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TEMPO-Copper(II) Diimine-Catalysed Oxidation of Benzylic Alcohols in Aqueous Media

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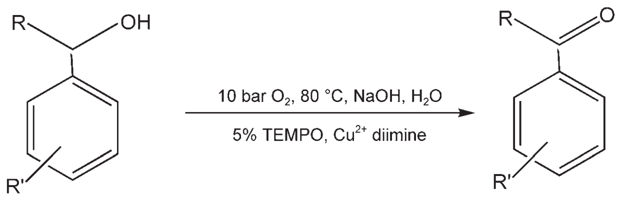
Abstract: *In situ* generated copper(II)-diimine complexes combined with TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl radical) were studied in the oxidation of benzylic alcohols, the focus being on enviromentally benign reaction conditions. In this respect, reactions were studied in aqueous alkaline solutions and dioxygen was used as an end oxidant. This simple catalytic system turned out to be highly efficient and selective in the oxidation of primary and secondary benzylic alcohols to their corresponding carbonyl compounds. Under optimised reaction conditions [5 mol% of TEMPO, 3 mol% of copper(II) diimine, pH 12.6–13.5, 80 °C, 10 bar O_2] benzyl alcohol was quantitatively and selectively oxidised to benzaldehyde. According to ESI-MS studies, coordination of TEMPO, as well as deprotonated benzyl alcohol to the parent copper-diimine complex in aqueous solutions is feasible. Supported by these observations a plausible reaction mechanism is proposed for the oxidation reaction.

Keywords: alcohols; aqueous-phase catalysis; copper; green chemistry; oxidation; TEMPO

Introduction

The selective catalytic oxidation of alcohols to their corresponding carbonyl compounds is an important but challenging task for modern organic synthesis and the chemical industry.[1] Selective oxidation of benzylic alcohols to aldehydes is a particularly useful chemical transformation, as these aldehydes are important intermediates in the synthesis of other organic compounds, ranging from pharmaceuticals to plastic additives as well as in the processing of perfume and flavouring compounds and in the preparation of certain aniline dyes in the textile industry.[2] Many stoichiometric oxidants are known for the oxidation of alcohols such as chromates, hypochlorite, permanganates, and others,[3] however their main disadvantage is that most of them are toxic and produce large amounts of waste. In this respect, non-waste-producing oxidants such as air, dioxygen or hydrogen peroxide, provide a base for more enviromentally friendly and relatively cheap systems but activation of these oxidants with catalysts is needed.[4]

The use of persistent (TEMPO – 2,2,6,6-tetramethylpiperidinyl-1-oxyl, and its derivatives) or non-persistent (PINO – phthalimide-*N*-oxyl) nitroxyl radicals in oxidation processes seems to offer a significant improvement for several catalytic systems with transition metal complexes[5]. Recently, Sheldon et al.[6] reported an efficient system for the air oxidation of alcohols that consists of TEMPO with Cu(II)/bipyridine complexes. Although this system permits the effective oxidation of primary alcohols under mild conditions, it requires water/acetonitrile (2/1) solutions and additional base (*t*-BuOK). To further develop oxidation reactions towards environmentally benign processes, consideration must also be given to the reaction media. Non-toxic solvents, including ionic and supercritical liquids, have recently become popular,[7] but from an economic and environmental viewpoint, water still remains the undisputed solvent of choice, and has recently been the subject of significant interest in catalytic reactions.[8] In the light of this, we extended our studies on the oxidation capability of *in-situ* generated copper(II) complexes[9] towards the TEMPO-mediated oxidation of benzylic alcohols in aqueous media. The combination of TEMPO and Cu(II) turned out to be an efficient oxidation system for both primary and secondary benzylic alcohols using water as the only solvent, and dioxygen as the oxidant (Scheme 1).



R = H, Me
R' = H, 3-MeO, 2,4-di-MeO, 2,5-di-MeO, 3,4-di-MeO, 2,4,5-tri-MeO, 3,4,5-tri-MeO, 3,4-di-Cl

Scheme 1.

