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VARIOUS TECHNOLOGIES

Study of Special Catalytic Behaviors of the Metal Porphyrins with Different Central Metal Ions in the Aerobic Oxidation of 4-Nitroethylbenzene to 4-Nitroacetophenone[1]

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Abstract—The special catalytic behaviors of metalloporphyrins with different central metal ions in the oxidation of 4-nitroethylbenzene to 4-nitroacetophenone with molecular oxygen as an oxidant were investigated, including the initiated temperature and catalytic activities of mettalloporphyrins, as well as the selectivity of 4-nitroacetophenone. The 55.3% conversion of 4-nitroethylbenzene and 87.8% selectivity to 4-nitroacetophenone were obtained in the above process with cobalt(II) meso-tetrakis (4-methoxyphenyl) porphyrin as a catalyst at 140°C reaction temperature for 12 h. In particular, when the above process was carried out with zinc(II) meso-tetrakis-(4-methoxyphenyl) porphyrin as a catalyst at the same reaction condition, a predicted intermediate bis(α-methyl-4-nitrobenzyl) peroxide was discovered and selectivity to the compound was realized as 44.0%. In addition, a possible oxidation mechanism of 4-nitroethylbenzene to 4-nitroacetophenone catalyzed by metalloporphyrins was proposed.

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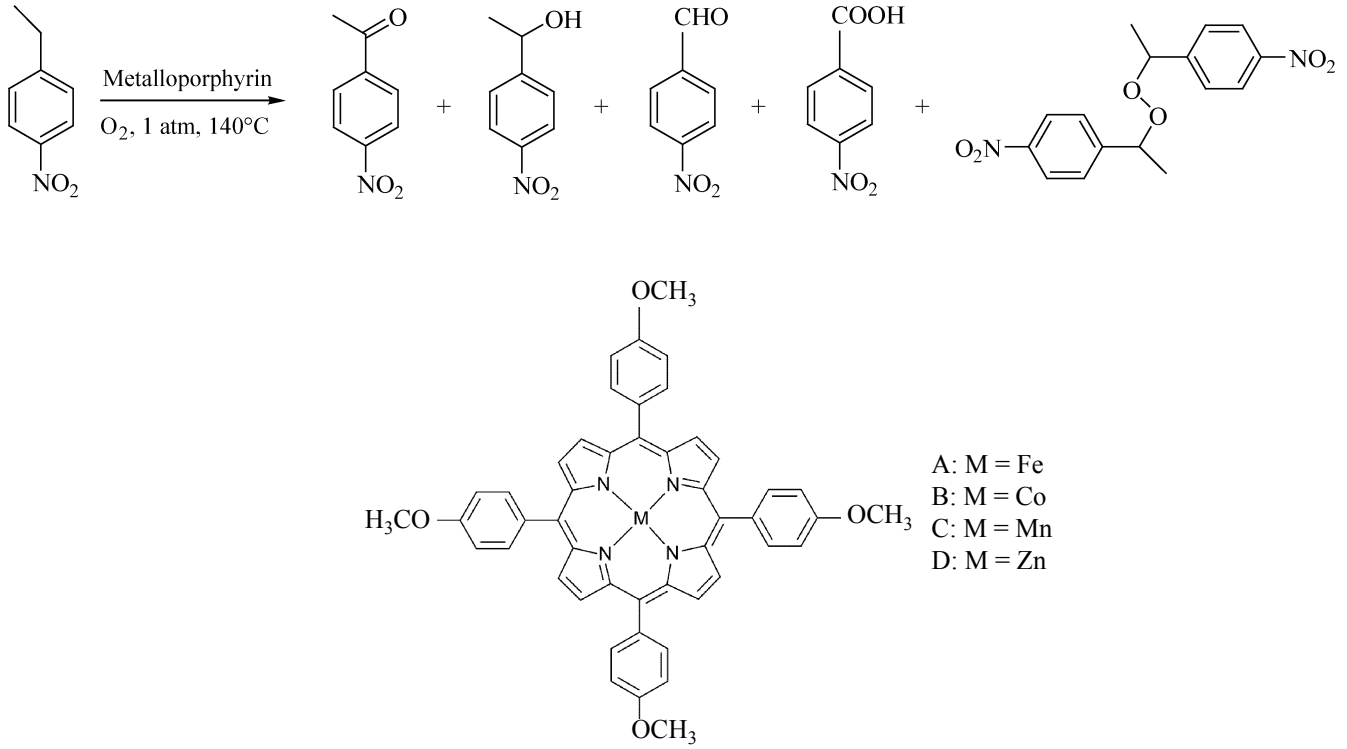
Metalloporphyrins, as the mimics of cytochrome P-450, can activate molecular oxygen to oxidize various organic compounds. Therefore, they have been widely used as the catalysts in the selective oxidation of hydrocarbons [1–7]. 4-Nitroacetophenone (PNAP) is an important organic intermediate with prochirality for the synthesis of pharmaceuticals [8, 9], pesticides [10], and chiral compounds [11, 12]. The aerobic oxidation of 4-nitroethylbenzene (PNEB) is one of the most promising methods for preparing PNAP [13] because the nitro and the acetyl are the second locating groups. Metalloporphyrins would be the effective catalysts in the aerobic oxidation of PNEB. However, the catalytic activities of metalloporphyrins and selectivities of aromatic ketones may be interrelated with the redox electric potential [14–17]. Thus, the catalytic performances of different metalloporphyrins may vary in the oxidation of PNEB.

