2,2,6,6-四甲基哌啶-1-氧自由基促进的钒基催化剂 催化苯直接氧化制苯酚

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摘要: 以钒基化合物为催化剂, 在 TEMPO (2,2,6,6-四甲基哌啶-1-氧自由基) 存在下, 能形成快速催化分子氧氧化苯制苯酚的催化体系. 在反应过程中, 由类似芬顿试剂反应过程生成的羟基自由基亲核进攻苯环, 形成羟基环己二烯自由基; 该羟基氢可在 TEMPO 存在的催化体系中消除, 同时苯环氢可立即转移至氧原子而生成苯酚. 在以 $[(\text{CH}_3)_4\text{N}]_4\text{-PMo}_{11}\text{VO}_{40}$ 为催化剂的体系中, 反应 1 h 苯酚收率可从不加 TEMPO 时的 1.2% 提高到 8.4%; 而以 V-AlPO₅ 为催化剂时, 苯酚收率可从不加 TEMPO 时的 5.0% 提高到 9.5%, 且选择性均较高.

关键词: 2,2,6,6-四甲基哌啶-1-氧自由基; 钒; 苯; 羟基化; 分子氧; 苯酚

中图分类号: O643 文献标识码: A

收稿日期: 2011-05-28. 接受日期: 2011-07-07.

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基金来源: 国家自然科学基金 (20643006); 国家重点基础研究发展计划 (973 计划, 2009CB623505).

本文的英文电子版(国际版)由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18722067>).

2,2,6,6-Tetramethylpiperidine-1-Oxyl-Promoted Hydroxylation of Benzene to Phenol over a Vanadium-Based Catalyst Using Molecular Oxygen

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Abstract: Rapid benzene hydroxylation was achieved using a reaction system that consisted of a vanadium-based catalyst, ascorbic acid, and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) with molecular oxygen as the oxidant. The hydroxyl radicals that form by a Fenton-type process attack the benzene ring to produce a hydroxycyclohexadienyl radical. The hydroxyl hydrogen is then abstracted quickly in the presence of TEMPO and phenol forms by the transfer of a hydrogen atom from the benzene ring to oxygen. Over the $[(\text{CH}_3)_4\text{N}]_4\text{-PMo}_{11}\text{VO}_{40}$ catalyst the phenol yield reached 8.3% with a selectivity of 95% in 1 h while trace amounts of phenol were obtained in the normal system without TEMPO.

Key words: 2,2,6,6-tetramethylpiperidine-1-oxyl; vanadium; benzene; hydroxylation; phenol; molecular oxygen

Received 28 May 2011. Accepted 7 July 2011.

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This work was supported by the National Natural Science Foundation of China (20643006) and the National Basic Research Program of China (973 Program, 2009CB623505).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

苯酚是重要的有机化工原料, 目前其工业上主要采用异丙苯法生产^[1]. 由于该方法在经济上受到

联产物丙酮市场价格的制约, 且能耗极大, 因此, 开发苯一步法高选择性制备苯酚新工艺具有重要意义.

义^[2~4]. 其中以分子氧直接催化氧化苯制苯酚极具吸引力和挑战性^[5~8].

用于共还原剂存在下分子氧直接催化氧化苯制苯酚的反应体系已有很多报道, 如金属负载的具有高比表面的催化材料 Cu/SBA15^[9], Pd-TS-1^[10], Pd-sil-1^[11]; 金属取代的杂多酸化合物 Cu-POM^[12], V-POM^[13~17]; 以及金属氧化物 CuO-Al₂O₃^[18], V-Al₂O₃^[19], VO-nanoplate^[20]. 但多数反应通常需要很长时间, 且苯酚选择性不高. 2,2,6,6-四甲基哌啶-1-氧自由基 (TEMPO) 可作醇氧化反应中氢转移试剂^[21], 且在苯羟基化制苯酚反应过程中, 苯环受到羟基自由基亲核进攻后发生氢转移可生成产物苯酚, 因此本文以分子氧为氧化剂, 钒基化合物为催化剂, 引入 TEMPO 为助催化剂, 进行苯催化氧化制苯酚.

