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A Novel and Simple Catalyst System ($CuBr_2$/TEMPO/Piperidine) for the Oxidation of Primary Benzylic Alcohols to Aldehydes by Oxygen

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Abstract: A novel and simple catalyst system ($CuBr_2$/TEMPO/piperidine) for the oxidation of primary benzylic alcohols to aldehydes by oxygen has been developed. This catalyst system shows high activity and excellent selectivity for the oxidation of various primary benzylic alcohols to the corresponding aldehydes by oxygen in acetonitrile at 50 ℃ without need of additional base as co-catalyst. However, the novel catalyst system is not effective in the oxidation of secondary benzylic alcohols, primary aliphatic alcohols and allylic alcohols.

Key words: benzylic alcohols; oxidation; $CuBr_2$; TEMPO; piperidine
CLC number: O643.32　　**Document code**: A

The oxidation of alcohols to their corresponding aldehydes and ketones is one of the most widely used classes of oxidation reactions in organic chemistry. Traditional methods to carry out this reaction involve the use of stoichiometric amounts of inorganic oxidants, such as chromium (VI) oxide[1-2], MnO_2 or hypervalent iodine compounds[3-7]. In most cases, these oxidants are usually expensive, toxic, or hazardous. Therefore, the development of selective and environmentally friendly oxidations catalyzed by transition-metal complexes is a very important and topical area of contemporary catalysis. From both an economical and environmental point of view, the development of effective catalytic oxidation processes with molecular oxygen as the terminal oxidant is most attractive. Therefore, many catalysts containing transition metals such as palladium[8-9], iridium[10], ruthenium[11], copper[12] and vanadium[13] have been developed for catalytic aerobic oxidation of alcohols. Except for copper, all the metals mentioned above are very expensive and not suitable for large-scale applications unless the recycling problem is resolved. Copper is an abundant metal on the earth's crust and presents in the active site of galactose oxidase-a mononuclear copper enzyme, and couples the oxidation of alcohols to aldehydes with the reduction of O_2 to H_2O_2 through an unusual Cu (II) phenoxyl-radical active species. Thus, a series of copper based catalysts or catalyst systems have been developed for the oxidation of alcohols to aldehydes and ketones with molecular oxygen as oxidant. In 1984, Semmelhack and co-workers[14] first reported the aerobic oxidation of benzylic and allylic alcohols with 10% CuCl/TEMPO in DMF as the solvent. Aliphatic alcohols proved to be substantially less reactive and required 2 equivalents of $CuCl_2$ to achieve good product yields. Since then a number of copper/TEMPO catalyst systems have been proved to be highly efficient for the transformation of a broad range of alcohols to aldehydes and ketones[15-39]. It has been found that chelating nitrogen ligands have beneficial effect on the oxidation reaction. Notable examples include a (bpy) $CuBr_2$/TEMPO catalyst system that employs *t*-BuOK as a cata-

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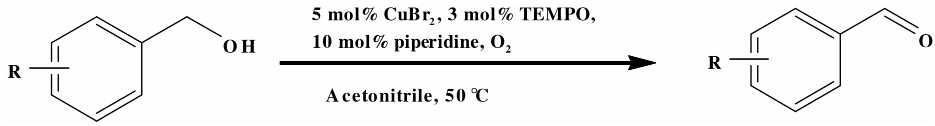
lytic base in CH_3CN/H_2O as the solvent, developed by Sheldon and co-workers[16-17], and a (bpy)Cu(OTf)$_2$/TEMPO catalyst system reported by Kumpulainen and Koskinen[39]. Stahl et al[19] made a breakthrough in the development of copper/TEMPO system. They disclosed a (bpy) CuI/TEMPO/NMI catalyst system (NMI = N-methylimidazole). It was observed that the replacement of Cu(II) with a Cu(I) source significantly enhanced the reaction rate. The catalyst system exhibits fast rates and high selectivities, even with unactivated aliphatic alcohols. Moreover, the method is compatible with substrates bearing diverse functional groups and uses ambient air as the source of the O_2 oxidant. Further investigation[22] revealed that the reaction proceeds via a two-stage catalytic mechanism consisting of (1)"catalyst oxidation" in which Cu(I) and TEMPO-H are oxidized by O_2 via a binuclear Cu_2O_2 intermediate and (2)"substrate oxidation" mediated by Cu(II) and the nitroxyl radical of TEMPO via a Cu(II)-alkoxide intermediate.

