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Highly efficient controllable oxidation of alcohols to aldehydes and acids with sodium periodate catalyzed by water-soluble metalloporphyrins as biomimetic catalyst

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ABSTRACT

Highly efficient controllable oxidation of alcohols to aldehydes or acids by sodium periodate in the presence of water-soluble manganese porphyrins (*meso*-tetrakis(*N*-ethylpyridinium-4-yl)manganese porphyrin, MnTEPyP) with different reaction media has been reported. The manganese porphyrin showed excellent activity for the controllable oxidation of various alcohols under mild conditions. Moreover, different factors influencing alcohol oxidation, for example, oxidant, catalyst amount, temperature, and solvent, have been investigated. A plausible mechanism for the controllable oxidation of alcohol has been proposed.

1. Introduction

Selective catalytic oxidation of alcohols to corresponding aldehydes or acids is of great importance for both laboratory and synthetic industrial applications.[1] As model catalysts of cytochrome P-450, metalloporphyrins could be used as intermediate of oxygen carriers for biological systems. Metalloporphyrins have been widely used as catalysts for various biomimetic oxidation reactions as well.[2] Oxidation of alcohols catalyzed by metalloporphyrins has been well investigated with PhIO,[3] Cl_2PyNO,[4] *t*-BuOOH,[5] and *m*-chloroperbenzoic acid[6] used as oxidants. In general, these oxidations were performed with organic solvents as reaction media.[7]

The development of green chemical processes has become one of the most important tasks for chemical researchers to date.[8] To reduce or eliminate emission of volatile organic compounds to the environment, the possibility of using water as solvent for organic reactions has gathered much attention. Taking the form of biomimetic compounds, water-soluble metalloporphyrins have good solubility in water due to the presence of hydrophilic groups. These compounds could be employed to simulate catalytic performance of enzymes in water. Accordingly, water-soluble metalloporphyrins-catalyzed oxidations have been developed in water or mixtures of water with organic solvents.[9] However, only few investigations on water-soluble metalloporphyrins-catalyzed oxidation of alcohols have been reported. Fu and co-workers reported the oxidation of a broad range of alcohol substrates by (TSPP)Rh^{III} in water using molecular oxygen as the terminal oxidant.[10] Fabbri et al. reported the oxidation of a series of α-alkyl-substituted mono and dimethoxylated benzyl alcohols catalyzed by FeTMPyPCl and FeTSPPCl with selectivity up to 49% in aqueous solutions.[11] Wietzerbin reported the catalytic oxidation of tertiary alcohols in water-soluble Mn-TMPyP/$KHSO_5$ systems, but many products were obtained with poor selectivity.[12]

Subsequently, as a part of our studies on metalloporphyrins-catalyzed oxidations,[13] a controllable oxidation procedure for alcohols for corresponding acids or aldehydes catalyzed by water-soluble metalloporphyrins (MnTEPyP), has been developed (Scheme 1). Various alcohols were oxidized readily and controllably to obtain the corresponding products under mild conditions. Furthermore, high-valent oxo intermediate was verified by UV–vis spectroscopy in the oxidation of benzyl alcohol. Finally, a plausible mechanism was proposed.

2. Experimental

2.1. Materials and instruments

Alcohols were of analytical grade and purchased from Alfa Aesar or Aldrich without further purification unless indicated. Other solvents were all of analytical grade.

UV–vis spectra were recorded on a Shimadzu UV-2450 UV–vis spectrophotometer. Mass spectra were obtained on a Shimadzu LCMS-2010A.