Results and Discussion

As shown in our previous studies, catalysts for veratryl alcohol oxidation can be prepared *in situ,* simply by mixing a ligand and metal ion precurssor in an alkaline water solution.[9] A similar approach for catalyst preparation, now accomplished with TEMPO, was applied here. Reaction conditions, optimised previously for Cu(II)(phen) catalyst, were chosen for primary studies and the oxidation of benzyl alcohol was chosen as a model reaction (Table 1).

In the presence of TEMPO, the oxidation capability of *in situ* generated Cu(II) diimine complexes is significantly improved, as can be seen for runs 10 and 7 in Table 1. The oxidation of benzyl alcohol at 80 °C in alkaline aqueous solution proceeds nearly quantitatively when a catalytic amount of TEMPO (5 mol% *vs.* substrate) together with *in situ* generated $CuBr_2$/phenanthroline (3 mol% *vs.* substrate) or $CuSO_4$/phenanthroline complexes were used (Table 1, runs 1 and 2). The selectivity of the catalysts was also excellent (98–99%). The system based on the bipyridine ligand gave also high conversions under similar reaction conditions while quantitative conversions of benzyl alcohol were achievable when the pH of the reaction solution is slightly lowered (Table 1, runs 3 and 4). We can assume that the reasons for the improved activity at lower pH are related to the complex distribution in alkaline aqueous solutions as previously described for $Cu(bipy)_2$ catalysts.[9e] When the alcohol/catalyst ratio is increased (100:1), the difference among the catalyst systems becomes more apparent. The catalyst based on $CuSO_4$ and phenanthroline gives high conversions and selectivities, while the $CuBr_2$/phen-based system also provides high selectivity, but with significantly reduced conversions (Table 1, runs 7 and 8). Bipyridine as a ligand also facilitates high conversions with a high alcohol/catalyst ratio, but with a marked reduction in selectivity due to benzoic acid formation (Table 1, run 5 and 6). Interestingly, in this case $CuBr_2$ as a metal source provided better efficiency than the $CuSO_4$ derivative.

This prompted us to study the influence of other Cu(II) salts including $Cu(NO_3)_2$, $Cu(OAc)_2$, $CuCl_2$. In general, they gave fairly similar conversions of benzyl alcohol as those with $CuSO_4$/phen and $CuBr_2$/bipy under similar reaction conditions. In addition, from a series of different bases, including LiOH, NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$ and *t*-BuOK, NaOH turned out to be the most efficient. Due to the fact that the $CuSO_4$/phen/TEMPO/NaOH combination provides high activity and selectivity, and because it is a halogen-free system, it was chosen for further studies. The time dependency of the activity of the $CuSO_4$/phenanthroline system was studied. After 1.5 h, only 25% of the alcohol was oxidised whereas after 3 h, 90% conversion was reached (Table 1, runs

Table 1. Oxidation of benzyl alcohol with in situ made TEMPO/[Cu]/ligand system.[a]

Run	*t* [h]	pH	Conversion[b] [%]	Selectivity[b] [%]	Catalytic system TEMPO	Catalyst (substrate:catalyst)	Ligand
1	5	13.5	100	98	+	$CuBr_2$ (33:1)	phen
2	5	13.5	100	99	+	$CuSO_4$ (33:1)	phen
3	5	13.5	92	100	+	$CuBr_2$ (33:1)	bipy
4	5	12.6	100	100	+	$CuBr_2$ (33:1)	bipy
5	5	12.6	89	78	+	$CuBr_2$ (100:1)	bipy
6	5	12.6	77	67	+	$CuSO_4$ (100:1)	bipy
7	3	13.5	90	99	+	$CuSO_4$ (100:1)	phen
8	3	13.5	77	99	+	$CuBr_2$ (100:1)	phen
9	1.5	13.5	25	100	+	$CuSO_4$ (100:1)	phen
10	3	13.5	44	100	-	$CuSO_4$ (100:1)	phen
11	3	13.5	3	100	+	-	phen
12	3	13.5	3	100	+	$CuSO_4$ (100:1)	-

[a] *Reaction conditions:* 3 mmol of alcohol, TEMPO (0.15 mmol , 5 mol% *vs.* substrate), $CuSO_4$ 0.09 mmol, 3 mol% and 1,10-phenanthroline (phen) or bypirydine (bipy) (runs 1–4) or 0.03 mmol of $CuSO_4$ and diimine (runs 5–11), 10 bar O_2, 80 °C, NaOH water solution up to 10 mL total volume.

