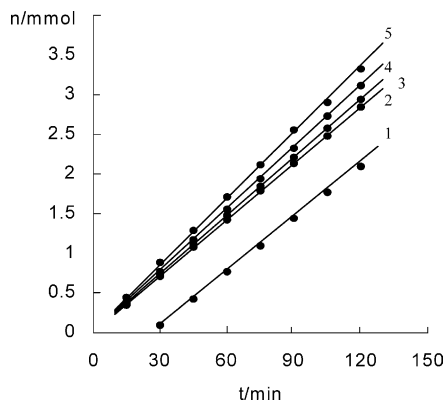

Fig. 1. Change of oxidation yields with time at the different ethylbenzene concentration: (1) 6.4 M; (2) 6.8 M; (3) 7.1 M; (4) 7.5 M; (5) 8.0 M.
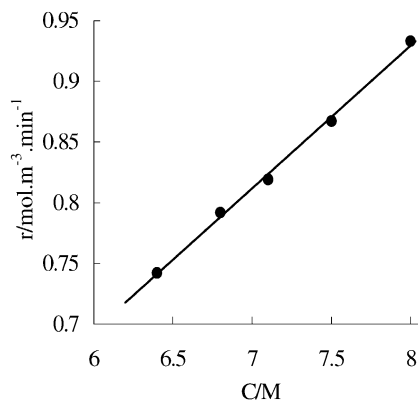

Fig. 2. Relationship between the reaction rates and the ethylbenzene concentrations.

Table 4
Effects of temperature on oxidation products[a]

	Temperature (°C)								
	60	65	70	75	80	85	90	95	100
Maximum yield time (h)	75	91	72	50	30	20	12	8	5
Ethylbenzene conversions (mol%)	3.39	6.33	6.53	6.62	6.70	6.84	7.90	8.25	9.53
Maximum yield of acetophenone (mol%)	3.08	4.94	5.15	5.06	4.97	4.92	4.66	4.46	4.31
Maximum yield of α-phenylethanol (mol%)	0.31	1.39	1.38	1.36	1.33	1.30	1.28	1.25	1.22
Total turnover number (mol/mol)	1120	2091	2157	2187	2213	2260	2510	2726	3148

[a] The flow rate of air is $0.06\,m^3/h$. Ethylbenzene in biphenyl is 8 M. Catalysts are 10 mg.

The hydrocarbon oxidation catalyzed by μ-oxo dimeric metalloporphyrins first from an active high-valence metal–oxygen positive radical intermediate, then this radical attracts a hydrogen atom of hydrocarbon to form an alkyl radical. The speed-determined step of the oxidation is one of above two steps [82]. The fact that the ethylbenzene oxidation is first-order reaction for the concentration of ethylbenzene shows that the speed of ethylbenzene oxidation with air is determined by the step of the active high-valence metal–oxygen positive radical intermediate attracting a hydrogen atom of hydrocarbon.

3.6. Effects of temperatures on oxidation yields

The catalyst $[TPPMn]_2O$ was used to study the effects of temperatures on the yields of the ethylbenzene oxidation. The changes of the oxidation yields of ethylbenzene with the changes of the reaction temperatures are listed in Table 4.

Results showed that there existed the optimum temperature for the air oxidation of the ethylbenzene catalyzed by $[TPPMn]_2O$. With the increasing of temperature from 60 to 70 °C, the maximum yields were increasing, but when the temperature increased from 70 to 100 °C, the maximum yield was decreasing continuously. As for the selectivity of the oxidation, the selectivity of α-oxidation products were greater than 99% when the temperature was lower than 90 °C. With the increasing of reaction temperature, the selectivity of α-oxidation products decreased. These proved further that in the reaction system of ethylbenzene oxidation catalyzed by $[TPPMn]_2O$ with air there existed the competing reaction between the self-oxidation of $[TPPMn]_2O$ and the catalysis of $[TPPMn]_2O$. The optimum temperature of $[TPPMn]_2O/O_2$

system is 70 °C, and the optimum temperature of $[TPPMn]_2O/PhIO$ system is 40 °C [84]. This showed that the stability of μ-oxo dimeric manganese porphyrin in $[TPPMn]_2O/O_2$ system is greater than one in $[TPPMn]_2O/PhIO$ system during the catalysis process.

3.7. Effects of reaction temperatures on the reaction rates

The reaction temperatures influence the reaction rates of the ethylbenzene oxidation. Changes of the total yields of acetophenone and α-phenylethanol with reaction time at the different temperatures were shown in Fig. 3. The reaction rates increased with the increase of the reaction temperatures. There was the Arrhenius
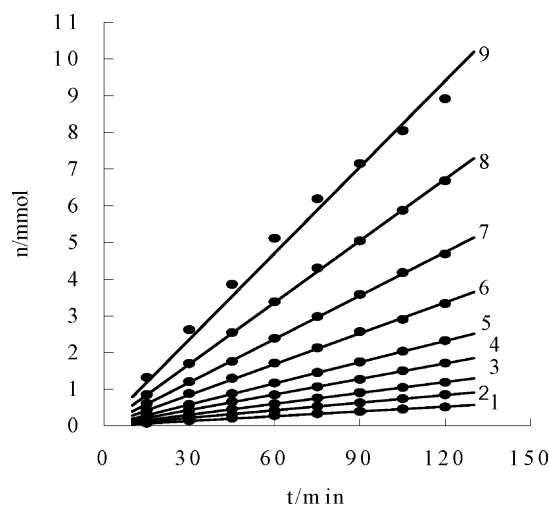
Fig. 3. Influences of the temperatures on the oxidation yields: (1) 333 K; (2) 338 K; (3) 343 K; (4) 348 K; (5) 353 K; (6) 358 K; (7) 363 K; (8) 368 K; (9) 373 K.
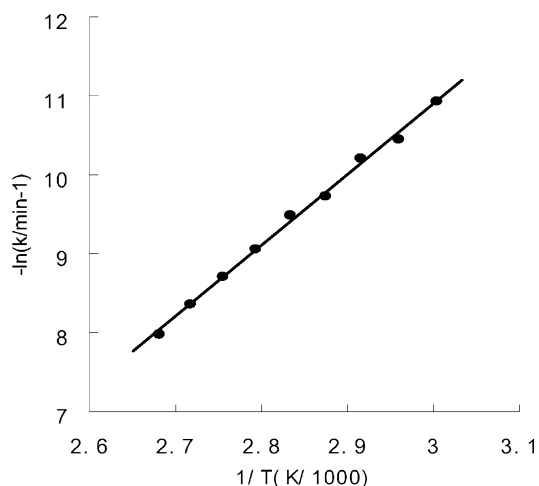
Fig. 4. Relationship between the rate constants and the reaction temperatures.

relationship as indicated in Fig. 4 between the observed rate constant (k) and reaction temperature (T). Its linear coefficient is -0.9978. From Fig. 4, we can obtain the following mathematical equation:

$$\ln k = -8744/T + 15.37$$

Its apparent activation energy is 72.66 kJ/mol.

Acknowledgements

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