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The effect of TEMPO in the hydroxylation of benzene to phenol on the $[(CH_3)_4N]_4PMo_{11}VO_{40}$/ascorbic acid/TEMPO/$O_2$ catalytic system: Formation of ascorbic acid radicals through hydrogen exchange of ascorbic acid and TEMPO

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ABSTRACT

Hydroxylation of benzene to phenol in the $[(CH_3)_4N]_4PMo_{11}VO_{40}$/ascorbic acid/TEMPO/$O_2$ catalytic system was carefully investigated. UV–vis, ESR and ^{1}H NMR studies showed ascorbic acid radicals were formed through the hydrogen exchange of ascorbic acid with TEMPO (2,2,6,6-tetramethyl-1-piperidine-N-oxyl radicals) during the reaction. In acetonitrile, the ascorbic acid would be partly oxidized to 2-hydroxy-2-buten-4-olide (α-tetronic acid, isotetronic acid, compound **1**) without TEMPO. The interaction of TEMPO and ascorbic acid restrained the oxidative dissociation of ascorbic acid and promoted the rate of the hydroxylation. Aqueous acetic acid solvent can also restrain the oxidative dissociation of ascorbic acid. In aqueous acetic acid, the yield of phenol could reach 18.9% in the $[(CH_3)_4N]_4PMo_{11}VO_{40}$/ascorbic acid/TEMPO/$O_2$ catalytic system with sufficient ascorbic acid after 400 min.

1. Introduction

Phenol is an important chemical material in producing phenol resins, bisphenol-A, dyes, antioxidation agents and pharmaceuticals [1–5]. The traditional method is the cumene process [6] which accounts for above 90% phenol production in the world. The cumene process is restricted by the co-product acetone, and causes a lot of environmental problems. Many new methods for hydroxylation of benzene to phenol have been developed in recent decades [7,8]. Among them the direct hydroxylation of benzene to phenol by molecular oxygen is preferred. In 1954, Udenfriend and co-workers first suggested an ideal oxidation system in which oxygen could be used as the oxidant in the oxidation of aromatic hydrocarbon [9,10]. In this process, ascorbic acid was used as the co-reductant, Fe^{2+}-EDTA as the catalyst, and the reaction vessel charged with oxygen as the oxidant. Since that time, various types of catalytic hydroxylation processes containing Cu [11,12], Pd [13–17], Pt [18,19] or Re [20,21] have appeared in the literature. In 1987, Orita [11] used CuCl as the catalyst and ascorbic acid as the co-reductant, and the phenol yield was 0.23%. In 1995 Tsuruya [12] used zeolites loaded with Cu as a catalyst, with a phenol yield of 1.69%. V-based catalysts [22–26] cooperating with ascorbic acid had been widely investigated and achieved good phenol yield. Tsuruya and co-workers [24] used $CsPMoV_2$ as the catalyst, aqueous acetic acid as the solvent, and the yield of phenol reached 7.2% after 1440 min. Later, Wang et al. [26] used $Py_3PMo_{10}V_2O_{40}$ as catalyst, aqueous acetic acid as the solvent, and the yield of phenol reached 11.5% after 600 min. However, most of the catalytic systems involving oxygen and ascorbic acid have a low rate of hydroxylation.

In our previous work [27], it was discovered that TEMPO can improve the rate of the hydroxylation in $[(CH_3)_4N]_4PMo_{11}VO_{40}$/ascorbic acid/$O_2$ catalytic system, but the real role of TEMPO was not very clear. In the present work, hydroxylation of benzene to phenol in the $[(CH_3)_4N]_4PMo_{11}VO_{40}$/ascorbic acid/TEMPO/$O_2$ catalytic system was carefully investigated.

2. Experimental

2.1. Catalyst preparation

$H_4PMo_{11}VO_{40}$ was prepared according to reference with minor modifications [28]. 7.16 g (20 mmol) of $Na_2HPO_4{\cdot}12H_2O$ and 3.16 g (20 mmol) of $NaVO_3{\cdot}2H_2O$ were dissolved in 80 mL of water at room temperature. 2 mL of concentrated H_2SO_4 was added and

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the mixture was acidified to a red color, 53.2 g (220 mmol) of $Na_2MoO_4{\cdot}2H_2O$ was dissolved in 80 mL of water, then added to this mixture. 34 mL of concentrated H_2SO_4 was added to the solution. After vigorous stirring of the mixture for 1 h, 160 mL of ethyl ether was added to extract the heteropoly acid. $H_4PMo_{11}VO_{40}$ was identified by IR spectra (see in Fig. S1). $[(CH_3)_4N]_4PMoV_{11}O_{40}$ was prepared by adding $H_4PMo_{11}VO_{40}$ into the solution of four equivalents of $(CH_3)_4NOH$ and characterized by IR (Fig. S1), elemental analysis (C/H/N was 4.05/11.76/1.00), ICP (P/Mo/V was 1.00/11.2/1.01), ^{31}P MAS NMR (Fig. S2), and XRD (Fig. S3) [29].