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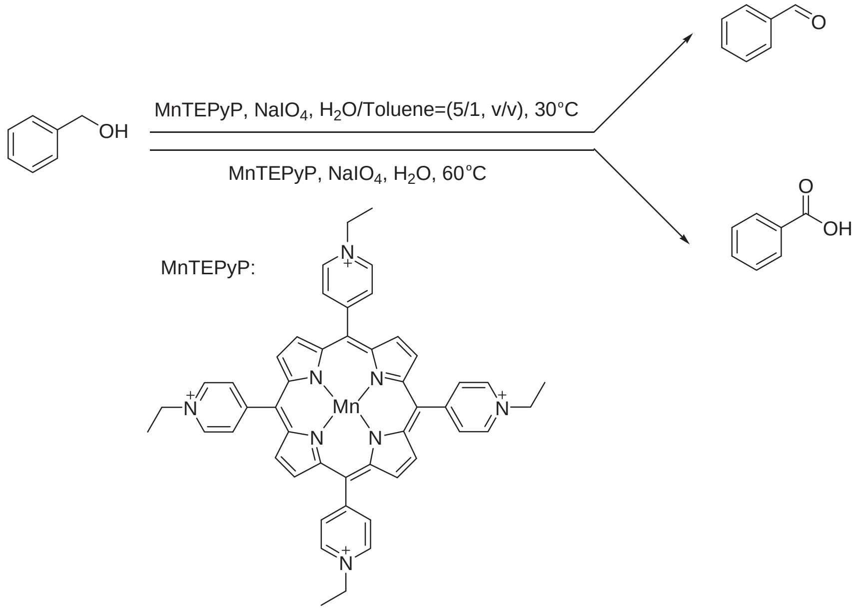


Scheme 1. Controllable oxidation of alcohols to acids or aldehydes catalyzed by MnTEPyP.

2.2. Synthesis of *meso*-tetrakis (*N*-ethylpyridinium-4-yl) manganese porphyrin

meso-Tetrakis(4-pyridyl) porphyrin (TPyP) was prepared according to reported works.[14] MnTPyP (0.15 g, 0.221 mmol) and fresh distilled iodoethane (0.62 mg, 4 mmol) were added to 20 mL dimethylformamide solution. The mixture was stirred for 4 h at 45 °C, and the solution was cooled to room temperature. Next, 20 mL ethyl ether was added, and the mixture was kept overnight. After filtration, the filter cake was washed thoroughly with ethyl ether and recrystallized with water/acetone (1:2) to obtain 0.189 g (71.4%) $[\text{MnTEPyP}]^{4+}$. EI-MS: *m/z* 787. UV–vis (H_2O): λ_{max}, nm (log ε) 464 (2.48), 559 (1.25), 675 (0.87), 769 (0.54). Anal. calcd for $[\text{MnTEPyP}]^{4+}$: C, 44.50; H, 3.42; N, 8.65. Found: C, 44.67; H, 3.51; N, 8.49.

2.3. General procedures for oxidation of alcohol to acid

Water (5 mL), benzyl alcohol (0.5 mmol), MnTEPyP (0.5×10^{-2} mmol), and $NaIO_4$ (2 mmol) were mixed at 60 °C while stirring for 4 h. Then, the aqueous solution was extracted with ethyl acetate (3 × 5 mL). Naphthalene (0.05 g) was added as internal standard. The consumption of alcohols and formation of oxidized products were monitored by gas chromatography (GC) (Shimadzu GC-14C) with a packed column and GC–mass spectrometry (MS) (Shimadzu GCMS-QP2010 plus) equipped with Rtx-5MS capillary column.

2.4. General procedures for oxidation of alcohol to aldehyde

Water (5 mL), toluene (1 mL), benzyl alcohol (0.5 mmol), MnTEPyP (0.5×10^{-2} mmol), and $NaIO_4$ (2 mmol) were mixed at 30 °C while stirring for 1.5 h. Then, the aqueous solution was extracted with ethyl acetate (3 × 5 mL). Naphthalene (0.05 g) was added as internal standard. The consumption of alcohols and formation of oxidized products were monitored by GC (Shimadzu GC-14C) with a packed column and GC–MS (Shimadzu GCMS-QP2010 plus) equipped with Rtx-5MS capillary column.

