Room Temperature Aerobic Copper–Catalysed Selective Oxidation of Primary Alcohols to Aldehydes

Patrick Gamez,[a,b] Isabel W. C. E. Arends,[b] Roger A. Sheldon,[b,*] Jan Reedijk[a]

[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P. O. Box 9502, 2300 RA Leiden, The Netherlands,
Fax: (+31)-71-527-4671

[b] Laboratory for Biocatalysis and Organic Chemistry, Department of Biotechnology, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
Fax: (+31)-15-278-1415, e-mail: r.a.sheldon@tnw.tudelft.nl

Received: March 3, 2004; Accepted: May 27, 2004

Dedicated to Joe Richmond on the occasion of his 60th birthday.

Abstract: A novel and very mild method for the oxidation of primary alcohols to aldehydes with excellent conversions has been developed. The reaction is carried out under air at room temperature and is catalysed using a [copper(II)-(N ligand)$_n$] complex with TEMPO and a base as co-catalysts. In this paper, the performance of a series of N-containing ligands, as well as different copper(II) salt precursors in different solvents are reported. Best results are obtained in acetonitrile/water as solvent using a copper(II) catalyst generated *in situ* from a Cu(II) salt with weak or non-coordinating anions and bipyridine ligands with electron-donating substituents. A reaction mechanism is postulated which resembles that of galactose oxidase, and in which TEMPO seems to be involved as a hydrogen acceptor.

Keywords: alcohols; aldehydes; biomimetic oxidation; copper; galactose oxidase; TEMPO

Introduction

The selective oxidation of primary alcohols to the corresponding aldehydes, which can be performed by a variety of methods, remains one of the most important functional transformations in the synthesis of fine chemicals.[1–5] Typically, the oxidation of alcohols is accomplished by stoichiometric amounts of metallic oxidants, mostly chromium(VI) reagents.[6,7] Safety hazards associated with these oxidants and their toxic by-products, and the difficulty to work-up the reaction mixtures are the main problems of such processes. Consequently, a number of catalytic methods using complexes containing transition metals, such as palladium, rhodium or ruthenium and clean oxidants, such as dioxygen or hydrogen peroxide has been developed.[8–13] Nevertheless, many of these catalytic systems still exhibit some drawbacks: (1) a low tolerance towards water, while water is formed stoichiometrically in the reaction; (2) the combination of flammable solvents with dioxygen at elevated temperatures, which may result in dangerous situations; and (3) an often tedious work-up procedure.

Copper is an essential trace element and it is, after iron and zinc, the most abundant transition metal in the human body.[14] Thus, copper is found in various metalloproteins, especially in enzymes implicated in the binding of molecular oxygen or in mild and highly selective aerobic oxidative transformations.[15] It is therefore surprising that only a few examples using cheap and "green" copper catalysts and molecular oxygen[16–18] or hydrogen peroxide are known so far.[19–26] Markó et al.[20] first reported the efficient use of CuCl(Phen-DEADH$_2$) (Phen = 1,10-phenanthroline; DEADH$_2$ = diethyl hydrazinodicarboxylate) catalytic system for the oxidation of primary and secondary alcohols under dioxygen at 90 °C. Stack et al.[21] described a Cu(II) species, namely [Cu(II)BSP] where BSP symbolises a salen-type ligand with a binaphthyl backbone and thioether functions, able to catalyse the oxidation of benzylic and allylic alcohols under dioxygen at room temperature. Wieghardt et al.[22] similarly reported the catalytic oxidation of primary and secondary alcohols by a dinuclear Cu(II)-phenoxyl complex at 20 °C under air with moderate conversions. More recently, Knochel et al.[23] followed by Gree et al.[25] developed CuCl-TEMPO catalytic systems for the oxidation of alcohols under dioxygen, at 90 °C under fluorous biphasic conditions and at 65 °C in an ionic liquid, respectively. Lately, Punniyamurthy et al.[26] reported the oxidation of alcohols to the corresponding carboxylic acid analogues and ketones catalysed by a salen-type Cu(II) complex with H_2O_2 as the source of oxygen, at 80 °C in acetonitrile.