The free radical autoxidation mechanism of the ethylbenzene catalyzed by iron porphyrins was confirmed by Evans and Smith [18]. In addition, they predicted a minor pathway [Eq. (1)], but was not able to detect it. According to the works [19, 20], this pathway forms peroxide. Moreover, the peroxide was only detected from the decomposition and coupling [Eq. (2)] of the peroxide radicals, instead of the hydrocarbon oxidation. However, nitro substituent as a strong electron-withdrawing group can enhance the stability of the phenylethyl radical

[1] The text was submitted by the authors in English.

Scheme 1. Aerobic oxidation of PNEB catalyzed by metalloporphyrins.



through the *p*-π conjugation. Thus, the Eq. (1) seems to occur when the substrate is PNEB.

$$ROO^{\cdot} + ROO^{\cdot} \rightarrow ROOR + O_2 \quad (1)$$

$$ROO^{\cdot} + R^{\cdot} \rightarrow ROOR + O_2 \quad (2)$$

Accordingly, PNEB was employed as the substrate and four metalloporphyrins were utilized as the catalysts in this study. The specificities of metalloporphyrins were investigated and the peroxide [21] was expected to be found as the oxidation product of PNEB.

EXPERIMENTAL

Aerobic oxidation of PNEB to PNAP was catalyzed by different metalloporphyrins, as represented in Scheme 1. Five products were identified by LC-MS (ESI), GC-MS (EI) or MS (FAB), in which, as the major products, PNAP ($[M + H]^+$: *m/z* 166), PNPE ($[M + H]^+$: *m/z* 168) and PNBA ($[M–H]^-$: *m/z* 166) were detected by LC–MS, while 4-nitrobenzaldehyde (PNBD) (M^+: *m/z* 151) by GC-MS. Further, there appeared a novel substance, bis(α-methyl-4-nitrobenzyl) peroxide (BMNP), which was separated by silica gel column chromatography using ethyl acetate/petroleum ether (80/20) as the eluting solvent and identified with melting point, IR, Raman, ^{1}H NMR, ^{13}C NMR, and FAB-MS.

BMNP: pale yellow solid; mp, °C, 55–56; IR (KBr, cm^{-1}): 2930, 2851, 1522, 1344, 1207, 908 and 856; Raman (KBr, cm^{-1}): 1598, 1334, 1106, 861, 627; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.23 (d, $^3J_{HH}$ = 8.4Hz, 4H), 7.55 (d, $^3J_{HH}$ = 8.4Hz, 4H), 5.18 (q, $^3J_{HH}$ = 6.4Hz, 2H) and 1.48 (d, $^3J_{HH}$ = 6.4Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 20.2, 82.7, 123.8, 127.2, 147.5, 149.5. FAB-MS *m/z*: 333($[M+H]^+$).

All solvents and reagents were AR reagent or chromatography pure reagent unless otherwise stated. PNEB was supplied by Anqin chemical Co., Ltd. of Funing County (purity: 99%). Deionized water was made by PALL PL5241. Catalysts were prepared by ourselves according to the process previously reported [22, 23].