3. Results and discussion

3.1. Effect of oxidant on the oxidation of alcohol to acid

Various oxidants were tested as oxygen resource for the metalloporphyrins-catalyzed aqueous oxidation of benzyl alcohol. The results are summarized in Table 1. Sodium periodate was more effective compared with O_2, *t*-BuOOH, H_2O_2, $NaIO_3$, and NaClO for the oxidation catalyzed by MnTEPyP in water. Although high conversion for benzyl alcohol could be obtained by using NaClO as oxidant, the oxidation system showed unsatisfactory selectivity for benzoic acid (entry 4). Compared with sodium periodate, sodium iodate presented poor activity (entry 5), indicating that IO_4^- ion is crucial for oxidation.[15]

The effects of sodium periodate contents on the catalytic oxidation of benzyl alcohol were also examined. It seemed that the conversion of benzyl alcohol and the selectivity of benzoic acid increased with increase in sodium periodate contents (entries 6 and 7). However, no significant difference was observed when the molar ratio of sodium periodate to substrate was over **4** for the sodium periodate oxidation system (entries 6–8).

Table 1
Effect of oxidant on the aqueous oxidation of benzyl alcohol catalyzed by MnTEPyP[a]

Entry	Oxidant	Conversion (%)	Yield (%)
1	O_2	1	1
2	H_2O_2	6	6
3	*t*-BuOOH	47	38
4	NaClO	90	75
5	$NaIO_3$	16	16
6[b]	$NaIO_4$	84	55
7	$NaIO_4$	100	94
8[c]	$NaIO_4$	100	95

[a] Benzyl alcohol (0.5 mmol), MnTEPyP (0.5×10^{-2} mmol), oxidant (2 mmol), H_2O (5 mL), 4 h, 60 °C.

[b] $NaIO_4$ (1 mmol).

[c] $NaIO_4$ (3 mmol).

3.2. Effect of catalyst contents on the oxidation of alcohol to acid

The effects of MnTEPyP contents on the oxidation of benzyl alcohol by sodium periodate were investigated. The results are summarized in Table 2.

As shown in Table 2, the reaction cannot take place in the absence of a catalyst, indicating that MnTEPyP is crucial in oxidation reaction (entry 1). When the molar ratio of catalyst to substrate was 1/1000, only 33% of benzyl alcohol could be converted, as the reaction continued for 4 h (entry 6). As depicted clearly in Table 2, the reaction rate and conversion increases with increasing catalyst contents. Benzyl alcohol could be converted completely when the molar ratio of the catalyst to substrate was 1/100 (entry 2), in which the yield for benzoic acid could reach 94%. Therefore, the optimal molar ratio of water-soluble metalloporphyrins to substrate for the aqueous oxidation of benzyl alcohol to benzoic acid was 1/100.

In addition, compared with other manganese cationic salts, water-soluble metalloporphyrins were proven to have the significant unique properties required in the selective oxidation of alcohols. Only 9% of benzyl alcohol could be converted when the catalyst was replaced to manganese(II) acetate tetrahydrate with the same catalytic amount as water-soluble metalloporphyrins, and the product was benzaldehyde (entry 7).

3.3. Effect of temperature on the oxidation of alcohol to acid

The effect of reaction temperature on the oxidation of benzyl alcohol to benzoic acid catalyzed by MnTEPyP was also investigated. Results are shown in Table 3.

From Table 3, it seemed that the conversion of benzyl alcohol was minimally influenced by reaction temperature. The conversion increased slightly with rising temperature from 30 to 60 °C and remained unchanged at temperature over 60 °C. Meanwhile, the selectivity for benzoic acid was closely related to reaction temperature. The selectivity for benzoic acid increased from 68% to 94% while temperature rose from 30 to 60 °C, and no obvious increase was observed at temperature over 60 °C. Therefore, the optimal reaction temperature for the oxidation of benzyl alcohol to benzoic acid was 60 °C.