 DOI: 10.1002/adsc.200404063

We recently developed a catalytic procedure for the selective aerobic oxidation of primary alcohols to aldehydes based on a $CuBr_2$(Bipy)-TEMPO system (Bipy = 2,2′-bipyridine).[27] This paper reports the use of a series of closely related N-donor-containing ligands for this reaction as well as different copper salts or solvents in order to determine which parameters can affect and/or improve the catalytic activity.

Results and Discussion

Oxidation of Benzyl Alcohol to Benzaldehyde Catalysed by [$CuBr_2$(2,2′-bipyridine)]-TEMPO

The oxidation of primary alcohols to their corresponding aldehydes can be carried out at room temperature in air with a [Cu(II)(N-ligand)$_n$] complex (where n = 1 for didentate ligands and n = 2 for monodentate ones) as catalyst and 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and a base as co-catalysts (Figure 1).

As shown in Table 1, the use of an N-donor ligand is essential. Only 6% of benzyl alcohol was converted to benzaldehyde in 1.5 h when no 2,2′-bipyridine (Bipy) was added (entry 1). This can well be due to the very poor solubility of the copper catalyst without ligand. The presence of TEMPO is crucial for the oxidation, as no catalytic activity could be observed without it (entry 2). The [$CuBr_2$(2,2′-bipyridine)]-TEMPO catalytic system is active without base, but 24 hours are required for the total conversion of benzyl alcohol to benzaldehyde (entry 3). With 5 mol % potassium *tert*-butoxide added, only 2.5 hours are needed to fully and selectively oxidise benzyl alcohol (entry 4). The function of the basic co-catalyst (sodium or potassium hydroxide could equally be employed in place of *t*-BuOK) is probably to deprotonate the alcohol and, thus, favour the coordination of the resulting alcoholate to the copper species, resulting in an increase of the activity.

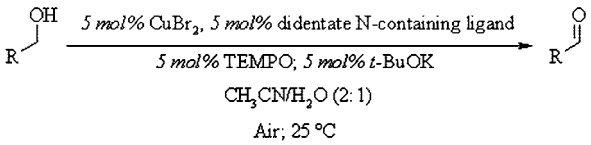

Figure 1. $CuBr_2$-catalysed oxidation of primary alcohols.

Table 1. $CuBr_2$-catalysed oxidation of benzyl alcohol to benzaldehyde.[a]

Entry	Bipy	TEMPO	*t*-BuOK	Conversion [%]
1	no	yes	yes	6
2	yes	no	yes	No reaction
3	yes	yes	no	27[b]
4	yes	yes	yes	83[c]

[a] Selectivity > 99% based on GC; conversions were determined after a reaction time of 1.5 h.
[b] 100% conversion after 24 h.
[c] 100% conversion after 2.5 h.

The exact role of TEMPO remains unclear. It might act as a hydrogen acceptor during the proposed catalytic cycle (Figure 2).[28] The alcoholate coordinates to the copper(II) complex **I** to lead to alkoxy species **II**. TEMPO most likely coordinates to the copper(II) ion in an η^2 manner (**III**) as reported by Caneshi et al.[29,30] The β-hydrogen is then transferred to TEMPO resulting in a radical-TEMPOH copper species (**IV**). Intramolecular one-electron transfer leads to the aldehyde, TEMPOH and Cu(I) species (**V**). Finally, species **I** are regenerated by the TEMPO-mediated oxidation of Cu(I) to Cu(II) species (**I**). The catalytic cycle is completed by the aerobic oxidation of the TEMPOH to TEMPO.