Ultraviolet-visible spectra were obtained on HITACHI U-3010; FT–IR, FT-Raman spectra on Bruker VERTEX 70, Bruker RFS 100/S; ^{1}H and ^{13}C NMR spectra on Bruker Avance 400; and FAB-MS on Thermo Finnigan MAT 90. HPLC analyses were performed by Agilent 1200

Table 1. Initiation temperatures and orbital energy levels of different metalloporphyrins in the oxidation of PNEB[a]

Entry	Catalysts[b]	Initiation temperature[c], ºC	E_{HOMO} of catalyst, eV	E_{LUMO} of catalyst, eV
1	Blank	190	–	–
2	T(*p*-OCH_3)PPCo	190	–3.861	–2.734
3	T(*p*-OCH_3)PPZn	170	–4.435	–2.791
4	T(*p*-OCH_3)PPFe	165	–4.575	–3.060
5	T(*p*-OCH_3)PPMn	155	–4.664	–3.469

[a] Reaction conditions: PNEB (14.1 g, 100 mmol), metalloporphyrins (0.1×10^{-2} mmol), and O_2 bubbling (1 atm). The reactions were initiated at the initiation temperature for 1 min and performed at 140ºC as a reaction temperature for 12 h.

[b] T(p-OCH_3)PPFe: iron(II) meso-tetrakis (4-methoxyphenyl) porphyrin; T(*p*-OCH_3)PPCo: cobalt(II) meso-tetrakis (4-methoxyphenyl) porphyrin; T(*p*-OCH_3)PPMn: manganese(II) meso-tetrakis (4-methoxyphenyl) porphyrin; T(*p*-OCH_3)PPZn: zinc(II) meso-tetrakis (4-methoxyphenyl)-porphyrin.

[c] Initiation temperature: the PNAP could be detected by HPLC when the oxidation reaction is maintained at this temperature for 1 min.

LC, LC-MS (ESI) were made on Bruker esquire 6000, and GC-MS (EI) were completed on Bruker Trace DSQ.

A typical reaction procedure was as follows: 14.1 g (100 mmol) of PNEB and 0.7 mg (1×10^{-3} mmol) of T(*p*-OCH_3)PPCo were loaded in the reactor and oxygen at a rate 40 mL min^{-1} was bubbled through the mixture obtained. The reaction mixture was heated to 190°C and kept at this temperature for 1 min, then it was quickly cooled to 140°C and kept at this temperature for 12 h under stirring with magnetic stirrer. The composition of reaction mixture was analyzed by means of HPLC.

RESULTS AND DISCUSSION

Various manifestations of the initiation temperature in the oxidation of PNEB. The initiation of the reaction is a key step for the PNEB oxidation [24], which is a free radical reaction. Therefore, the initiation temperature was investigated. In addition, the orbital energy levels of the central metal ions in diverse metalloporphyrins were calculated by Dmol3 program [25]. The results were summarized in Table 1.

As shown in Table 1, the initiation temperatures varied with various metalloporphyrins. In comparison with the blank reaction without catalyst (Entry 1), the metalloporphyrins served as the effective catalysts to lower the initiation temperatures, except for cobalt (II) *meso*-tetrakis(4-methoxyphenyl)porphyrin (T(*p*-OCH_3)PPCo). In particular, manganese(II) meso-tetrakis(4-methoxyphenyl)porphyrin (T(*p*-OCH_3)PPMn) lowered the initiation temperature from 190°C to 155ºC (Entry 5). Notably, a positive correlation existed between the initiation temperature and E_{HOMO} or E_{LUMO} of T(*p*-OCH_3)PPFe, T(*p*-OCH_3)PPCo, T(*p*-OCH_3)PPMn and T(*p*-OCH_3)PPZn. Therefore, the lower the E_{HOMO} or E_{LUMO} was, the lower the initiation temperature became (entries 2–5). According to the frontier molecular orbital theory [26], if the E_{HOMO} and E_{LUMO} of the central metal ions in metalloporphyrins are closer to the E_{LUMO} and E_{HOMO} of molecular oxygen (under the same calculated levels, the E_{HOMO} and E_{LUMO} of O_2 are –8.698 and –6.631 eV), the energy needed for the initiation of the reaction decreases. Therefore, the initiation temperature would be lowered.

In addition, the by-products sharply increased when the reaction was conducted above 140°C. Thus, the initiation and reaction temperatures must be controlled precisely to obtain the high yields for products.

Catalytic activities and selectivities of metalloporphyrins in the aerobic oxidation of PNEB to PNAP. The catalytic performances of metalloporphyrins with the different central metal ions were discussed. The results were summarized in Table 2.