3.4. Effect of axial ligands on the oxidation of alcohol to acid

The presence of axial ligands can improve the catalytic performance of catalysts by facilitating the formation and stabilization of the proposed high-valence metalloporphyrin intermediate.[16] The effect of different axial ligands on the oxidation rate of benzyl alcohol was investigated. As shown in Table 4, no significant differences for the conversion of benzyl alcohol can be found with or without axial ligands. However, the presence of axial ligands slightly and positively affected the selectivity of benzoic acid (entries 1–4). Oxidations were carried out in the absence of axial ligands in subsequent testing.

Table 2
Effect of MnTEPyP contents on the oxidation of benzyl alcohol[a]

Entry	Catalyst/substrate (molar ratio)	Conversion (%)	Yield of benzoic acid (%)
1	0	0	0
2	1:100	100	94
3	1:300	51	33
4	1:500	40	27
5	1:800	37	28
6	1:1000	33	27
7[b]	1:100	8	8

[a] Benzyl alcohol (0.5 mmol), $NaIO_4$ (2 mmol), catalyst (MnTEPyP), H_2O (5 mL), 4 h, 60 °C.

[b] The catalyst was manganese(II) acetate tetrahydrate. The product was benzaldehyde.

Table 3
Effect of temperature on benzyl alcohol oxidation catalyzed by MnTEPyP[a]

Entry	T (°C)	Conversion (%)	Yield (%)
1	30	94	68
2	40	96	77
3	50	95	85
4	60	100	94
5	70	100	95

[a] Benzyl alcohol (0.5 mmol), MnTEPyP (0.5×10^{-2} mmol), $NaIO_4$ (2 mmol), H_2O (5 mL), 4 h.

Table 4
Effect of different axial ligands on the oxidation of benzyl alcohol catalyzed by MnTEPyP[a]

Entry	Axial ligand	Conversion (%)	Yield (%)
1	NH_4Ac	100	97
2	Imidazole	100	99
3	Pyridine	100	99
4	*N*-Methylimidazole	100	99
5	No axial base	100	94

[a] Benzyl alcohol (0.5 mmol), MnTEPyP (0.5×10^{-2} mmol), axial ligand (0.03 mmol), $NaIO_4$ (2 mmol), H_2O (5 mL), 4 h, 60 °C.

3.5. Controllable oxidation of benzyl alcohol to benzyaldehyde

The profiles for oxidation of benzyl alcohol by sodium periodate in the presence of MnTEPyP are shown in Figure 1, demonstrating that reaction proceeds via two steps: (1) oxidation of benzyl alcohol to benzyaldehyde and (2) oxidation of benzyaldehyde to benzoic acid. Benzyaldehyde was used as the reaction intermediate.

Similar to the reaction intermediate during the oxidation process, benzyaldehyde showed solubility that much lower than that of benzyl alcohol in water. If organic solvents were added onto the reaction mixture, benzyaldehyde might be enriched in the organic phase. If the reaction intermediate could be selectively distributed onto the reaction media, the reaction process would be influenced to some extent, and the selectivity of product would be adjusted. Based on these considerations, non-polar organic solvents like toluene (1 mL) was chosen. The mixture was stirred at

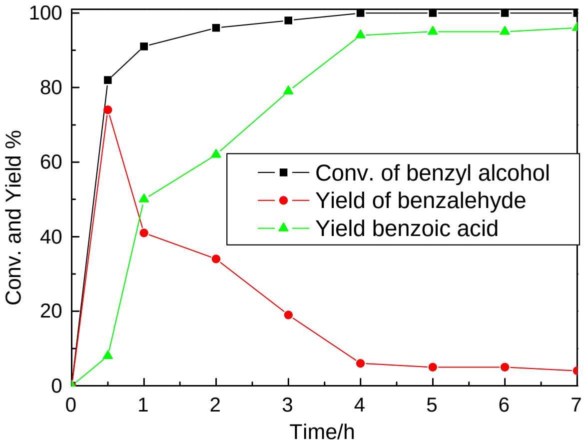


Figure 1. Reaction profile for the oxidation of benzyl alcohol by sodium periodate in the presence of MnTEPyP. Benzyl alcohol (0.5 mmol), MnTEPyP (0.5×10^{-2} mmol), $NaIO_4$ (2 mmol), H_2O (5 mL), 60 °C.