2.2. The hydroxylation of benzene

The hydroxylation of benzene was carried out in a stainless steel reactor equipped with a 40 mL PTFE liner. In a typical reaction, 0.105 g (0.05 mmol) of catalyst $[(CH_3)_4N]_4PMo_{11}VO_{40}$, 0.78 g (10 mmol) of benzene, 0.156 g (1 mmol) of TEMPO, 0.9 g (5 mmol) of ascorbic acid were added into 6.8 mL of acetonitrile or 50% aqueous acetic acid. The reactor was pressurized with O_2 to 2.0 MPa and put into a water bath at 80 °C for 80 min. A magnetic stirrer was used during the process. After reaction, 1,4-dioxane was added as an internal standard.

2.3. Materials and characterization

$Na_2HPO_4{\cdot}12H_2O$ (99%, Tianjin Kermel Chemical Reagent Co., Ltd.), $Na_2MoO_4{\cdot}2H_2O$ (99%, Tianjin Kermel Chemical Reagent Co., Ltd.), $NaVO_3{\cdot}2H_2O$ (98%, Tianjin Kermel Chemical Reagent Co., Ltd.), $(CH_3)_4NOH$ (97%, Aladdin Chemistry Co., Ltd.), benzene (99.5%, Beijing Chemical Works), acetic acid (99.5%, Guangdong Guanghua Chemical Factory Co., Ltd.), acetonitrile (99.5%, Beijing Chemical Works), ascorbic acid (99.7%, Tianjin Kermel Chemical Reagent Co., Ltd.) and TEMPO (98%, Aladdin Chemistry Co., Ltd.) were of analytical grade and were used as received without further purification.

The GC of the samples was analyzed by a GC-Agilent 7890 series instrument equipped with a capillary column (Agilent, SE-30) and a flame ionization detector (FID).

The GC–MS of the samples was analyzed by a Shimadzu-15 A GC–MS equipped with a capillary column (GL Sciences, TC-FFAP) and a flame ionization detector (FID).

The UV–vis spectra of the samples were recorded on a Shimadzu-2550 UV–vis spectrophotometer. Quartz sample cells were of 10-mm path length. The backgrounds of UV–vis spectra were subtracted using only solvent (acetonitrile) as a reference sample. The samples were recorded at ambient temperature.

The ESR spectra of the samples were recorded on a JEOL ES-ED3X spectrometer at X-band at ambient temperature.

The ^1H NMR spectra of each sample were recorded on a Bruker DPX 400 MHz type spectrometer at ambient temperature in DMSO-d6 using TMS as an internal standard with reference shift at 0 ppm.

3. Results and discussion

3.1. Oxygen uptake in different reaction conditions

The oxygen uptakes under different reaction conditions were firstly investigated (Fig. 1). Without catalyst and TEMPO, the oxygen pressure variation was almost negligible (Fig. 1, curve a), showing that the reaction between ascorbic acid and oxygen was slow.

With the addition of catalyst, it can be seen that the oxygen uptake was slightly increased in the initial 40 min (Fig. 1, curve b). It was confirmed that catalyst slightly accelerated the oxygen uptake in the reaction in the initial 40 min. Beyond 40 min, acceleration by the catalyst was more obvious.

After TEMPO was added in the reaction (Fig. 1, curve c), there was a drastic increase in oxygen uptake in the first 10 min. This

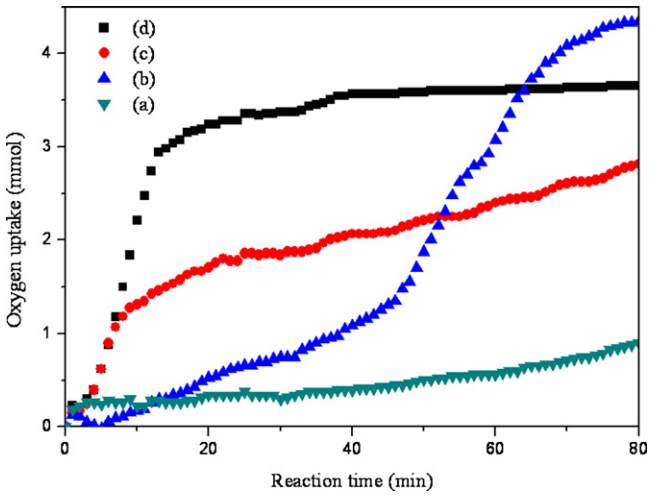
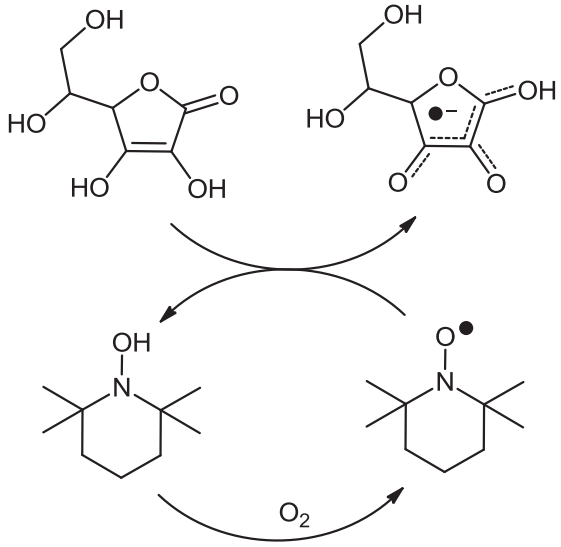