Although these systems permit the effective oxidation of primary alcohols under mild conditions, the chelating nitrogen ligands are generally expensive and additional bases are required to accelerate the reaction in most cases. Therefore, seeking novel catalysts or catalyst systems with low cost and simple composition for the aerobic oxidation of alcohols to aldehydes and ketones is still of great significance. Herein, we report a novel, highly active $CuBr_2$/TEMPO/ piperidine catalyst system that can catalyze selective aerobic oxidation of primary benzylic alcohols to the corresponding aldehydes in acetonitrile (Scheme 1).



Scheme 1 Aerobic oxidation of primary benzylic alcohols to the corresponding aldehydes catalyzed by $CuBr_2$/TEMPO/piperidine

1 Experimental

1.1 Materials and methods

2, 2, 6, 6-Tetramethylpiperidine-1-oxyl(TEMPO) and alcohols were purchased from Acros Organics. Other chemicals were obtained from Tianjin Fuchen Chemical Reagents Factory, China. All the chemicals were used as received without further purification.

1.2 Catalytic reaction

Oxidation reactions were performed in a 5 mL two-necked round bottomed flask equipped with a magnetic stirrer and a condenser, immersed in a temperature-controlled water bath. A balloon filled with oxygen was connected to the top of the condenser. Typically, the alcohol (2 mmol) was dissolved in 1.5 mL CH_3CN. TEMPO (0.06 mmol) and $CuBr_2$(0.1 mmol) were added successively, resulting in a green solution. Finally, piperidine (0.2 mmol) was added, and the green color of the reaction solution rapidly faded and emerged again, and slowly turned reddish brown. The system was purged with oxygen and sealed. Oxygen was passed into the system under stirring from the balloon to start the reaction. Samples of the reaction mixture were taken out regularly and analyzed by a Shandong Lunan Ruihong Gas Chromatograph (GC) SP-6800A equipped with a 30 m×0.5 μm PEG-20 m capillary column and an FID detector. Upon completion, the reaction mixture was neutralized with appropriate amounts of 0.5 mol/L HCl and then extracted with cyclohexane or ethyl acetate. The organic phase was analyzed by GC in the presence of decane as an internal standard.

1.3 Computational Methods

According to the research practice[40-41], the four methyl groups in TEMPO have been replaced by H atoms in our reaction model to improve the efficiency of calculation. All of the geometry optimizations and frequency calculations were performed with the B3LYP functional implemented in Gaussian 09[42]. The LANL2DZ basis set was used for copper and the 6-31G (d) basis set for the other atoms. The transition state was verified by the existence of imaginary frequency and the connectivity between the reactant and transition sate confirmed by intrinsic reaction coordinate (IRC)[43] calculation. Computational details are given in the Supporting Information.

2 Results and discussion

The novel $CuBr_2$/TEMPO/piperidine catalyst system was discovered occasionally in an experiment for the oxidation of benzyl alcohol into benzaldehyde by oxygen catalyzed by TEMPO in combination with $CuBr_2$ in presence of silica supported bidentate nitrogen ligands, and K_2CO_3 as co-catalyst in a 2 ∶ 1 acetonitrile/water mixture. It was found that the supported bidentate nitrogen ligands were poorly dispersed in the mixture solvent, which retarded the oxidation. To resolve this problem, we used piperidine instead of K_2CO_3 as a base and pure acetonitrile as the solvent, and the reaction proceeded smoothly. Then, an additional blank experiment was carried out in the absence of the supported bidentate nitrogen ligands. Surprisingly, the reaction still proceeded very well. The interesting results promoted us to undertake a thorough study of $CuBr_2$/TEMPO/piperidine-catalyzed oxidation of alcohol by oxygen.