Solvent Effect

The choice to use acetonitrile as a solvent was not arbitrary. Indeed, a dramatic effect of acetonitrile on a similar reaction, namely the Cu(II)-catalysed oxidative coupling of 2,6-dimethylphenol has previously been reported.[31] One explanation was the stabilisation of Cu(I) species during the catalytic cycle caused by the coordination of acetonitrile molecules. Therefore, the oxidation reactions were performed in a 2:1 (v/v) acetonitrile/water solvent mixture. As shown in Table 2, water is necessary to obtain catalytic activity (entries 1 and 2). This is probably due to the insolubility of the base in pure acetonitrile. In addition, the amount of water also has an effect on the catalyst performance (entries 2 and 3): only 47% conversion was achieved in 1.5 h. with a 1:2 acetonitrile/water solvent mixture instead of 83% with the 2:1 combination. This may be explained by a decrease in the solubility of the benzyl alcohol in this mixture.

A range of other water-miscible co-solvents in a 2:1 (v/v) ratio with water in the oxidation of benzyl alcohol were tested (Table 2; entries 4 to 6). The use of acetone

Table 2. Influence of the co-solvent/water mixture on the [$CuBr_2$(Bipy)]-catalysed oxidation of benzyl alcohol.

Entry	Solvent mixture (v/v)	Conversion [%]	
		0.5 h	1.5 h
1	Acetonitrile	No reaction	
2	Acetonitrile/Water (2/1)	38	83
3	Acetonitrile/Water (1/2)	24	47
4	Acetone/Water (2/1)	17	48
5	Dioxane/Water (2/1)	9	78
6	Sulfolane/Water (2/1)	36	75
7	Toluene/Water (2/1)[a]	5	9

[a] Biphasic reaction.

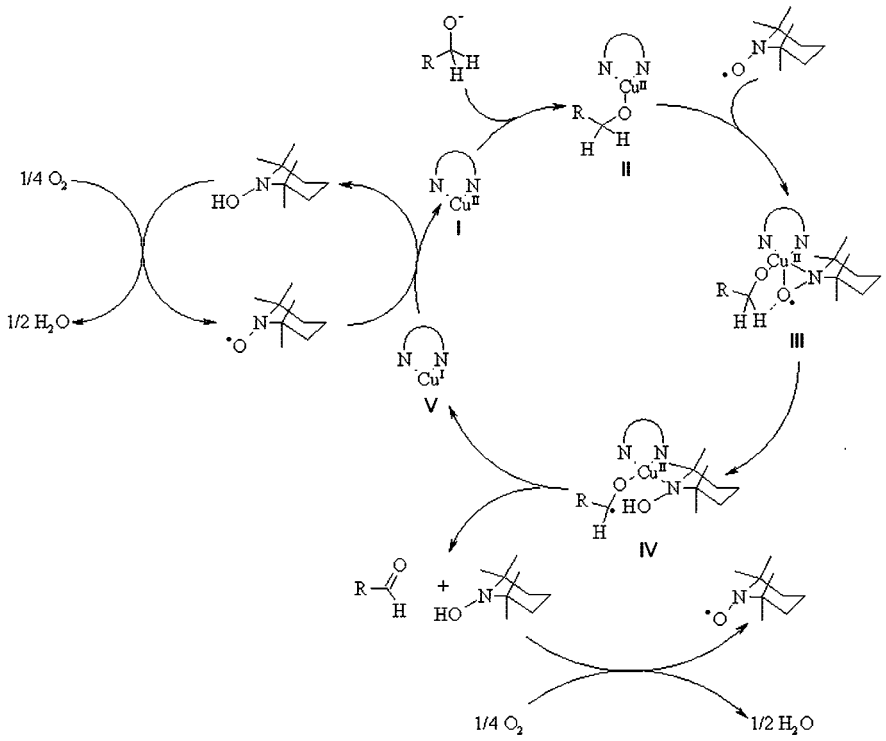

Figure 2. Proposed mechanism of (Cu-N-ligand-TEMPO)-catalysed oxidation of primary alcohols.

instead of acetonitrile led to a lower activity (entry 4). This decrease may be due to the non-coordination of solvent molecules to the metal centre. On the contrary, a very good conversion is achieved with dioxane (entry 5), which is also known to coordinate to copper species albeit weakly.[32] Similar reaction rates to the ones obtained with acetonitrile were obtained when sulfolane was used as co-solvent (entry 6). Once again, the coordination of sulfolane molecules during the catalytic cycle is possible,[33] which probably enhances the activity. Finally, the biphasic oxidation resulting from the utilization of toluene (entry 7) showed a very poor catalytic activity because of an unsatisfactory mixing of the reactants.