30 °C for 1.5 h. Surprisingly, the selectivity for benzaldehyde soared to 97%.

Catalytic oxidations with the addition of different organic solvents were well investigated. The solvents used included polar and non-polar organic solvents with different dielectric constants. The results are summarized in Table 5.

Results showed that the oxidation of benzyl alcohol in 1:5 (v/v) mixture of C_7H_8/H_2O resulted in benzaldehyde. The selectivity of benzaldehyde also decreased with the increase in polarity of the organic solvent. When the reaction was carried out in water, the main product was benzoic acid and the yield for benzaldehyde was only 33%. The increasing selectivity for benzaldehyde in non-polar solvents attributable to the solubility of benzaldehyde in non-polar solvent is much higher compared with those in polar solvents. In addition, by adding non-polar solvent onto the system, the formed benzaldehyde could be removed from the aqueous phase, resulting in the increase in selectivity for benzaldehyde.

Benzaldehyde or benzyl alcohol could be obtained from the oxidation of toluene by molecular oxygen in the presence of metalloporphyrin under high pressure.[17] For the present system, no benzaldehyde or benzyl alcohol could be detected by GC–MS (entry 8) in the absence of benzyl alcohol, indicating that toluene could not be oxidized in the present work. Nevertheless, in the present protocol, the oxidation of benzyl alcohol could be well controlled to obtain benzaldehyde with excellent selectivity under mild conditions.

In the reaction system adopted in this study, two phases (aqueous and organic) were employed. The catalyst and $NaIO_4$ were dissolved in the aqueous phase. The solubility of benzaldehyde in water was much lower compared with those in toluene. Therefore, benzaldehyde could be removed easily from the aqueous system and then protected from over-oxidation to benzoic acid when benzyl alcohol was oxidized to benzaldehyde. The oxidant was also dissolved in aqueous phase, and benzaldehyde could not be transferred to the benzoic acid in the organic phase due to the absence of oxidant. From the viewpoint of mass transfer, the presence of the organic solvent is favorable for benzaldehyde when diffusing into the organic phase.[18] The process for controllable oxidation of benzyl alcohol to benzaldehyde or benzoic acid is shown in Figure 2.

Table 5

Effect of organic solvent on the selectivity of benzaldehyde in the oxidation of benzyl alcohol catalyzed by MnTEPyP[a]

Entry	Solvent	Conversion (%)	Yield (%)	Selectivity (%)
1	C_7H_8/H_2O	98	97	99
2	$CHCl_3/H_2O$	64	63	98
3	CH_2Cl_2/H_2O	98	89	91
4	$(CH_3)_2CHOH/H_2O$	92	41	45
5	CH_3CN/H_2O	79	34	43
6	H_2O	99	33	33
7[b]	C_7H_8/H_2O	–	–	–

[a] Benzyl alcohol (0.5 mmol), MnTEPyP (0.5 × 10^{-2} mmol), $NaIO_4$ (2 mmol), 1.5 h, 30 °C, solvent/H_2O = 5/1 (v/v).

[b] No substrate was added.