Fig. 1. Oxygen uptake in different reaction conditions. *Reaction conditions*: Ascorbic acid 0.9 g (5 mmol), benzene 0.78 g (10 mmol), acetonitrile 6.8 mL, 80 °C, initial pressure of 0.8 MPa O_2. (a) No $[(CH_3)_4N]_4PMo_{11}VO_{40}$ and TEMPO, (b) $[(CH_3)_4N]_4PMo_{11}VO_{40}$ 0.105 g (0.05 mmol), (c) TEMPO 0.156 g (1 mmol), and (d) $[(CH_3)_4N]_4PMo_{11}VO_{40}$ 0.105 g (0.05 mmol), TEMPO 0.156 g (1 mmol).

indicated that TEMPO accelerated the uptake of oxygen in the reaction. It was reported that ascorbate could react quickly with TEMPO [30,31] with the loss of a proton and an electron [32], generating ascorbic acid radicals and TEMPOH. We supposed that the reaction between ascorbic acid and TEMPO is a similar process (proved in Section 3.2). It was probable that the drastic increase of oxygen was caused by the reaction between ascorbic acid radicals and oxygen, and the reoxidation of TEMPOH. We used GC to follow the interaction of TEMPO, ascorbic acid and oxygen: after TEMPO and ascorbic acid (1:5 molar ratio) was mixed, TEMPO was detected to form TEMPOH by GC. After the mixture was charged with oxygen, TEMPOH could change back to TEMPO. TEMPO and TEMPOH were detected to coexist in the mixture by GC. The mechanism involved in ascorbic acid and TEMPO was proposed as shown in Scheme 1.

The oxygen uptake was partly promoted by the interaction between ascorbic acid and TEMPO (Fig. 1, curve c) and was further promoted by the catalyst together with TEMPO (Fig. 1, curve d). Therefore, the most drastic oxygen uptake must be caused by



Scheme 1. Mechanism for the reaction between TEMPO and ascorbic acid in acetonitrile.

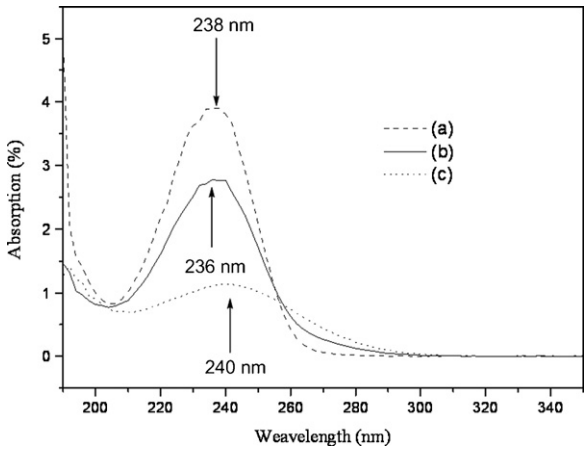


Fig. 2. UV–vis spectrum of (a) ascorbic acid, (b) ascorbic acid mixed with TEMPO and (c) TEMPO. *Reaction conditions*: (a) 2.5 mM ascorbic acid in acetonitrile, (b) 0.5 mM TEMPO, 2.5 mM ascorbic acid in acetonitrile, and (c) 0.5 mM TEMPO in acetonitrile.

the combined catalytic system involving ascorbic acid, catalyst and TEMPO.

3.2. Identification of ascorbic acid radicals by UV–vis, ESR and ^1H NMR

To elucidate the nature of the interaction between ascorbic acid and TEMPO, the mixture of ascorbic acid and TEMPO was measured by UV–vis (Fig. 2) and followed over 80 min (Fig. 3). The maximum absorption band around 238 nm was designated as ascorbic acid (Fig. 2, curve a). The maximum absorption band of TEMPO was 240 nm (Fig. 2, curve c). The UV–vis spectrum of ascorbic acid and TEMPO were constant within 80 min. However, when ascorbic acid and TEMPO were mixed together, a new absorption band was quickly generated (Fig. 2, curve b).

The maximum absorption band of 236 nm decreased with the increase of reaction time (Fig. 3). This band was suggested to be the absorption of ascorbic acid radicals. Because of the decaying of ascorbic acid radicals, this signal slowly decreased during the 80 min.