Effect of the Ligand Structure and the Copper(II) Salt Precursor

Several N-containing ligands were tested with $CuBr_2$ and the results are reported in Table 3. All N-donors employed led to reasonable to very good conversions. The copper complexes from monodentate ligands are less active than those from the didentate ones, which is most likely related to the smaller association constants. Activities with 1-methylimidazole and 1-benzylimidazole (entries 1 and 2) are comparable while 4-cyanopyridine and 4-methoxypyridine (entries 3 and 4) behave in completely different manners. The reason is certainly the electron-withdrawing and -donating effects of the substituents on the pyridine ring. This is confirmed with the 2,2′-bipyridine derivatives (entries 7, 9 and 10). Indeed, the catalytic activities increase with the donating character of the *para*-substituents, from 83% conversion in 1.5 h for 2,2′-bipyridine (entry 7) to total conversion in 1.5 h for 4,4′-dimethyl-2,2′-bipyridine (MeBipy; entry 9) and in 1 h for 4,4′-dimethoxy-2,2′-bipyridine (MeOBipy; entry 10). The last ligand tried was 1,10-phenanthroline (entry 11) which showed a good catalytic activity of its copper complex.

At this point, it has to be mentioned that, after the end of the oxidation reaction, the copper catalyst is still active. For example, the addition of one more equivalent of benzyl alcohol to the reaction mixture using MeOBipy as ligand led to its total conversion in 3 h. (entry 10). However, the addition of another 5 mol % of TEMPO was necessary (entry 10) for this oxidation to proceed. Indeed, the concentration of TEMPO (determined by GC) stays constant during the course of the reaction and dramatically drops when all the substrate is consumed. TEMPO is deactivated[28,34] through a mechanism which is currently under investigation.

Different copper(II) salts were tested with 2,2′-bipyridine as catalyst precursors for the oxidation of benzyl alcohol and the results are reported in Table 3. Copper(II) chloride and copper(II) nitrate gave the least active catalysts with only 60 and 66% conversion, respectively, after 1.5 h (entries 5 and 6). Copper(II) bromide led to the formation of 83% benzaldehyde in the same reaction time (entry 7). Copper(II) perchlorate was found to be

Table 3. Influence of the copper(II) salt and the ligand on the [CuX_2(ligand)]-catalysed oxidation of benzyl alcohol to benzaldehyde.

Entry	Cu(II) salt + ligand	Conversion [%]	
		0.5 h	1.5 h
1	$CuBr_2$ + 1-methylimidazole	26	53
2	$CuBr_2$ + 1-benzylimidazole	22	68
3	$CuBr_2$ + 4-cyanopyridine	11	12
4	$CuBr_2$ + 4-methoxypyridine	9	78
5	$CuCl_2$ + 2,2′-bipyridine	30	60
6	$Cu(NO_3)_2$ + 2,2′-bipyridine	30	66
7	$CuBr_2$ + 2,2′-bipyridine	38	83
8	$Cu(ClO_4)_2$ + 2,2′-bipyridine	42	90
9	$CuBr_2$ + 4,4′-dimethyl-2,2′-bipyridine	78	100
10	$CuBr_2$ + 4,4′-dimethoxy-2,2′-bipyridine	85	100[a, b]
11	$CuBr_2$ + 1,10-phenanthroline	36	75

[a] 100% conversion to benzaldehyde reached within one hour.
[b] After 2 h reaction time, 10 more mmol of benzyl alcohol were added as well as 0.5 mmol of TEMPO. 100% conversion to benzaldehyde was achieved in 3 h.