2.1 Aerobic oxidation of alcohols

As shown in Table 1, both $CuBr_2$ and TEMPO are crucial for the oxidation (Table 1, entries 1, 2), as reported in literature[16-17]. The use of piperidine is essential too. Only 4.4% of benzyl alcohol was converted to benzaldehyde in 2 h when no piperidine was added (Table 1, entry 3). The $CuBr_2$/TEMPO/piperidine catalyst system showed high activity in the absence of additional base, which is different from the other copper based catalyst systems[16-18]. When a mount of 10% of piperidine was added, benzyl alcohol was fully and selectively converted to benzaldehyde in 2 h (Table 1, entry 4). It was revealed that piperidine acting as a ligand can coordinate with copper to generate a complex[44]. Therefore, it can be concluded that piperidine coordinates with copper ion in situ to form a complex in the present oxidation system; the complex in combination with TEMPO catalyzed the aerobic oxidation of benzyl alcohol. Besides, piperidine also acts as a base to deprotonate the alcohol facilitating the coordination of alcohol to the central copper ion as shown in Scheme 2, resulting in enhancement of the activity.

Table 1 $CuBr_2$-catalyzed oxidation of benzyl alcohol to benzaldehyde by O_2.

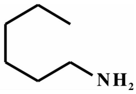
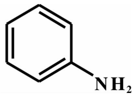
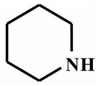
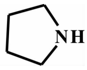
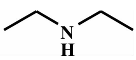
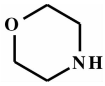
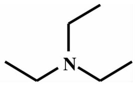
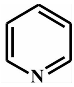
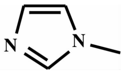
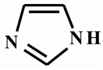
Entry	Piperidine /(mol%)	TEMPO /(mol%)	$CuBr_2$ /(mol%)	Yield[a] /%
1	10	5	0	2.4
2	10	0	5	-
3	0	5	5	4.4
4	10	5	5	>99

Reaction conditions: 2 mmol benzyl alcohol, 3 mL CH_3CN, atmospheric oxygen pressure, reaction temperature 50 ℃, reaction time 2 h.

a. The yield is determined by GC, and the selectivity is 100%.

As piperidine can promote the copper-catalyzed aerobic oxidation of benzyl alcohol, a range of other amines were evaluated as alternatives of piperidine in the oxidation reaction. The results are shown in Table 2. It can be seen that only secondary amines are efficient in the oxidation reaction (Table 2, entries 3-6), whether they are cyclic or acylic; both primary and tertiary amines are inefficient in the oxidation (Table 2, entries 1, 2, 7-10). As described above, amines such as piperidine acted as both bases and ligands in the catalytic oxidation of benzyl alcohol with oxygen, the base strength might be the key factor to determine the performances of the amines in the reaction. Besides, among all the employed secondary amines the performances of piperidine and diethylamine (Table 2, entries 3, 5) were comparable, while pyrrolidine and morpholine (Table 2, entries 4, 6) behaved poorly. Low activity was received when morpholine was used instead of piperidine , which might be ascribed to the

Table 2 Effects of different bases on the aerobic oxidation of benzyl alcohol

Entry	Amines	pKa^b	Time/h	Selectivity/%	$Yield^a$/%
1		-	4	86.6	6.2
2		4.6	4	54.1	0.7
3		11.0	2	100	>99
4		11.2	4	100	30.7
5^c		11.0	4	100	94.5
6		8.3	4	100	73.7
7		10.8	4	98.3	18.0
8		5.2	4	76.3	6.2
9		7.4	4	92.7	17.1
10		7.0	4	88.5	8.3

Reaction conditions: 2 mmol benzyl alcohol, 10 mol% amine, 5 mol% TEMPO, 5 mol% $CuBr_2$, 3 mL CH_3CN, atmospheric oxygen pressure, reaction temperature 50 ℃.

a. The yield is determined by GC; b. The pK_a values are proportional to the base strength of the amines; c. The reaction temperature is 35 ℃.

low basicity of morpholine compared to piperidine due to the electron-withdrawing effect of the oxygen in the molecular structure of morpholine. Surprisingly, only 30.7% of benzaldehyde was received in 4 h under the same reaction conditions when pyrrolidine was used as an additive, which is difficult to explain only from the viewpoint of basicity, because the basicity of pyrrolidine is slightly stronger than that of piperidine. The poor performance of pyrrolidine may be ascribed to the big steric hindrance as it coordinated with Cu^{2+} during the catalytic oxidation process.