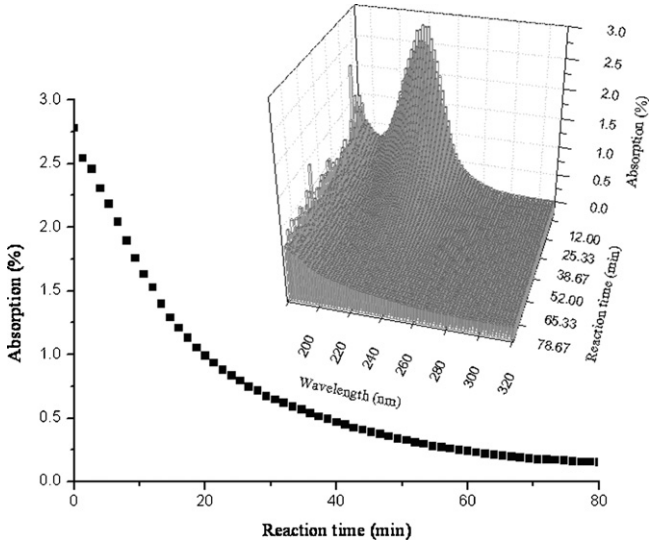


Fig. 3. UV–vis absorption decaying of the maximum of the mixture of TEMPO and ascorbic acid. *Reaction conditions*: 0.5 mM TEMPO reacted with 2.5 mM ascorbic acid in acetonitrile over 80 min.

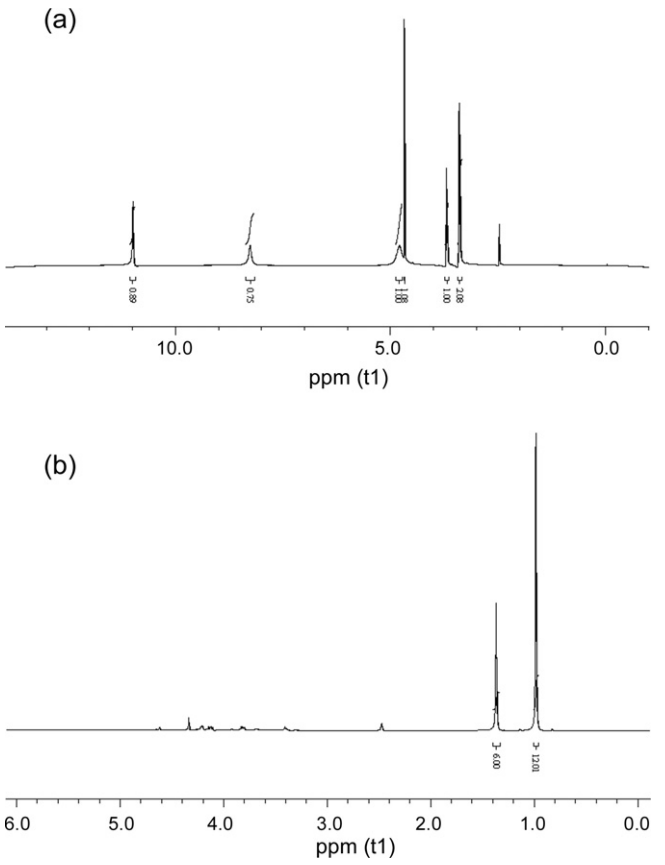


Fig. 4. ^1H NMR of ascorbic acid, the mixture of ascorbic acid and TEMPOH DMSO-d6 as the solvent. *Reaction conditions*: (a) 0.049 g ascorbic acid dissolved in 0.5 mL DMSO-d6 and (b) 0.049 g ascorbic acid and 0.065 g TEMPO dissolved in 0.5 mL DMSO-d6.

To further illustrate the interaction between ascorbic acid and TEMPO, ascorbic acid (Fig. 4a) and the mixture of TEMPO and ascorbic acid (Fig. 4b) were analyzed by ^1H NMR. Ascorbic acid was stable at ambient temperature, and its ^1H NMR is shown in Fig. 4. After the mixing of ascorbic acid and TEMPO, the ^1H NMR signals of ascorbic acid disappeared from the ^1H NMR spectrum. Instead, two new signals caused by the formation of TEMPOH appeared in the ^1H NMR spectrum. The ratio of the chemical shift at around 1.4–1.0 ppm was 6:12, and designated as the hydrogen of methylene and methyl of TEMPOH.

To identify the new species, the interaction of ascorbic acid and TEMPO was also followed by ESR. The sample of TEMPO in acetonitrile gave a strong ESR signal ($g = 2.0055$) at ambient temperature as shown in Fig. 5a. The same amounts of ascorbic acid and TEMPO were added to the solvent above and the ESR signals were transformed to the new signal (Fig. 5b). This transformation of ESR spectroscopy was caused by the formation of another species with an unpaired electron. The signal was centered at $g = 2.0059$, which was the same as the report of ascorbic acid radicals in acetonitrile [31] and confirmed our assignment.