[b] Conversions and selectivities are based on GC measurements. Accuracy ±1%. The main side product in these reactions is benzoic acid.

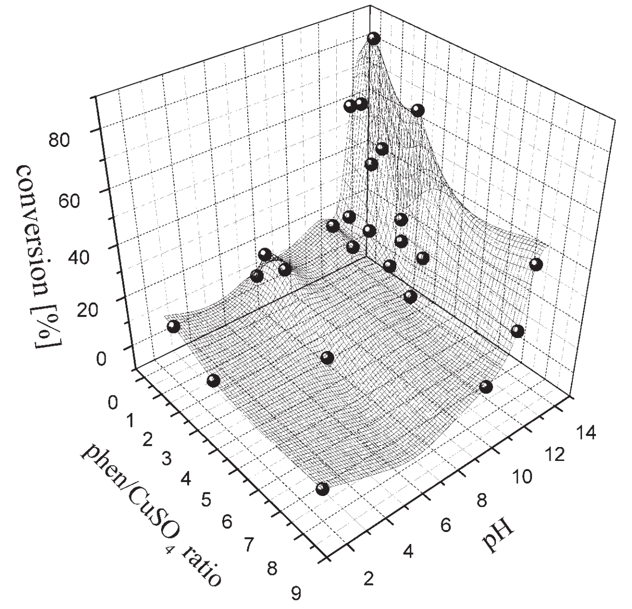


Figure 1. Optimisation of the catalytic system. Black dots represent the experimental points. *Reaction conditions:* Benzyl alcohol (3 mmol), TEMPO (5 mol%), $CuSO_4$ (1 mol%) and phen (0–8%) at differrent pH (1–14). Reaction time 3 h.

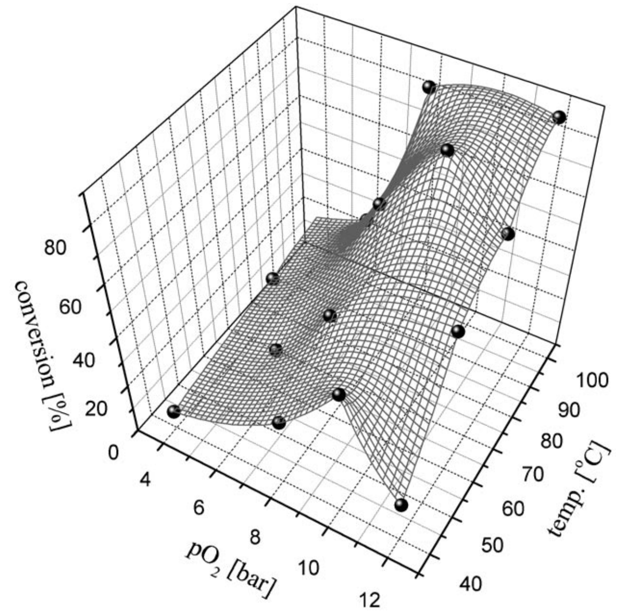


Figure 2. The effect of reaction temperature and pressure as a function of benzyl alcohol conversion. *Reaction conditions:* 5 mol% of TEMPO and 1 mol% of $CuSO_4$/phen (1:1), 3 h.

9 and 7), which indicates not only the lengthy induction time but also the stability of the catalyst system under the applied reaction conditions. The control reaction without TEMPO gave a conversion of 44% after 3 h, while reactions without $CuSO_4$ or phenanthroline produced approximately 3% benzaldehyde (Table 1, runs 10–12). These results underline the importance of each catalyst component for the efficient oxidation reaction.

As shown previously for the *in situ* made Cu(phen) catalyst, pH and ligand concentration are crucial factors which determine catalytic activity in aqueous solution and these two parameters have a strong interdependency.[9] The three-dimentional plot in Figure 1 summarises the optimisation results for the $CuSO_4$/phen/TEMPO/NaOH system with the focus being on maximum benzyl alcohol conversion. Apparently, the most effective system is achieved with rather high pH (12–14) and with a 1:1 ligand/metal ratio. Interestingly, for the $Cu(phen)_n$ systems without TEMPO the optimised ligand to metal ratio was 2:1, which leads to pentacoordinated Cu(II) complexes of the type $Cu(phen)(OH)_2$.[9e] In these Cu(II) complexes two coordination sites are available for further coordination, e.g., for the substrate. Also, the results herein indicate that for optimum activity at least two coordination sites should be available. Presumably the coordination of both substrate and TEMPO to one catalytic centre might be beneficial.