TEMPO is very expensive and hazard to environment. Therefore, it is essential to minimize the loading of TEMPO. Table 4 presents the effect of the TEMPO loading on the reaction. It can be seen that when the TEMPO loading was reduced from 5% to 3%, the reaction finished in 2 h, which is still acceptable (Table 3, entry 3). However, when the TEMPO loading was decreased to 2%, the yield was 96.1% in 6 h, and the reaction did not proceed with further prolonging reaction time (Table 3, entry 2). For the purpose to minimize the loading of TEMPO, the the optimal loading of TEMPO is 3% for the aerobic oxidations of alcohols.

Table 3 Effect of TEMPO loading on the oxidation of benzyl alcohol[a]

Entry	TEMPO/(mol%)	Time/h	Yield/%
1[b]	1	5	72.7
2[b]	2	6	96.1
3	3	2	>99
4	5	1.67	>99

Reaction conditions: 2 mmol of benzyl alcohol, 10 mol% piperidine, 5 mol% $CuBr_2$, 1.5 mL CH_3CN, reaction temperature 50 ℃.

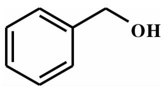
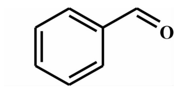
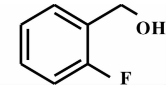
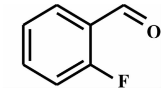
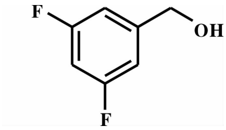
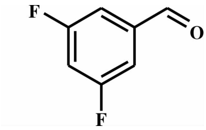
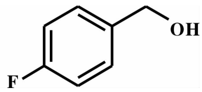
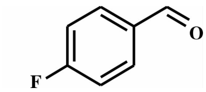
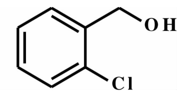
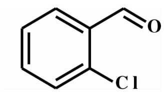
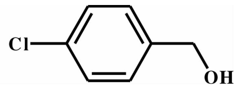
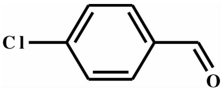
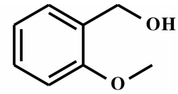
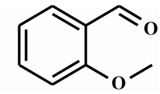
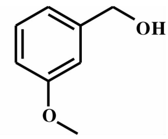
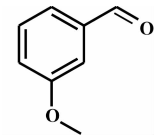
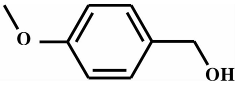
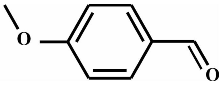
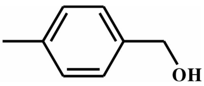
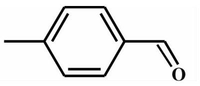
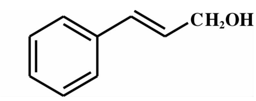
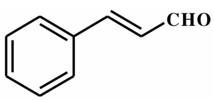
a. The yield is determined by GC;

b. The yield is no longer increased by prolonging reaction time.