3.3. Tracking analysis of the hydroxylation process by GC in situ

When the hydroxylation of benzene to phenol was carried out without TEMPO, a new compound in addition to phenol was found in acetonitrile (Fig. 6). This compound was 2-hydroxy-2-buten-4-olide (α-tetronic acid, isotetronic acid), which was determined by GC–MS (Fig. S4) and named as compound **1**. According to the structure of compound **1**, it was regarded as a product of oxidative dissociation of ascorbic acid. The phenomenon of the oxidative

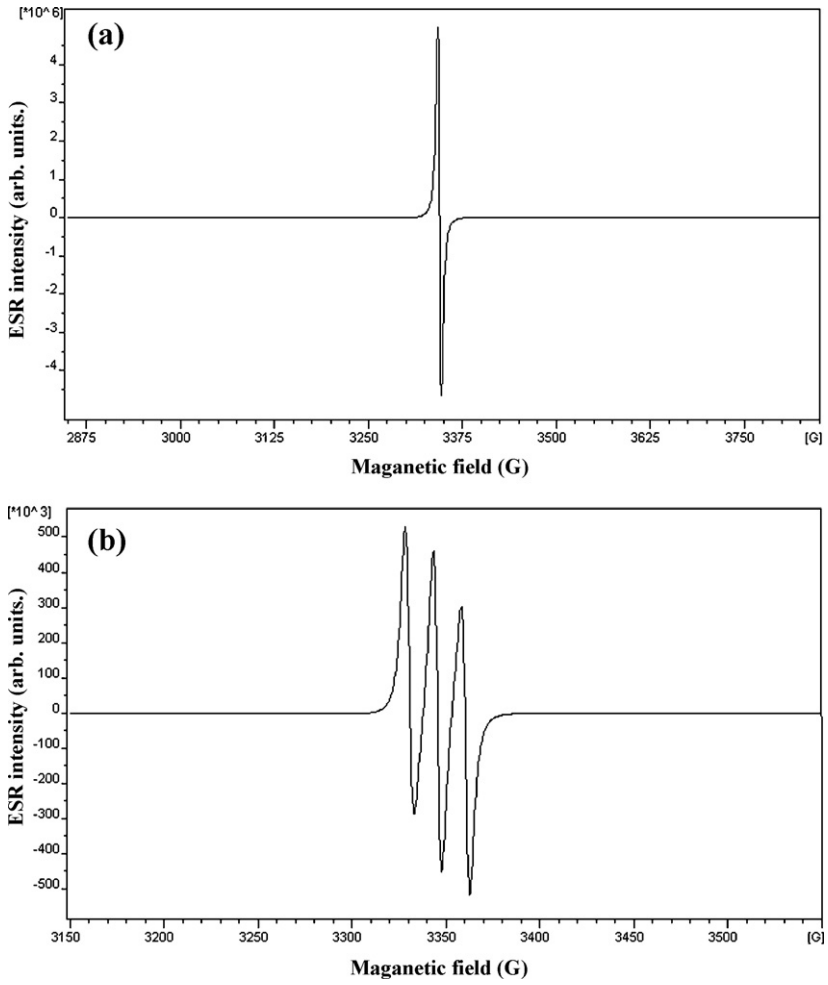


Fig. 5. ESR spectroscopy of TEMPO and ascorbic acid radicals. *Reaction conditions*: (a) 0.5 M TEMPO, acetonitrile as the solvent and (b) 0.5 M ascorbic acid, 0.5 M TEMPO, acetonitrile as the solvent.

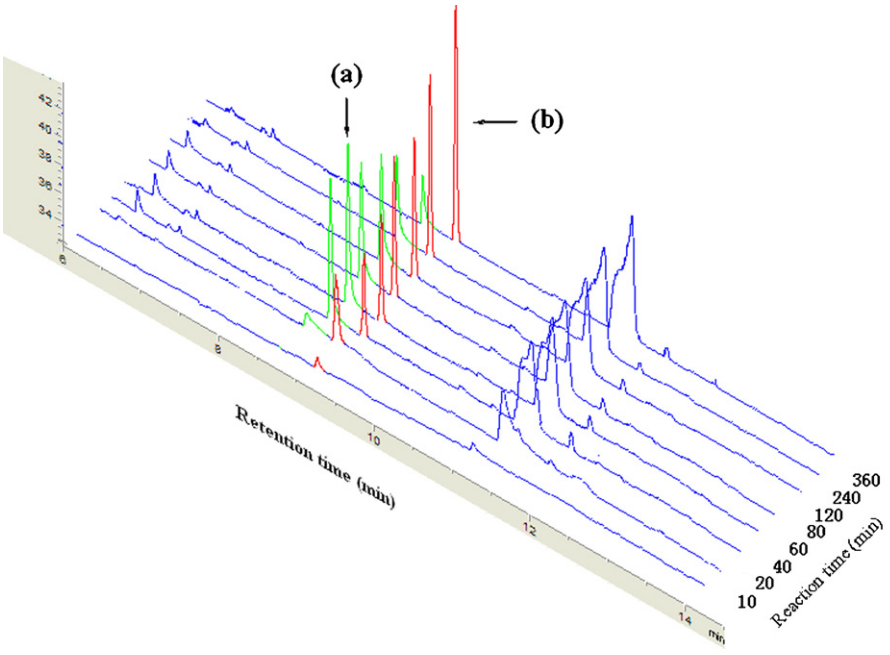


Fig. 6. Hydroxylation of benzene to phenol without the addition of TEMPO (red line indicated phenol, green line indicated compound **1**). *Reaction conditions*: $[(CH_3)_4N]_4PMo_{11}VO_{40}$ 0.105 g (0.05 mmol), ascorbic acid 0.9 g (5 mmol), benzene 0.78 g (10 mmol), acetonitrile 6.8 mL, 80 °C, 2 MPa O_2. (a) Compound **1** (retention time is 8.7 min) and (b) phenol (retention time is 9.1 min). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