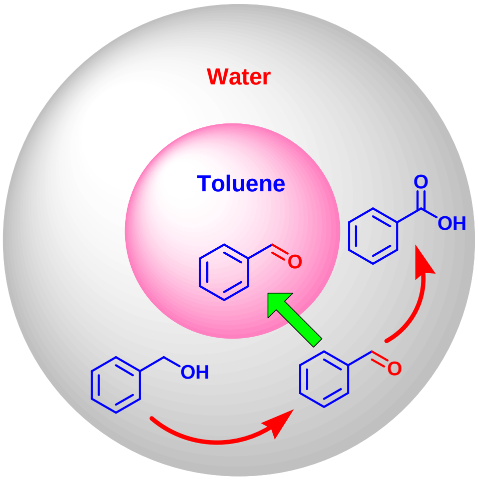
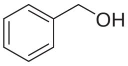
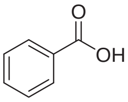
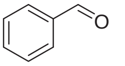
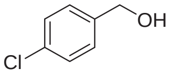
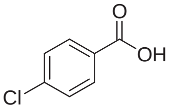
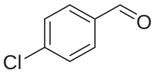
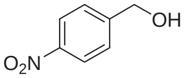
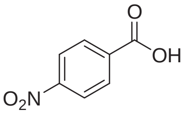
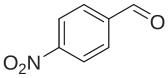
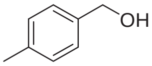
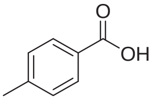
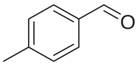
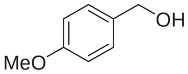
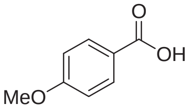
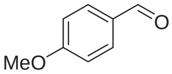
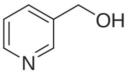
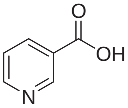
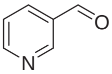
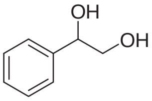
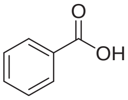
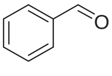


Figure 2. The schematic of controllable oxidation of benzyl alcohol to benzaldehyde or benzoic acid catalyzed by MnTEPyP.

Table 6

Controllable oxidation of alcohols to acids and aldehydes catalyzed by MnTEPyP

Entry	Substrate	Product	
		Acid[a]	Aldehyde[b]
1		 (4h, 98%) (4 h, 98%)	 (1.5h, 97%) (1.5 h, 97%)
2		 (4h, 94%) (4 h, 94%)	 (2h, 94%) (2 h, 94%)
3		 (4h, 50%) (4 h, 50%)	 (1h, 96%) (1 h, 96%)
4		 (4h, 96%) (4 h, 96%)	 (2h, 93%) (2 h, 93%)
5		 (4h, 98%) (4 h, 98%)	 (2h, 84%) (2 h, 84%)
6		 (4h, 50%) (4 h, 50%)	 (3h, 27%) (3 h, 27%)
7		 (4h, 96%) (4 h, 96%)	 (0.5h, 97%) (0.5 h, 97%)

[a] Alcohol (0.5 mmol), MnTEPyP (0.5 × 10^{-2} mmol), $NaIO_4$ (2 mmol), H_2O (5 mL), 60 °C. The values in parentheses are reaction time and yield.

[b] Alcohol (0.5 mmol), MnTEPyP (0.5 × 10^{-2} mmol), $NaIO_4$ (2 mmol), H_2O (5 mL), toluene (1 mL), 30 °C. The values in parentheses are reaction time and yield.

3.6. Controllable oxidation of various alcohols to aldehydes and acids

To evaluate the scope of the controllable oxidation, various aromatic alcohols were subjected to the reaction system catalyzed by MnTEPyP. The results are summarized in Table 6.

As shown in Table 6, most aromatic alcohols can be smoothly converted to the corresponding acids or aldehydes in high yields except 4-pyridinemethanol (entry 6). It seemed that catalytic efficiency was not affected by the electronic property of substrates with electron-donating groups (entries 4 and 5). However, for the substrate with strong electron-withdrawing group, such as 4-nitrobenzyl alcohol, the catalytic system seemed favorable for oxidation to aldehyde (entry 3). The catalytic system also exhibited high activity for the oxidation of diols like 1-phenyl-1, 2-ethanediol (entry 7). The main products, benzaldehyde and benzoic acid, were obtained from the oxidative cleavage of C–C bonds. Diols that could be cleaved to the corresponding aldehydes were also reported in previous works with ruthenium porphyrins used as catalyst.[7a]

3.7. Plausible mechanism for controllable oxidation of benzyl alcohol

In the blank experiments without catalyst, no products could be detected for the oxidation of benzyl alcohol even if they were conducted in either water or 1:5 mixture of toluene/water. Results clearly suggest that manganese porphyrin is crucial for the oxidation of benzyl alcohol. High-valent porphyrin intermediate is generally accepted as the active species for metalloporphyrins-catalyzed oxidations. The presence of manganese-oxo porphyrin was confirmed by in situ UV–vis spectra for the oxidation of benzyl alcohol (Fig. 3).