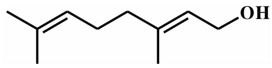
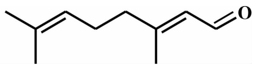
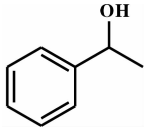
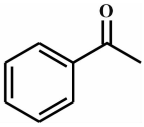
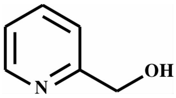
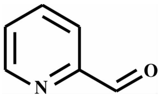
The $CuBr_2$/TEMPO/piperidine catalyst system was then evaluated in the oxidation of a series of primary and secondary alcohols, under the optimized conditions. The results are listed in Table 4. As shown in Table 4, various primary benzylic alcohols were successfully oxidized to their corresponding aldehydes. Benzyl alcohol was totally and selectively converted to benzaldehyde in 2 hours at 50 ℃ or in 6 h at 25 ℃ (Table 4, entries 1, 2), corresponding to a TON of 33 per mole of TEMPO. All *para*-substituted benzyl alcohols, including those bearing both electron-withdrawing and electron-donating groups, were selectively oxidized to the corresponding aldehydes in less than 2 hours (Table 4, entries 5, 7, 11, 12). In general, the electron-donating groups can accelerate the reaction but not significantly, indicating the oxidation is not sensitive to electronic effects of the substituent. Similar phenomenon was observed in the oxidation of *meta*-substituted benzyl alcohols (Table 4, entries 4, 10). However, long reaction time was required to finish the oxidation reaction in the cases of *ortho*-substituted benzyl alcohols as substrates, whether the substituent is electron-withdrawing or electron-donating (Table 4, entries 3, 6, 8, 9). The bigger size of the substituent is, the slower the reaction proceeds. This may be explained by the steric hindance between the *ortho*-substituent and the coordinated TEMPO in the transition state from intermediate Ⅳ to Ⅴ (Fig. 1) in the catalytic cycle (Scheme 2).

As shown in Table 4, almost no products were detected in the cases of 1-phenylethanol and octan-1-ol as substrates respectively (Table 4, entries 16, 18). The low reactivity of the secondary alcohols was ascribed to the steric effects of the methyl and lack of the second β-hydrogen to stabilize the radical intermediate in the catalytic cycle in literature[16-17]. In the case of the mixture of benzyl alcohol and 1-phenylethanol as substrate (Table 4, entry 19), 99% of benzyl alcohol was converted to benzyl aldehyde, whereas no 1-phenylethanol was oxidized. This chemoselectivity may be useful in the selective oxidations of alcohols in synthetic organic chemistry. It was noted that the novel catalyst system was less active than the other copper-based catalyst systems reported in literature[14, 16, 45] in the oxidation of primary aliphatic alcohols. This can be ascribed to the weak basicity of piperidine, which makes it difficult for piperidine to remove protons from primary aliphatic alcohols in the catalytic cycle.

Table 4 Oxidation of alcohols to the corresponding aldehydes and ketones with oxygen catalyzed by the piperidine/$CuBr_2$/TEMPO catalyst system [a]

Entry	Substrate	Product	Time /h	Yield[b] /%	TON/ TEMPO	TON/ Cu
1[c]			6	>99	33	20
2			2	>99 (93.2)	33	20
3			5	>99	33	20
4			3	>99	33	20
5			2	>99	33	20
6			9	>99	33	20
7			1.5	>99	33	20
8			8.5	77.3	26	15
9[d]			8	87.6	29	18
10			1.5	>99 (94.6)	33	20
11			1.0	>99 (85.7)	33	20
12			1.5	>99	33	20
13[e]			6.5	24.1	8	5

（续表 4）

Entry	Substrate	Product	Time h	Yield^{b} /%	TON/ TEMPO	TON/ Cu
14			10	–	–	–
15	Geraniol + Benzyl alcohol	Geranial + Benzyl aldehyde	3	–/3.6	–	–
16			2.5	–	–	–
17			12	6.3	–	–
18			10	–	–	–
19	Benzyl alcohol +1-phenylethanol	Benzyl aldehyde +Acetophenone	2	99/-	33/-	20/-

Reaction conditions: 2 mmol substrate, 1.5 mL CH_3CN, 3 mol% TEMPO, 5 mol% $CuBr_2$, 10 mol% piperidine, atmospheric oxygen pressure, reaction temperature 50 ℃.

a. Unless otherwise specified, the selectivity is 100% based on GC; b. The data in the parentheses are the isolated yields; c. The reaction temperature is 25 ℃; d. TEMPO is 5 mol%; e. The selectivity is 73.1% based on GC.