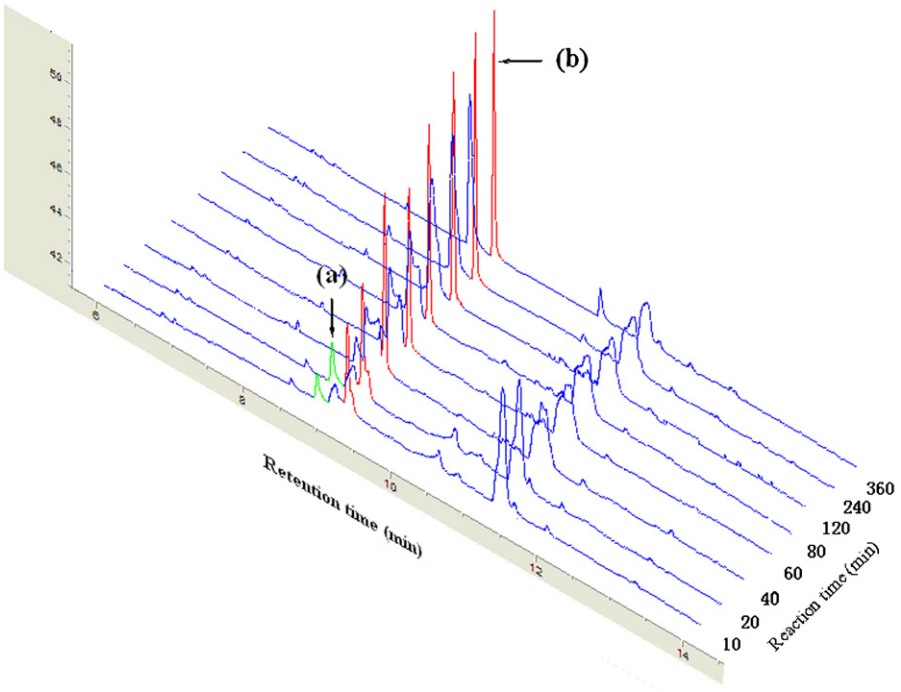


Fig. 7. Compound **1** was depressed by the addition of TEMPO (red line indicated phenol, green line indicated compound **1**). *Reaction conditions*: $[(CH_3)_4N]_4PMo_{11}VO_{40}$ 0.105 g (0.05 mmol), TEMPO 0.156 g (1 mmol), ascorbic acid 0.9 g (5 mmol), benzene 0.78 g (10 mmol), acetonitrile 6.8 mL. 80 °C, 2 MPa O_2. (a) Compound **1** (retention time is 8.7 min) and (b) phenol (retention time is 9.1 min). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

dissociation of ascorbic acid has never been reported in the hydroxylation of benzene. The low rate of hydroxylation is likely to be caused by the oxidative dissociation of ascorbic acid that decreased its efficiency in the hydroxylation (Table 1, right).

After TEMPO was added into the reaction, the formation of compound **1** was restrained (Fig. 7). Only traces of compound **1** can be detected in the first 40 min, then it cannot be detected at all. It was supposed that the oxidative dissociation of ascorbic acid was restrained by the interaction of TEMPO and ascorbic acid (Fig. S5). The oxidative dissociation of ascorbic acid decreased its efficiency and was a negative factor for the hydroxylation process. Therefore, the restraint of this oxidative dissociation of ascorbic acid enhanced its efficiency and increased the yield of phenol (Table 1, left).

To confirm that the oxidative dissociation of ascorbic acid was restrained by the interaction of TEMPO and ascorbic acid, the controlled experiments were carried out as shown in Fig. S5. Compared with Fig. 6, only trace levels of compound **1** can be detected with the addition of TEMPO. In acetonitrile, the mechanism for the hydroxylation rate promoted by TEMPO in acetonitrile was proposed as shown in Scheme 2.