The influence of both reaction temperature and O_2 pressure was studied for the optimised catalyst system. As shown in a 3-D plot (Figure 2) at lower pressure (< 6 bar) and temperature (< 60 °C) conversions are rather low (< 10%), whereas at temperatures above 60–80 °C and pressure of about 8–10 bar the alcohol conversions markedly increased (up to 90%). Although thermally rather stable, the catalytic activity does not unexpectedly increase linearly with the O_2 pressure, but reaches its maximum at 8–10 bar. The available results do not provide adequate reasons for the reduced activity but we can assume that this phenomenon is linked to stability of the catalytic system at high O_2 concentrations.

Although Cu(diimine) alone can oxidise benzyl alcohol with moderate activity (40%, Table 1), addition of a catalytic amount of TEMPO markedly improved the catalytic system, and in the best case leds to quantitative substrate oxidation. The influence of the Cu(II)-diimine catalyst and TEMPO concentrations on the efficiency of the catalytic system were further studied. As illustrated in Figure 3, an increase in the catalyst concentration in the absence of TEMPO significantly improves the activity when more than 5% catalyst loading is applied, however, the conversion remains under 80%. Similar conversions are also attainable if a 1% catalyst loading combined with high TEMPO concentration (above 8%) is used. For a quantitative conversion of benzyl alcohol, catalyst concentrations between 3 and 4% and 5–8% TEMPO are needed.

To demonstrate the applicability and limits of this simple catalyst system, the optimised reaction conditions (5 mol% of TEMPO, 3 mol% of Cu^{2+}, ligand to

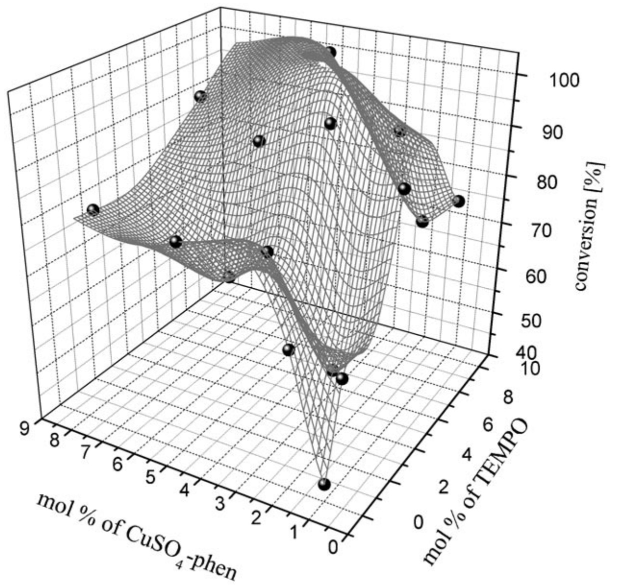


Figure 3. The effect of catalyst and TEMPO concentration on the conversion of benzyl alcohol. *Reaction conditions:* Cu:phen = 1:1, 10 bar of O_2, 80 °C, 3 h

metal ratio = 1:1, high pH) were chosen for a further study of the catalyst in the oxidation of different alcohols. Besides benzyl alcohol, also trimethoxy-substituted primary benzylic alcohols, as well as di- and mono-substitued ones can be smoothly and selectively oxidised to their corresponding aldehydes with moderate to good yields (Table 2).

Based on extended oxidation experiments with a series of substrates, the optimal reaction conditions evidently depend on the substrate as well. For example, with the substrates in runs 2, 7 and 8, a lower pH (12.6) gave higher conversions than those measured at pH 13.5. In addition with some substrates higher catalyst loadings (5 mol%) were beneficial. Further fine tuning of the structure of the phenanthroline did not improve the efficiency of the catalyst, for example, only with a few substrates, like 3,5-di-MeO-benzyl alcohol did the use of 4,7-dihydroxyphenanthroline gave better conversions (Table 2, runs 6 and 7. See also S1 in Suplementary Information).