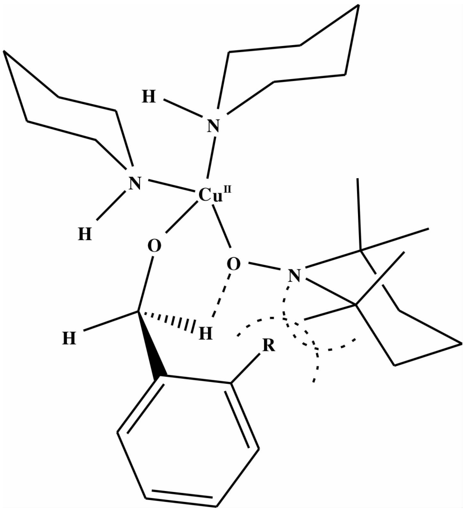


Fig. 1 Steric hindrance present in thetransition state of the α-H abstraction with *ortho*-substituted benzyl alcohols as substrate

Surprisingly, the system is also not active for the oxidation of allylic alcohols by oxygen. Cinnamic alcohol was converted to cinnamic aldehyde only in low yield and selectivity (Table 4, entry 13), and no reaction was observed with geraniol as a substrate (Table 4, entry 14). Generally, these allylic alcohols were easily converted to their corresponding aldehydes by other copper-based catalyst systems[16, 45]. More surprisingly, the oxidation of benzyl alcohol can be stopped when geraniol was added to the reaction system (Table 4, entry 15). It is difficult to know what caused these results. We suppose that this lack of reactivity of allylic alcohols with the novel catalyst system is due to the coordination of the allylic alcohol molecule with copper ion in the reaction mixture. Here, because of the weak coordination of piperidine with copper ion compared to bidentate nitrogen ligands such as 2, 2’-bipyridine, allyl alcohol molecule can chelate with copper to replace one piperidine, resulting in the alcohol moiety being fixed (Fig. 2). We tried to confirm this assumption by recording UV-Vis spectra of the reaction mixture, but no information was observed.

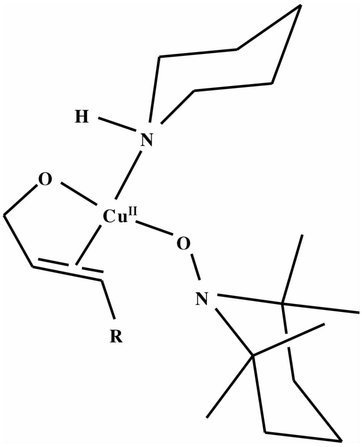
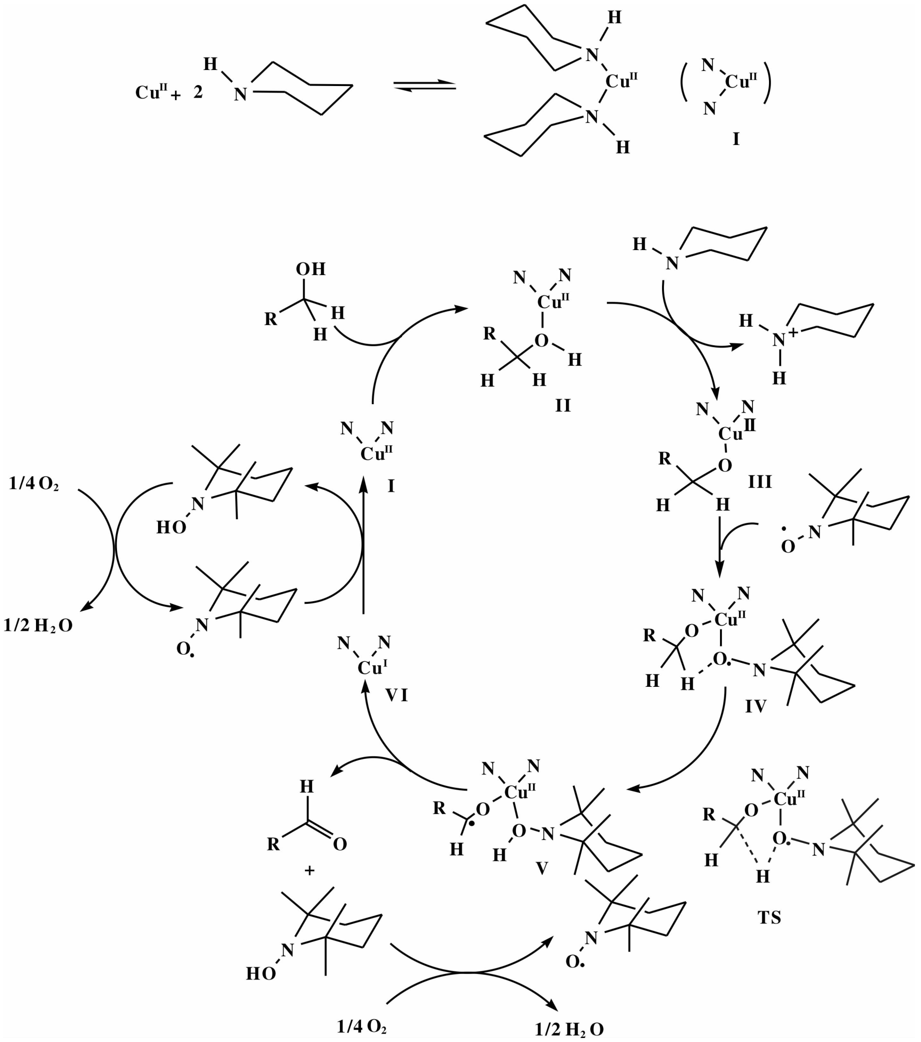