3.4. Effect of aqueous acetic acid on the hydroxylation reaction

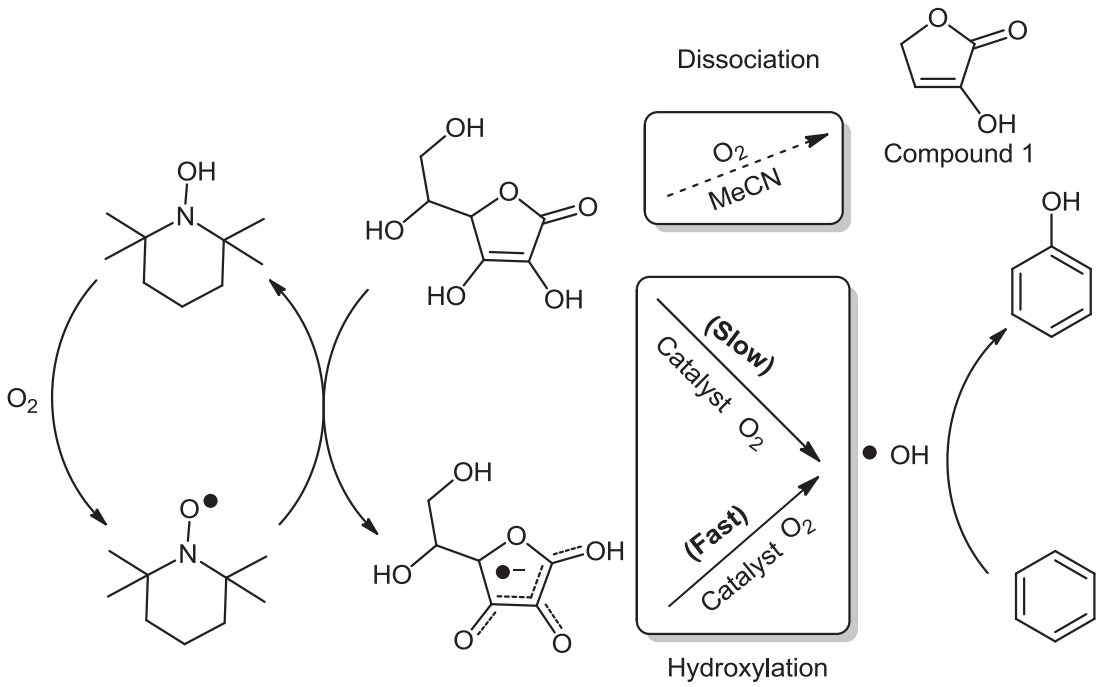
Aqueous acetic acid was widely used as a solvent in the hydroxylation of benzene to phenol [23–26]. Why is aqueous acetic acid good for the hydroxylation of benzene? We found compound **1** cannot be detected when aqueous acetic acid was used as the solvent. That is to say, the oxidative dissociation of ascorbic acid did not happen, meaning its efficiency was higher in aqueous acetic acid than in acetonitrile. Table 2 shows that the yield of phenol was up to 6.6% using aqueous acetic acid as the solvent. With the addition of TEMPO, there was a further increase of the phenol yield from 6.60% to 9.00%. It was found that the interaction of ascorbic acid and TEMPO was still happening in acetic acid/water. The extra phenol yield may be attributed to the interaction between TEMPO and ascorbic acid.

TEMPOH can be reoxidized to TEMPO by oxygen in acetonitrile with or without catalyst (Scheme 1). However, at acidic pH, it was proposed by Neumann [33] that the reoxidation of TEMPOH to TEMPO may be rate-determining, and it was very slow. Sheldon [34] also reported that the nitrogen atom of TEMPOH was protonated and less susceptible to oxidation. In our catalytic

Table 1
Effect of the reaction time on the phenol yield.

Reaction time (min)	Yield of phenol (%)[a]	Selectivity to phenol (%)[a]	Yield of phenol (%)[b]	Selectivity to phenol (%)[b]
10	3.76	>99	2.51	>99
20	4.25	>99	2.66	>99
40	5.12	>99	2.97	>99
60	5.95	>99	3.17	>99
80	6.96	>99	3.48	>99
120	7.25	>99	3.87	>99
240	7.35	>99	4.55	>99
360	7.40	>99	5.26	>99

Reaction conditions: Catalyst 0.105 g (0.05 mmol), ascorbic acid 0.9 g (5 mmol), benzene 0.78 g (10 mmol), acetonitrile 6.8 mL, 80 °C, 2 MPa O_2.
[a] With the addition of TEMPO 0.156 g (1 mmol).
[b] Without TEMPO 0.156 g (1 mmol).



Scheme 2. Mechanism for the hydroxylation rate promoted by TEMPO in acetonitrile.

Table 2
Effect of the solvents on the phenol yield.