As shown in Table 2, the metalloporphyrins work effectively in the oxidation of PNEB compared with the blank experiment (entry 1). Notably, the selectivity for PNAP was substantially increase when the metalloporphyrins used as catalysts. However, the catalytic performances of the metalloporphyrins distinctly exhibited diversities (entries 2–5). This finding suggested that the catalytic activities of metalloporphyrins and selectivities of PNAP depend on the nature of central ions. Based on the results of this study, T(*p*-OCH_3)PPCo has presented

Scheme 2. The possible oxidation mechanism of PNEB to PNAP catalyzed by metalloporphyrins with variable valence metal ions.

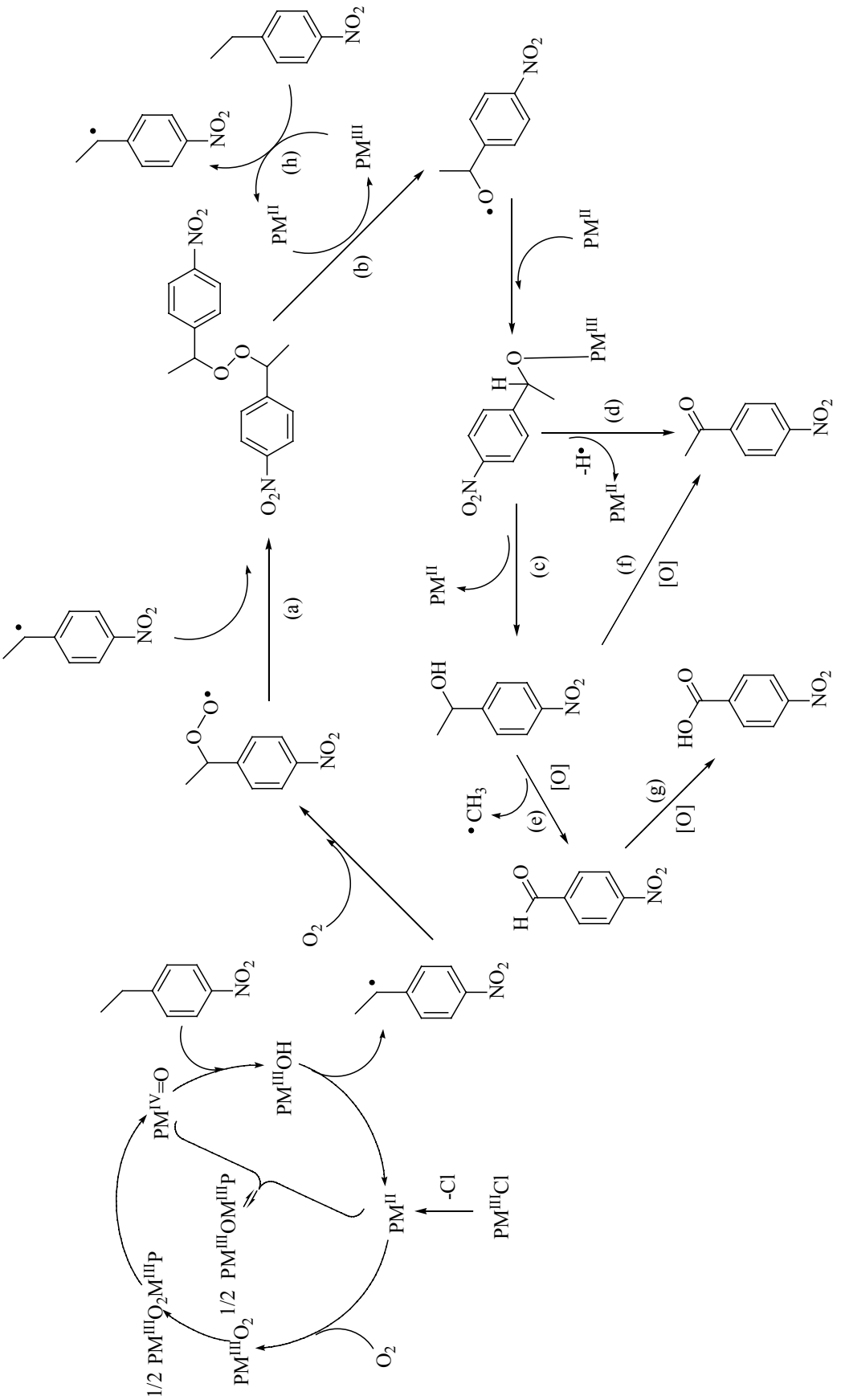


Table 2. Oxidation of PNEB catalyzed by different metalloporphyrins in the presence of molecular oxygen[a]