根据文献[22]合成催化剂[(CH₃)₄N]₄-PMo₁₁VO₄₀ (TMA-PMoV); 采用类似文献[23]中所述方法合成催化剂 V-AlPO₅. 将 2.0 g 异丙醇铝加入预先溶有 3.84 g 磷酸的 7.0 g 去离子水中, 并在 0 °C 搅拌 2 h. 再加入 0.3348 g 硫酸氧钒, 持续搅拌 2 h 后, 将该溶液转移至 150 ml 聚四氟乙烯 (PTFE) 内衬中, 于 180 °C 静置晶化 6 h. 最后经过洗涤和干燥, 并在 600 °C 焙烧后即得 V-AlPO₅ 分子筛.

氧化反应在 25 ml PTFE 内衬中进行, 加入 5 g 乙腈, 0.78 g 苯, 0.2 g 催化剂 TMA-PMoV (或 0.172 g V-AlPO₅), 0.15 g TEMPO 和 0.9 g 抗坏血酸, 再将内衬转至不锈钢压力釜中, 充入 2.0 MPa 的 O₂, 并在 80 °C 搅拌反应 1 h. 反应结束后, 冰浴冷却至 10 °C, 加入 1,4-二氧六环为内标, 用 Agilent 4890 型气相色谱进行定量分析, 色谱柱为 SE-30 毛细柱.

表 1 为苯羟基化制苯酚系列实验结果. 可以看出, 以 TMA-PMoV 为催化剂, 只添加抗坏血酸时, 该

表 1 氧气氧化苯制苯酚的对比实验

Table 1 Comparative reaction of oxidation of benzene to phenol with O₂

Entry	TMA-PMoV (mmol)	TEMPO (mmol)	Ascorbic acid (mmol)	<i>Y</i> _{phenol} /%
1	0.1	—	5.0	trace
2	0.1	1.0	5.0	8.3
3	—	1.0	—	no reaction
4	0.1	1.0	—	no reaction
5	—	1.0	5.0	no reaction

Reaction conditions: benzene 0.78 g, acetonitrile 5.0 g, O₂ 2.0 MPa, 80 °C, 1 h. TEMPO—2,2,6,6-tetramethylpiperidine-1-oxyl.

反应几乎无活性 (实验 1). 当加入 TEMPO 时, 在短时间内苯酚收率可提高至 8.3%, 苯酚选择性为 95% (实验 2). 由实验 3~5 可知, 只加 TEMPO, 或 TEMPO 和催化剂, 或 TEMPO 和抗坏血酸时, 反应活性均低. 因此, 只有 TMA-PMoV 催化剂、抗坏血酸和 TEMPO 共存条件下反应才能发生.

图 1 为不同反应条件下苯羟基化反应结果. 由图可见, 不加 TEMPO 时, 经过 6 小时反应, 苯酚收率依然较低; 而加入 TEMPO 后, 反应 1 h 苯酚收率即达 8.3%, 继续反应至 3 h 苯酚收率未见增加. 为了考察该现象是否由于 TEMPO 消耗所致, 在反应 1 h 后, 向反应体系中加入相同量的 TEMPO, 结果发现, 反应 1 h 后苯酚收率反而降至 7.6%, 可见, 并非 TEMPO 的消耗使反应不再继续. 在苯羟基化反应中, 抗坏血酸会被消耗, 在反应 2 h 后, 向体系中补加抗坏血酸, 继续反应 1 h, 苯酚收率上升至 11.3% 并保持稳定; 继续补加抗坏血酸, 苯酚收率继续提高. 这表明抗坏血酸的补加可使该催化体系得以循环累积反应.

图 1 不同条件下的苯羟基化反应

Fig. 1. Benzene hydroxylation under different conditions. Reaction conditions: catalyst [(CH₃)₄N]₄PMo₁₁VO₄₀ 0.21 g, benzene 0.78 g, acetonitrile 5.0 g, TEMPO 0.156 g, ascorbic acid 0.9 g, O₂ 2.0 MPa, 80 °C. (1) TMA-PMoV and ascorbic acid; (2) TMA-PMoV, TEMPO, and ascorbic acid; (3) TMA-PMoV, TEMPO, and ascorbic acid upon adding another 0.156 g TEMPO after 1 h; (4) TMA-PMoV, TEMPO, and ascorbic acid upon adding 0.9 g ascorbic acid at 0 h, 2 h, and 4 h.

Chen 等^[22]以过氧化氢为氧化剂, [(CH₃)₄N]₄-PMo₁₁VO₄₀ 为催化剂进行苯羟基化制苯酚反应. 结果发现, 加入 TEMPO 后, 完全没有苯酚的生成 (见图式 1). 图式 2 中路线 A 为过氧化氢反应的示意图, 即在过氧化氢作用下, 钒金属活性中心首先生成五价

图式 1 TEMPO 作用下的苯羟基化反应

Scheme 1. Benzene hydroxylation with TEMPO.