Unlike the previously reported Cu/TEMPO catalyst,[6] the current catalyst system can also oxidise secondary benzylic alcohols. Under the applied conditions, 1-phenyl-1-ethanol can be oxidised to acetophenone with good yield and 3-MeO-α-Me-benzyl alcohol can be converted to the corresponding ketone in moderate yield (Table 2, runs 10 and 11). Both of these oxidations are also highly selective. As a limitation, aliphatic alcohols, both primary (1-hexanol), and secondary (2-pentanol), were not oxidised (Table 2, runs 12 and 13). These results clearly point out that benzylic activation of alcohol is needed for the efficient catalytic oxidation.

There are several mechanisms proposed for the TEMPO-copper assisted alcohol oxidation, mainly based on UV-Vis or kinetic experiments.[10a] Some of the most recent publications suggest the simultaneous coordination of TEMPO and alcohol to the metal centre and reaction in the coordination sphere[6,8,10] whereas other proposed mechanisms are based on the activity of the nitrozium cation.[11] The role of basic conditions remains unclear, but the presence of sodium hydroxide likely facilitates the formation of Cu(diimine)(OH) species and assists the deprotonation of alcohol.[6,9]

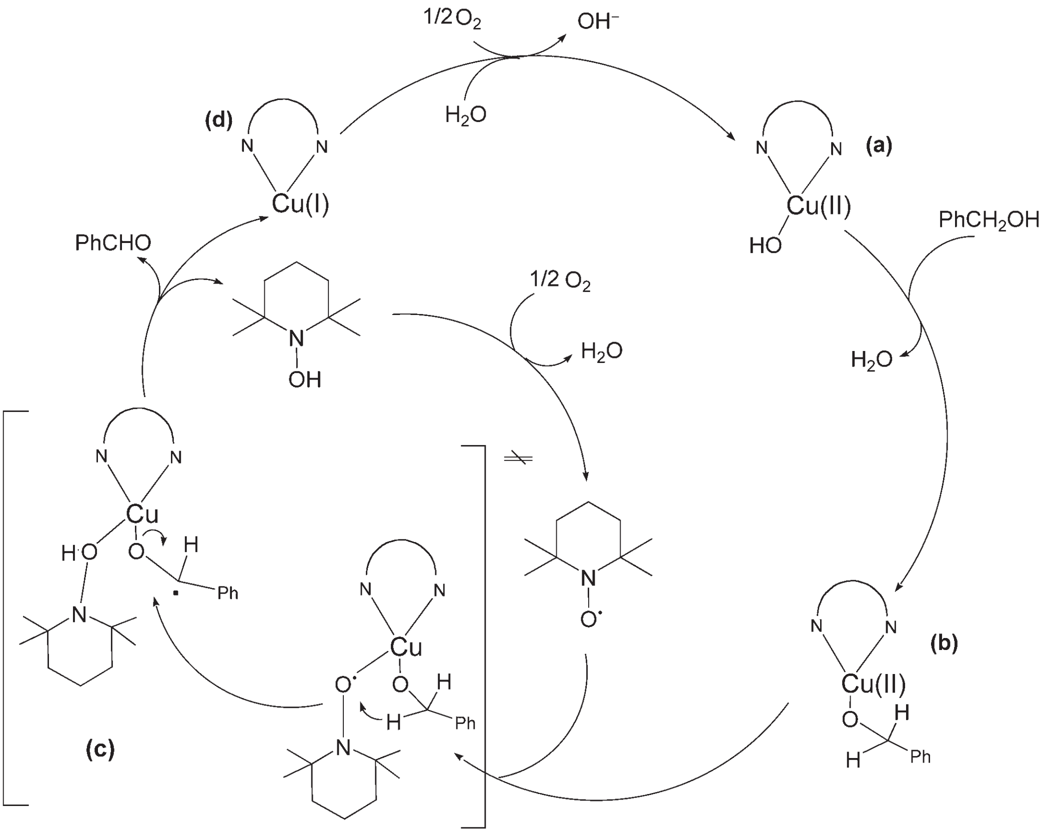
ESI-mass spectrometry is an effective method for the characterisation of the reaction intermediates.[12] To adapt this technique to the present system, and to avoid the excessive formation of sodium adducts in the ionisation, we applied neutral conditions (pH ~ 7) for the measurements. In the water solutions consisting of $CuSO_4$ and bipyridine or phenanthroline, few