Entry	Catalysts	Conversion, %	Selectivity for PNAP, %	Selectivity for PNPE[b], %	Selectivity for PNBA, %	Selectivity for BMNP, %	Selectivity for PNBD, %
1	Blank	11.3	52.5	2.9	44.4	0	0.2
2	T(*p*-OCH_3)PPCo	55.3	87.8	5.9	6.3	0	0
3	T(*p*-OCH_3)PPZn	16.2	38.9	10.0	6.9	44.0	0.2
4	T(*p*-OCH_3)PPFe	48.1	80.6	7.8	7.5	2.1	2.0
5	T(*p*-OCH_3)PPMn	53.2	77.8	6.8	8.5	5.7	1.2

[a] Reaction conditions: PNEB (14.1 g, 100 mmol), metalloporphyrins (0.1×10^{-2} mmol), and O_2 bubbling (1 atm). The reactions were initiated at the initiation temperature for 1 min and performed at 140°C as the reaction temperature for 12 h.

[b] PNPE: 1-(4-nitrophenyl) ethanol, PNBA: 4-nitrobenzoic acid, BMNP: bis(α-methyl-4-nitrobenzyl) peroxide, PNBD: 4-nitrobenzaldehyde.

high conversion of PNEB and good selectivity for PNAP, and BMNP cannot be detected (entry 2). As for the T(*p*-OCH_3)PPZn (entry 3), the great volume of BMNP product indicated that BMNP cannot be effectively converted into PNAP with the T(*p*-OCH_3)PPZn as the catalyst. This result suggested that the conversion of BMNP required the variable valence metalloporphyrins[27,28]. According to the above discussion, the specificities of metalloporphyrins functioning as metal ions were remarkable.

Possible oxidation mechanism of PNEB to PNAP catalyzed by the metalloporphyrins with variable valences. Combining the researches of Smith [18], Ba1ci [26], Taylor [28] and their co-workers, a possible oxidation mechanism of PNEB to PNAP catalyzed by the metalloporphyrins with variable valence metal ions has been proposed according to the above results (Scheme 2).

The nitro group as the *para*-substituent of the ethylbenzene enhanced the structural stability of the phenylethyl radical because of conjugative effect. Furthermore, the path (a) was a fast reaction because the hydroperoxide was not observed when PPh_3 was applied to the PNEB oxidation mixture. BMNP was decomposed by metalloporphyrins with variable valence metal ions (PM^{II}) according to Haber–Weiss recycle mechanism [29] [path (b)] to PNAP and PNPE [path (c) and (d)], and then PNPE was oxidized to PNAP and PNBD [path (e) and (f)]. These pathways were further confirmed with the oxidative reaction of BMNP and PNPE as the reactants respectively. In addition, two oxidation reactions of PNEB, which were catalyzed by T(*p*-OCH_3)PPCo or T(*p*-OCH_3)PPZn, were desired and investigated. It was shown that, when oxidation lasted for 3 h, the temperature was reduced from 140 to 25°C, maintained for 1 h, and the again rose to 140°C and maintained for 6 h, reaction in presence of T(*p*-OCH_3)PPZn continued due to the presence of BMNP as the free radical initiator. However, no change was observed in other cases. It means that the oxidation of PNEB at the addition of BNMP can proceed without heating to the initiation temperature.

CONCLUSIONS

In conclusion, the remarkable catalytic specificities of metalloporphyrins, such as catalytic activities and selectivities, in the aerobic oxidation of PNEB were observed, including the effects on the initiation temperatures and diverse selectivities for different products. The initiation temperature was low when T(*p*-OCH_3)PPMn was used as the catalyst, whereas it was the highest when the oxidation of PNEB was catalyzed by T(*p*-OCH_3)PPCo. However, T(*p*-OCH_3)PPCo was demonstrated to have a reasonable catalytic activity for the oxidation of PNEB (55.3%) and a high selectivity for PNAP (87.8%). In particular, bis(α-methyl-4-nitrobenzyl)peroxide (BMNP) as a predicted intermediate was produced at 44.0% selectivity in the oxidation of PNEB with T(*p*-OCH_3)PPZn as the catalyst. Finally, the radical mechanism of the above reaction was proposed and confirmed for this oxidation process.

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