Fig. 2 Coordination of allyl alcohol moiety as a bidentate ligand with copper ion

2.2 The possible Mechanism

Several mechanisms have been proposed for the Cu^{2+} or Cu^{+}/TEMPO catalyzed oxidation of alcohols by oxygen. The first mechanism proposed by Semmelhack et al[14] involving oxoammonium ion ($TEMPO^{+}$) proved to be inaccurate[46]. Later Sheldon et al[17, 47] proposed an alternative mechanism, in which the TEMPO radical and the alkoxide anion are both coordinated to Cu (II) confirmed by others[46]. Very recently, a non-coordinated mechanism was proposed by Stahl[22], but it can not explain the big difference of the oxidation of primary and secondary benzylic alcohols. Based on our experimental results in combination with the mec- hanism proposed by Sheldon[17, 47], we proposed a possible mechanism (Scheme 2) for the novel catalyst system catalyzed oxidation of alcohols.



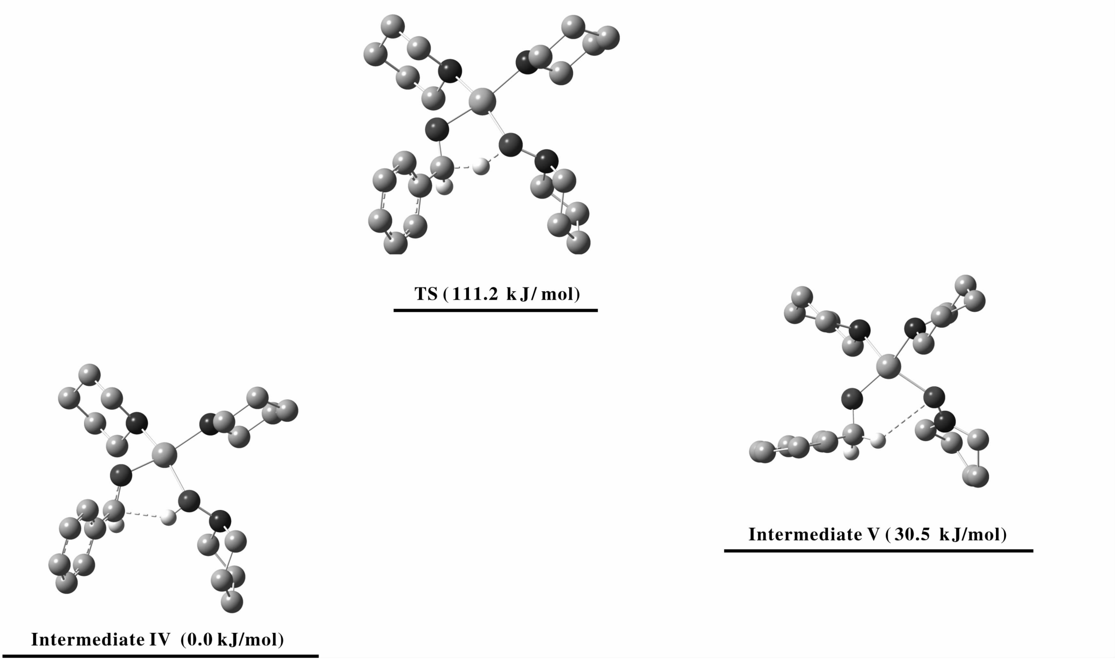
Scheme 2 Proposed possible mechanism for the oxidation of alcohols catalyzed by $CuBr_2$/TEMPO/piperidine