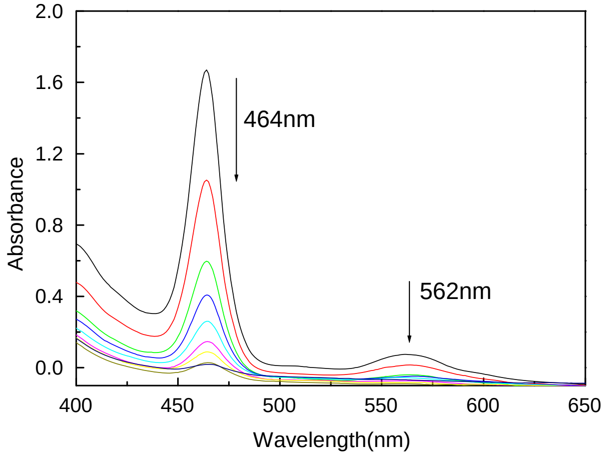


Figure 3. In situ UV–vis spectra of manganese porphyrin in the solution of benzyl alcohol oxidation in the presence of sodium periodate (time scan: 5 min). Benzyl alcohol (0.5 mmol), $NaIO_4$ (2 mmol), MnTEPyP (0.5×10^{-2} mmol), H_2O, 60 °C.

In Figure 3, the initial characteristic absorption peaks of MnTEPyP were at 464 and 562 nm. After adding sodium periodate and benzyl alcohol onto the reaction system, in situ determination revealed that the characteristic absorption peak of MnTEPyP weakened gradually, suggesting the consumption of oxidant active species ($Mn^{IV}{=}O$) by substrate.[19] In addition, color changes of the reaction mixture from dark green to tinge also indicate valence change of manganese. GC analysis of these reaction products revealed the formation of benzoic acid and benzyaldehyde, indicative of the presence of active oxidation species.

Based on these presented observations, a plausible reaction mechanism for the oxidation of benzyl alcohol using water-soluble manganese porphyrin (MnTEPyP) as catalyst was proposed (Fig. 4). The reaction mechanism could involve the use of oxo-manganese intermediate generated from the reaction between manganese porphyrin and sodium periodate. The formation of benzaldehyde was attributed to the reaction of benzyl alcohol with Mn-oxo species, followed by the β-hydride elimination.[10] Benzoic acid was generated by the further reaction of benzaldehyde to Mn-oxo species.

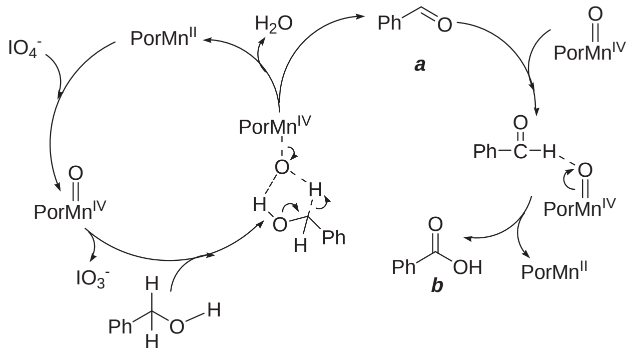


Figure 4. Plausible reaction mechanism for the oxidation of benzyl alcohol by sodium periodate in the presence of MnTEPyP.

4. Conclusion

A controllable procedure for selective oxidation of alcohols to acids or aldehydes has been developed in the presence of water-soluble manganese porphyrin and sodium periodate with different reaction media. A plausible reaction mechanism involved the formation of Mn-oxo species has been proposed.

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