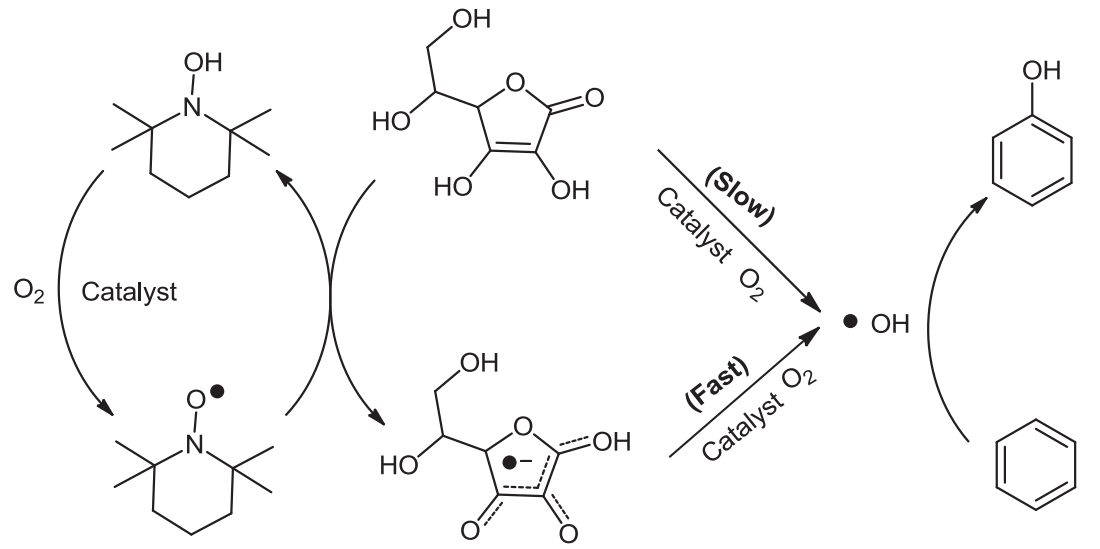
	Yield of phenol (%)[a]	Selectivity to phenol (%)[a]	Yield of phenol (%)[b]	Selectivity to phenol (%)[b]
Acetonitrile	6.96	>99	3.48	>99
Aqueous acetic acid	9.00	>99	6.60	>99

Reaction conditions: Catalyst 0.105 g (0.05 mmol), ascorbic acid 0.9 g (5 mmol), benzene 0.78 g (10 mmol), acetonitrile or 50% aqueous acetic acid 6.8 mL, 80 °C, 2 MPa O_2, 80 min.

[a] With the addition of TEMPO 0.156 g (1 mmol).

[b] Without TEMPO 0.156 g (1 mmol).

system, did the reoxidation of TEMPOH happen using aqueous acetic acid as solvent? Some controlled experiments were carried out to determine this. In aqueous acetic acid, the TEMPOH generated from the interaction between TEMPO and ascorbic acid could not be reoxidized to TEMPO without catalyst. After the addition of catalyst, TEMPO can be detected. This showed that the reoxidation of TEMPOH could happen with the assistance of the catalyst in aqueous acetic acid (Scheme 3). To confirm the recycling of TEMPO in the hydroxylation process, TEMPO as the co-catalyst was added just once, ascorbic acid was added a further five



Scheme 3. Mechanism for the hydroxylation rate promoted by TEMPO in aqueous acetic acid.

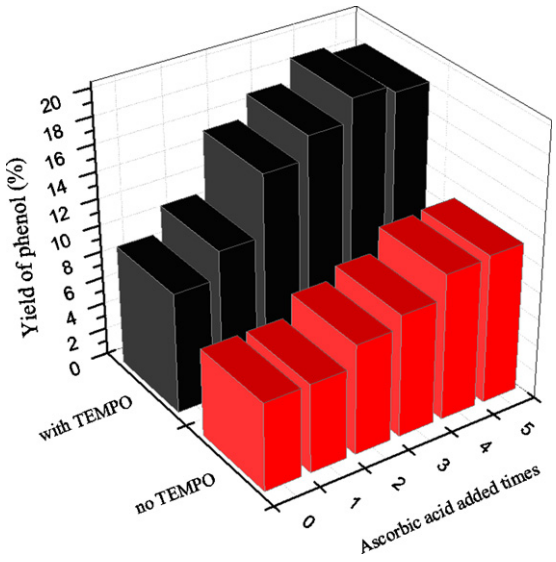


Fig. 8. The yield of phenol in aqueous acetic acid. *Reaction conditions*: Catalyst 0.105 g (0.05 mmol), TEMPO 0.156 g (1 mmol), ascorbic acid 0.9 g (5 mmol, for each addition), benzene 0.78 g (10 mmol), 50% aqueous acetic acid 6.8 mL. 80 °C, 2 MPa O_2, 80 min (for each addition of ascorbic acid).

times, and the yield of phenol could reach up to 18.9% in 400 min (Fig. 8).

4. Conclusions

1. The oxidative dissociation of ascorbic acid happened in the $[(CH_3)_4N]_4PMo_{11}VO_{40}$/ascorbic acid/$O_2$ catalytic system and decreased ascorbic acid efficiency for the hydroxylation reaction in acetonitrile. With TEMPO addition, the interaction of TEMPO and ascorbic acid could restrain the oxidative dissociation of ascorbic acid and increase the rate of the hydroxylation.
2. TEMPO can react quickly with ascorbic acid and generate ascorbic acid radicals and TEMPOH. TEMPO can be recycled in the reaction through the reoxidation of TEMPOH. However, in aqueous acetic acid, catalytic assistance is needed for the recycling process. Ascorbic acid radicals are more reactive than ascorbic acid for the hydroxylation of benzene to phenol.
3. Aqueous acetic acid can protect ascorbic acid from oxidative dissociation and TEMPO can also promote the rate of hydroxylation in aqueous acetic acid.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.11.032.

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