图式 2 TEMPO 在过氧化氢催化苯羟基化体系中的阻断作用

Scheme 2. The interruption of TEMPO in the catalytic system for benzene hydroxylation in a catalytic system containing H_2O_2 .

的钒过氧中间体, 该含有活性氧的中间体失水后能形成更为稳定的带有三元过氧环的钒活性物种, 后者进攻苯环生成含有芳环的金属过氧中间体. 然而, TEMPO 的加入阻碍了路线 A, 而使反应按照路线 B 进行. 这是因为 TEMPO 易夺取钒过氧中间体的羟基氢, 导致使该活性物种无法失水形成能够进攻苯环的三元环过氧的钒活性物种, 因此不能按照路线 A 继续进行. 因此, 在过氧化氢体系下加入 TEMPO 是无法使苯羟基化反应正常进行的.

如图式 3 中 Circle A 所示, 在 O_2 为氧化剂, 抗坏血酸存在下, 利用过渡金属钒整合了类似于过氧化氢体系芬顿反应体系中产生活性氧羟基自由基的过程^[24]. 因此对于产生羟基自由基这一步过程, O_2 , 抗坏血酸和钒催化剂缺一不可. 由该路线可知, V(V) 首先被抗坏血酸还原为 V(IV), 而后者能在酸性条件下将 O_2 原位还原成过氧化氢, 该再在 V(IV) 作用下分解得到羟基自由基. 羟基自由基进攻苯环可形成羟基环己二烯自由基 (图式 3 中的过渡态 A). 据此推测, 过氧化氢的合成在反应初始阶段是非常重要的, 因此, 本文在反应初期添加微量的过氧化氢进行实验, 结果发现, 反应 1 h 后苯酚收率由 8.3% 升到 11.3%, 进一步证实了我们的猜测. 当在反应体系中加入自由基捕捉剂 BHT (2,6-di-tert-butyl-4-methylphenol) 时, 反应收率急速下降, 因此该反应由自由基引发.

在没有添加 TEMPO 的普通反应体系中, 也能生成苯酚, 但反应时间相对较长, 收率也较低. 我们用图式 3 中的 Circle B 来进行推测 TEMPO 存在的反应

图式 3 TEMPO 促进的苯羟基化反应机理的推测

Scheme 3. The proposal of the reaction mechanism for benzene hydroxylation promoted by TEMPO.

体系中反应加快的原因. 由 Circle A 产生的羟基环己二烯自由基将进入 Circle B 进行反应, 进而得到苯酚. 为此, 本文进行了苯羟基化反应的氘代苯同位素示踪实验, 由 GC-MS 的结果表明, 所得苯酚均为 PhOD, 即酚羟基中氢来自于苯环. 因此, TEMPO 的加入加快了羟基自由基上氢转移过程而提高了苯酚生成速度. 然而氢转移能垒相对较高, 仅靠 TEMPO 是很难完成的, 因此离不开钒催化剂与 TEMPO 的共同作用. 在反应后的体系中检测到少量 TEMPH, 这由 TEMPOH 转变而来的^[25], 也证明了 TEMPO 确实和氢转移有一定的关系. 添加 TEMPO 反应体系的特点是将羟基自由基的生成与对苯环亲核进攻和氢转移过程结合起来, 从而加快了苯酚的生成. 以 V-AIPO₅ 为催化剂的苯羟基化反应体系 (见表 2), 添加 TEMPO 后也具有类似的效果, 苯酚收率可从 5.0% 提高至 9.5%, 选择性为 99%.

表 2 以 V-AIPO₅ 为催化剂的苯羟基化制苯酚的反应

Table 2 Benzene hydroxylation over V-AIPO₅ with TEMPO

Sample	$Y_{\text{phenol}}^a/\%$	$Y_{\text{phenol}}^b/\%$	$S_{\text{phenol}}^c/\%$
V-AIPO ₅ ^d	5.0	9.5	99.0
V-AIPO ₅ ^e	4.4	11.8	99.0

^aYield obtained in the reaction without adding TEMPO.

^bYield obtained in the reaction with TEMPO.

^cSelectivity for phenol in the reaction with TEMPO.

^dReaction conditions: catalyst V-AIPO₅ 0.172 g, benzene 0.78 g, acetonitrile 5.0 g, TEMPO 0.156 g, ascorbic acid 1.343 g, O₂ 2.0 MPa, 80 °C, 1 h.