Table 2. Oxidation of selected alcohols with TEMPO/$CuSO_4$/phen system.[a]

Run	Substrate	Time [h]	Temp. [°C]	Substrate/catalyst	pH	Conversion [%]	Selectivity [%]
1	2,4,5-tri-MeO-benzyl alcohol	5	100	20	13,5	100	99
2	3,4,5-tri-MeO-benzyl alcohol	5	100	20	12,6	77	99
3	2,5-di-MeO-benzyl alcohol	5	100	20	13,5	96	99
4	2,4-di-MeO-benzyl alcohol	5	100	20	13,5	100	100
5	3,4-di-MeO-benzyl alcohol	5	100	20	13,5	99	97
6	3,5-di-MeO-benzyl alcohol	5	100	20	13,5	55	94
7[b]	3,5-di-MeO-benzyl alcohol	5	100	20	12,6	100	99
8	3,4-di-Cl-benzyl alcohol	3	80	100	12.6	68	100
9	3-MeO-benzyl alcohol	3	80	100	13.5	65	100
10	1-Ph-1-ethanol	3	80	100	13.5	82	100
11	3-MeO-α-Me-benzyl alcohol	5	100	20	13.5	62	99
12	1-hexanol	3	80	100	12.6/13.5	no reaction	-
13	2-pentanol	3	80	100	12.6/13.5	no reaction	-

[a] *Conditions:* 3 mmol of substrate, 5 mol% of TEMPO, 10 bar O_2. Conversions and selectivities based on GC.

[b] 4,7-Dihydoxyphenanthroline was used instead of phenanthroline.



Scheme 2. Proposed mechanism for the catalytic oxidation of benzyl alcohols by O_2 and a TEMPO-Cu(II)-diimine system in alkaline aqueous media.

peaks appeared in ESI-MS ($m/z = 316$ and 375 for bipy, $m/z = 339$ and 423 for phen) due to the formation of [Cu(diimine)(SO_4)] and $[Cu(diimine)_2]^{2+}$ complexes. This is in accordance with the results obtained from the optimisation of the ligand to metal ratio and supports the discussion therein. The addition of TEMPO to these solutions induced new peaks coresponding to Cu(TEMPO)(phen) or Cu(TEMPO)(bipy) species (ESI-MS signals at $m/z = 399$ and 375, respectively). Similarly, even in these neutral conditions, benzyl alcohol alone can coordinate to the Cu-diimine complexes and adequate alkoxide species are formed. In fact, the peaks corresponding to Cu($PhCH_2O$)(bipy) ($m/z = 327$) and Cu($PhCH_2O$)(phen) ($m/z = 351$) were also observable when TEMPO was present. Thus, both Cu(TEMPO)(diimine) and Cu($PhCH_2O$)(diimine) complexes can coexist, but the presence of the Cu(TEMPO)($PhCH_2O$)(bipy) complex could not be confirmed. It is likely that, when formed, this species reacts further rapidly and aldehyde is released.

On the basis of the oxidation results and the ESI-MS measurements for the model system, a mechanism for the Cu(II)/TEMPO system is proposed (Scheme 2). Our previous studies on the Cu(II) diimine complexes in alkaline media and the present optimisation results suggest that the *in situ* formation of a Cu(diimine)(OH) [or Cu(diimine)] complex is needed for an efficient oxidation reaction.[9] As shown by ESI-MS measurements, this complex can coordinate benzyl alcohol ($PhCH_2OH$), and water is released as a side product (Scheme 2a). Obviously, the abstraction of β-hydrogen from coordinated alcohol should occur, after which the aldehyde is produced (Scheme 2c). We assume that this fundamental step in the current system requires a benzylic activation and is driven by TEMPO (Scheme 2c). TEMPO-OH is formed simultaneously and is latter reoxidised to TEMPO by dioxygen, as described in previously proposed mechanisms.[6] The nascent Cu(I)(diimine) complex formed (Scheme 2d) can be then reoxidised by O_2 to Cu(II), which is a well-known step for catalytic systems containing copper complexes,[13] although, alternatievely TEMPO can be involved in that process as well.[6]