the best catalyst precursor with 90% conversion achieved after 1.5 h (entry 8). These differences are likely associated to the propensity for dissociation of the anion from the copper centre. Chloride and nitrate ions are more strongly coordinated to copper than bromide or perchlorate anions, the latest even being non-coordinating. Therefore, it is easier, for the alcoholate, to enter the copper coordination sphere when perchlorate is the counter-ion rather than chloride. In this regard, counter-ions like tetrafluoroborate or triflate are expected to lead to the same results. This is a plausible explanation for the different activities observed.

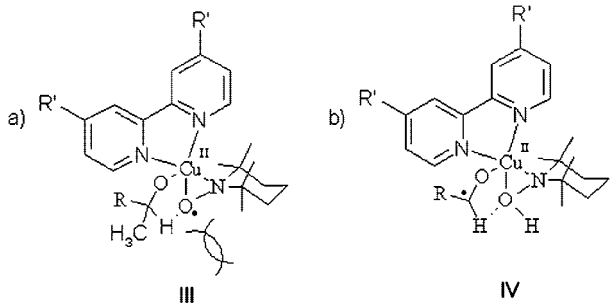

Figure 3. Possible explanations for the lack of reactivity of secondary alcohols: a) Steric hindrance due to the methyl group of the secondary alcohol preventing the formation of species **III** in the catalytic cycle; b) Stabilisation of the radical species **IV** by the second β-hydrogen of the primary alcohol.

Substrate Scope

Various primary benzylic, allylic and aliphatic alcohols have been successfully oxidized to their corresponding carbonyl derivatives (Table 4). Benzyl alcohol is totally and selectively converted to benzaldehyde in 2.5 hours (entry 1). The same result can be achieved in 1 hour when MeOBipy is used as a ligand (see Table 3, entry 10). This corresponds to a TOF of 20 h^{-1} which is an excellent result for a room temperature oxidation reaction involving a copper catalyst. Surprisingly, no reaction was observed with 1-phenylethanol, an activated secondary benzylic alcohol (entry 2). Recently, we have described a Cu(I)-TEMPO system able to catalyse the oxidation of primary and secondary alcohols in DMF,[28] indicating the involvement of different active species in the present study. This lack of reactivity of secondary alcohols with the [Cu(II)(N ligand)] catalyst may be explained by two factors affecting the catalytic cycle. Steric effects of the methyl group can hinder the formation of species **III** (Figures 2 and 3), crucial for the C–H abstraction from the alcohol by the coordinated TEMPO molecule. Furthermore, in the case of primary alcohols, the second β-hydrogen atom can be bonded to the oxygen atom of TEMPOH, stabilising the radical intermediate **IV** (Figure 3). This is obviously not possible with secondary alcohols.

These results are indeed confirmed when octan-1-ol and octan-2-ol are used (Table 4, entries 5 and 7). Octan-1-ol was oxidised in 61% conversion and > 99% selectivity after one day at room temperature (95% at 40 °C, entry 6) while no octan-2-one formation is observed with octan-2-ol. Allylic alcohols, crotyl alcohol and geraniol (entries 3 and 4) were converted to the corresponding aldehydes in excellent yields (91 and 100%, respectively) and selectivities as no by-products were detected by gas chromatography. These data (entries 1, 3, 4 and 5) clearly demonstrate that the oxidation of activated alcohols is faster than aliphatic ones, indicating that the hydrogen abstraction from the α-carbon atom

Table 4. [$CuBr_2$(Bipy)]-catalysed oxidation of alcohols to aldehydes under air.