^eReaction conditions: catalyst V-AIPO₅ 0.172 g, benzene 0.78 g, acetonitrile 5.0 g, TEMPO 0.156 g, ascorbic acid 2.238 g, O₂ 2.0 MPa, 60 °C, 1 h.

总之, 以 TEMPO 为助催化剂, O₂ 为氧化剂, 钒基化合物为催化剂, 抗坏血酸为共还原剂的条件下, 实现苯快速催化氧化制苯酚. 这也是 TEMPO 在苯羟基化反应中的首次应用, 为苯羟基化制苯酚的研究提供了一条新的思路.

致谢 感谢中国科学院大连化学物理研究所徐杰研究员在 GC-MS 上的热忱帮助.

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英 译 文

English Text

Phenol is an important industrial intermediate for the production of various chemicals and it is mainly produced by the cumene method [1]. However, the "cumene process" is a laborious, three-step reaction which not only suffers from an economic dependence on the byproduct acetone but also requires a vast amount of energy. The development of a phenol from benzene route by a single-step and co-product(s)-free reaction is, therefore, urgent. The one-step synthesis of phenol by the direct insertion of oxygen into a benzene ring is an attractive and challenging process [2–4],

especially hydroxylation with molecular oxygen as the oxidant, which is desirable from an environmental and synthetic chemical point of view [5–8].

The direct hydroxylation of benzene with molecular oxygen as an oxidant in the presence of a co-reductant has been extensively investigated. Many catalytic systems have been developed such as metal-supported high-surfaces materials Cu/SBA15 [9], Pd-TS-1 [10], Pd-sil-1 [11], metal substituted polyoxometalates Cu-POM [12], V-POM [13–17], and metal oxides CuO-Al₂O₃ [18], V-Al₂O₃ [19], VO-nanoplate [20]. However, a lengthy reaction time is usually required and moderate phenol selectivities are obtained in most catalytic systems for the direct hydroxylation of benzene with molecular oxygen as oxidant. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) has been used as a hydrogen transfer reagent for the oxidation of alcohols [21]. During benzene hydroxylation phenol can be obtained by hydrogen transfer after a nucleophilic attack on a benzene ring by a hydroxyl radical. Therefore, a novel catalytic system consisting of vanadium-based catalysts, ascorbic acid, and TEMPO was developed for the direct hydroxylation of benzene to phenol by molecular oxygen.

The heteropoly compound [(CH₃)₄N]₄-PMo₁₁VO₄₀ (TMA-PMoV) was prepared by the method described by Chen [22]. The preparation of V-AlPO₅ was carried out according to the method of Xu [23]. First, 2.0 g aluminum isopropoxide was added to a mixture of 7.0 g H₂O and 3.84 g H₃PO₄, and then aluminum isopropoxide was added with stirring at 0 °C for 2 h. After that, VOSO₄ (0.3348 g) was added under constant stirring for 2 h. The solution was poured into a 150 ml PTFE liner. The raw material was obtained after crystallization for 6 h at 180 °C. V-AlPO₅ was synthesized by washing, drying, and calcining in air at 600 °C.

For a typical reaction: 0.2 g catalyst [(CH₃)₄N]₄-PMo₁₁VO₄₀ (or 0.172 g V-AlPO₅), 5 g acetonitrile as solvent containing 0.78 g benzene, 0.15 g TEMPO, and 0.9 g ascorbic acid were added into a 25 ml PTFE liner. The liner was put into a stainless steel reactor and subsequently pressurized with O₂ at 2.0 MPa. After stirring for 1 h at 80 °C the reactor was cooled to 10 °C. The 1,4-dioxane was added as an internal standard. Quantification of the products was carried out using a GC-Agilent 4890 series instrument with a SE-30 capillary column (internal standard method).

A series of control experiments for benzene hydroxylation is shown in Table 1. The reaction was first investigated over the catalyst TMA-PMoV with ascorbic acid but phenol was only obtained in trace amounts (Table 1, entry 1). Surprisingly, when TEMPO was added the phenol yield increased to 8.3% with a high selectivity of 95% in a relatively short reaction time (Table 1, entry 2). We also found that the reaction activity was poor when using TEMPO alone (Table 1,

entry 3) and when using both TEMPO and the catalyst (Table 1, entry 4) or ascorbic acid (Table 1, entry 5). The efficient benzene hydroxylation catalytic system only worked when the three ingredients- TMA-PMoV, ascorbic acid and TEMPO were used.