This mechanism shares similarities with those of our previous studies on Cu-catalysed oxidations[9] accomplished with some previously-published TEMPO-based systems.[6] The, intermediate species observed by ESI-MS, Cu(diimine)(TEMPO) and Cu(diimine)($PhCH_2O$) may have a role in the replenishment of the active species as postulated in former publications.[5a,6,10]

Conclusions

In conclusion, a novel catalytic system for the efficient and selective oxidation of benzylic alcohols, in alkaline aqueous solutions has been developed. The effects of different reaction conditions were carefully studied to achieve the maximum substrate conversion. These studies have shown that high pH, temperature and O_2 pressure, as well as a 1:1 ratio of ligand:Cu are needed for effective benzaldehyde production. The former Cu(II)-diimine system used mainly for the oxidation of veratryl alcohol in water, is now markedly improved by the use of a catalytic amount of TEMPO radical. Conversion of primary and secondary alcohols into their corresponding carbonyl products was achieved both efficiently and selectively. The use of "green" reagents, such as dioxygen as an oxidant and water as the only solvent makes the system attractive for environmentally sustainable processes. It is important to note that the ESI-MS experiments confirmed the existence of the Cu(diimine)(TEMPO) and Cu(diimine)($PhCH_2O$) species, thus providing an insight into the catalytic system.

Experimental Section

Materials

Benzyl alcohols and other reagents were used as received from commercial sources without further purification.

General Procedure

The oxidation reactions were carried out as described previously in standard glass test tubes (up to 14 test tubes per one run) placed in a 1-L steel reactor.[9b] The reactor was placed on a magnetic stirrer and thermostated in an oil bath. Reaction products were isolated by extraction with 10 mL of ethyl acetate, and analysed quantitatively by GC (Agilent 6890 chromatograph, Agilent 19091 J-413 capilary column 0.32 mm × 30 m × 0.25 μm, FID detector) using internal standards. To estimate the amount of benzoic acid formed during the reaction, samples were acidified with hydrochloric acid before extraction with ethyl acetate, then the acid was converted into a methyl ester by reaction with 0.1 mL 0.25 M TMSH (trimethylsulfonium hydroxide, Fluka reagent) prior to GC analysis. Products were identified by GC-MS analyses (Agilent 6890N equiped with Agilent 5973 mass selective detector, HP 19091 L-102 capilary column, 200 mm × 24 m × 0.31 μm).

Mass Spectrometry

High resolution ESI-MS measurements were performed using a Bruker Microtof LC mass spectrometer in water solutions, with sodium formate as a reference standard. The peaks observed for the mixture of $CuSO_4$ and phenanthroline were: $m/z = 339.9586$ corresponding to $Cu(SO_4)$(phen) (calculated: 339.9573, error −3.9 ppm) and $m/z = 423.0659$, $Cu(phen)_2$ complex (calculated: 423.0665, error 1.3 ppm). After the addition of TEMPO the following peaks were observed: $m/z = 399.1369$ due to Cu(phen)(TEMPO) formation (calculated: 399.1366, error −0.8 ppm), after addition of benzyl alcohol a peak at $m/z = 351.0574$ appears for Cu($PhCH_2O$)(phen) (calculated: 351.0553, error 5.9 ppm).

For the mixture of $CuSO_4$ and bipyridine the following peaks were observed: $m/z = 315.9587$ corresponding to Cu(bipy)(SO_4) (calculated: 315.9574, error −4.12 ppm) and $m/z = 375.0677$ corresponding to $Cu(bipy)_2$ (calculated: 375.0665, error −3.0 ppm). The addition of TEMPO results in the formation of a peak at $m/z = 375.1339$ due to the Cu(bipy)(TEMPO) complex (calculated: 375.1366, error 7.2 ppm), while after the addition of benzyl alcohol a peak at $m/z = 327.0579$ appears for Cu($PhCH_2O$)(bipy) (calculated: 327.0553, error 7.9 ppm).

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