First, two piperidine molecules coordinate with copper (II) to generate complex I. Then a alcohol coordinates to the copper(II) complex I to give complex II, which is converted to the alkoxide complex III by the abstraction of proton with piperidine as base. The subsequent steps are the same as those in the mechanism proposed by Sheldon[17, 47]. TEMPO coordinates to the copper (II) ion with O→Cu bond to give IV. Then the α-hydrogen is transferred to the oxygen atom of TEMPO resulting in a copper complex of TEMPOH and a RHC · -O$^-$ radical V. The intramolecular transfer of one electron from the RHC · -O$^-$ radical to Cu (II) leads to the aldehyde, TEMPOH and a Cu(I) species VI. Complex I is then regenerated by the TEMPO-mediated oxidation of VI, and TEMPO is regenerated by the aerobic oxidation of TEMPOH.

To test the possible mechanism, we have computationally studied the key intermediates IV, V and the transition state by density functional theory (DFT). The geometric and energetic parameters of intermediates and possible transition state are listed in Table 5 and structures are displayed in Fig. 3.

Table 5 Gibbs free energies and interatomic distances for the intermediates and transition state calculated at the B3LYP/6-31G(d)/LANL2DZ level

Intermediates or transition state	Gibbs free energy /(kJ · mol^{-1})	Distance/nm			
		N-**O**-**H**-C(OH)	N-O-**H**-**C**(OH)	N-O	C-O
IV	0	0.2796	0.1102	0.1293	0.1408
TS	111.2	0.1266	0.1374	0.1404	0.1354
V	30.5	0.0997	0.2092	0.1419	0.1342


TS (111.2 kJ/mol)

Intermediate V (30.5 kJ/mol)

Intermediate IV (0.0 kJ/mol)

Fig. 3 Geometries and energies of intermediates IV, V and the transition state, calculated at B3LYP/6-31G(d)/LANL2DZ level

As shown in Table 5 and Fig. 3, when the α H transfers from the carbon atom to the oxygen atom, simultaneously with this, the N-O bond length is increased and the C-O bond is gradually shortened to the double bond. Our calculation results show that the reaction mechanism that we hypothesized is reasonable.

3 Conclusion

In conclusion, a novel and simple catalyst system, composed of $CuBr_2$, TEMPO and piperidine, for the oxidation of primary benzylic alcohols to aldehydes has been developed. Piperidine, in the catalyst system, acts as both a base and a N-donor ligand. Various primary benzylic alcohols are quantitatively oxidized to the corresponding aldehydes by oxygen in acetonitrile catalyzed by the catalyst system at 50 ℃. However, the novel catalyst system is not effective in the oxidation of secondary benzylic alcohols, primary aliphatic alcohols and allylic alcohols. This chemoselectivity may be useful for selective oxidations of alcohol in synthetic organic chemistry.

Acknowledgment

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用于催化氧气氧化苄醇到醛的新型且简单的催化体系(溴化铜/TEMPO/哌啶)

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摘要: 构建了一个可用于催化氧气氧化苄醇类醇到醛的新型催化体系(溴化铜/四甲基哌啶氧化物/哌啶). 该体系以乙腈为溶剂, 可以在50 ℃下高活性和选择性地催化氧气将含不同取代基的苄醇氧化为相应的醛. 然而, 该体系对于仲醇、脂肪族伯醇以及烯丙醇类型醇的氧化没有催化活性.

关键词: 苄醇类醇; 氧化; 溴化铜; 四甲基哌啶氧化物; 哌啶