Figure 1 shows that the phenol yield remains low even after 6 h in the absence of TEMPO. A higher phenol yield was obtained 1 h after the addition of TEMPO but the yield remained the same at 3 h. To determine whether TEMPO was consumed in this reaction extra TEMPO was added 1 h after the reaction beginning but the yield decreased to 7.6% in the subsequent hour, indicating that TEMPO was not consumed. Ascorbic acid is known to be spent during the hydroxylation of benzene with oxygen, therefore, extra ascorbic acid was added after 2 h in another reaction. The phenol yield increased to nearly 11.3% in the subsequent hour and then remained constant. Interestingly, the phenol yield improved if ascorbic acid was repeatedly added after 4 h, which meant that the catalytic system could be regenerated by supplementing with ascorbic acid.

The H₂O₂ system with the vanadium-based catalyst has been studied previously [22] and here TEMPO was added to the H₂O₂ system to improve the reactivity but no phenol product was obtained (Scheme 1). With the normal hydrogen peroxide approach described in Scheme 2 (Route A) the catalyst TMA-PMoV reacts with H₂O₂ to form a V(V) peroxo species, which then interacts with the substrate benzene to produce a metallo-peroxy-arene intermediate species. However, Route A is interrupted and replaced by Route B upon adding TEMPO where hydroxyl hydrogen transfer occurs and the vanadium species loses the capability to attack the benzene ring. Therefore, the reactivity of the H₂O₂ system with TEMPO is hardly significant.

As described in Scheme 3 (Circle A), the OH radical can be produced by the plausible Fenton-type process [24]. Both the oxidant oxygen and the reductant ascorbic acid are necessary for the production of phenol from benzene oxidation upon catalysis by the vanadium-based catalyst. This shows that the V(V) species is reduced to V(IV) by ascorbic acid. The resulting V(IV) species causes the O₂ reduction to form hydrogen peroxide in the presence of H⁺. The OH radicals are generated by the decomposition of the formed H₂O₂ in the presence of the V(IV) species and a proton attacks benzene to form a hydroxycyclohexadienyl radical (the transition state A in Scheme 3). According to the hypothesis in Circle A, H₂O₂ should be useful particularly during the initial stage of benzene oxidation. When a small amount of H₂O₂ (50%) was added to the reaction using oxygen as an oxidant the phenol yield increased to 11.3% within 1 h, which supports the assertion in Circle A. Furthermore, BHT (2, 6-di-tert-butyl-4-methylphenol) was added to the O₂ system with TEMPO and the phenol yield reduced sharply to the micro scale thus

indicating that this hydroxylation process was initiated by radicals.

In a normal system over V(V) the transition state **A** produces phenol although this reaction requires a long time. In the catalytic system containing TEMPO the hydroxycyclohexadienyl radical follows the process described in Scheme 3 (Circle B). Here, a labelling experiment was carried out to obtain mechanistic information about the benzene hydroxylation shown in Circle B. C_6D_6 was used as the substrate to track benzene hydrogen. We found that C_6D_6 afforded PhOD, which was detected by GC-MS and this indicates that the hydrogen atom from the benzene ring transfers to the oxygen atom. We propose that adding TEMPO improves the reaction rate by accelerating hydrogen transfer in transition state **A** to form phenol. Direct hydrogen transfer using TEMPO alone is difficult to achieve because the activation energy barrier is high. Therefore, it can be assumed that the process can be carried out over both TEMPO and the V-catalyst (marked by the * in Circle B). A small amount of the TEMPH generated from TEMPOH in the reaction solution was also detected by GC-MS, which supports the combination of TEMPO with

hydrogen [25]. The system over the V-based catalyst with TEMPO is unique because of the successive hydroxyl radical generation, nucleophilic attack, and hydrogen transfer. Benzene hydroxylation over V-AlPO₅ was also carried out using TEMPO. The phenol yield improved from 5.0% to 9.5% with a high selectivity of 99% (Table 2).

In conclusion, we developed a novel catalytic system consisting of a V-based catalyst, ascorbic acid, and TEMPO for benzene hydroxylation to phenol using oxygen as the oxidant. This is the first report on the acceleration of the reaction rate of benzene hydroxylation by the addition of TEMPO. This provides a clear path for research into the direct hydroxylation of benzene to phenol.

Acknowledgements

We thank Prof. Jie XU for technical assistance during the GC-MS analysis.

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