Entry	Alcohol	Time [h]	Conversion [%][a]
1	Benzyl alcohol	2.5	100
2	1-Phenylethanol	5	No reaction
3	Crotyl alcohol	5	91
4	Geraniol	5	100
5	Octan-1-ol	24	61
6	Octan-1-ol	24	95[b]
7	Octan-2-ol	5	No reaction[c]
8	Benzyl alcohol + Octan-2-ol	1.5	67/0[d]
9	Benzyl alcohol + 1-Phenylethanol	1.5	63/0[e]

[a] Selectivity in aldehyde > 99%, based on GC.
[b] Reaction performed at 40 ^{0}C.
[c] No oxidation after 24 h.
[d] 67% Benzaldehyde and no octan-2-one detected.
[e] 72% Benzaldehyde after 2.5 h. and no acetophenone detected.

by TEMPO (**III** to **IV**, Figure 2) is rate-determining in the reaction.

Finally, a mixture of benzyl alcohol and octan-2-ol was reacted with air in the presence of the copper(II)-TEMPO-base catalyst (entry 8). The result shows the specificity of the catalytic system towards primary alcohols. Thus, 67% of the benzyl alcohol was converted whereas octan-2-ol remained unreacted. The same feature was observed with a mixture of benzyl alcohol and 1-phenylethanol (entry 9) where 63% benzaldehyde was produced within 1.5 h while no acetophenone could be detected. The oxidation of 72% benzyl alcohol after 2.5 h (entry 9) instead of 100% (entry 1) tends to indicate that both benzylic alcohols are able to coordinate to the Cu(II) ion. This competitive coordination may lead to a lower formation of benzaldehyde as less binding sites are available for benzyl alcohol. This chemoselectivity is a typical characteristic of the natural copper protein galactose oxidase (GOase). GOase is a mononuclear type-2 copper enzyme that selectively catalyses the two-electron oxidation of a large number of primary alcohols to their corresponding aldehydes, coupled with the reduction of dioxygen to hydrogen peroxide (Figure 4).[35–37]

The reaction mechanism proposed for the TEMPO-mediated oxidation reaction (Figure 2) is very similar to one suggested for GOase (Figure 4b), with TEMPO playing the role of the protein-bound phenoxyl radical. Furthermore, the key catalytic species **III** and **IV** (Figure 2) are analogous to the species **B** and **C** found in the copper protein (Figure 4b) which also oxidises benzylic and allylic alcohols to aldehydes.[38]

Conclusion

A new and mild catalytic system for the effective and selective aerobic oxidation of primary alcohol to aldehyde has been developed. The optimum catalyst consists of a copper(II) salt and an aromatic didentate nitrogen-containing ligand such as 4,4′-dimethoxy-2,2′-bipyridine. In addition, the reaction requires a base and TEMPO as co-catalysts. The catalytic activity is enhanced when a water-miscible co-solvent (acetonitrile, dioxane or sulfolane), which may act as a labile copper ligand during the catalytic cycle, is used. The reaction rates are also dependent on the copper salt precursor and the electron-donating character of the *para*-substituent on the aromatic rings of the ligand. This catalytic system can be considered as a synthetic model of galactose oxidase as both the observed chemoselectivity and the proposed reaction mechanism are close to those of the natural copper enzyme. The mechanism of the oxidation is the subject of further investigations, and specifically UV-Vis, EPR and EXAFS measurements are expected to lead to more insights.

Experimental Section

General Remarks

The solvents, the copper(II) salts, the primary alcohols and the corresponding aldehydes are commercially available and were used without further purification. The yields of aldehydes were determined by GC analyses, carried out with a Varian Star 3400 instrument equipped with a CP Sil 5-CB column (50 m × 0.53 mm) or carbowax column (50 m × 0.53 mm) using decane as internal standard.

Typical Oxidation Procedure

The oxidation of alcohols was carried out under air in a 50-mL three-necked, round-bottom flask equipped with a magnetic stirrer. Typically, the alcohol (10.0 mmol) and decane (2.0 mmol; GC internal standard) were dissolved in 15 mL of a CH_3CN/H_2O (2:1) solvent mixture. 56 mg (0.5 mmol) of potassium *tert*-butoxide (potassium hydroxide can be used as

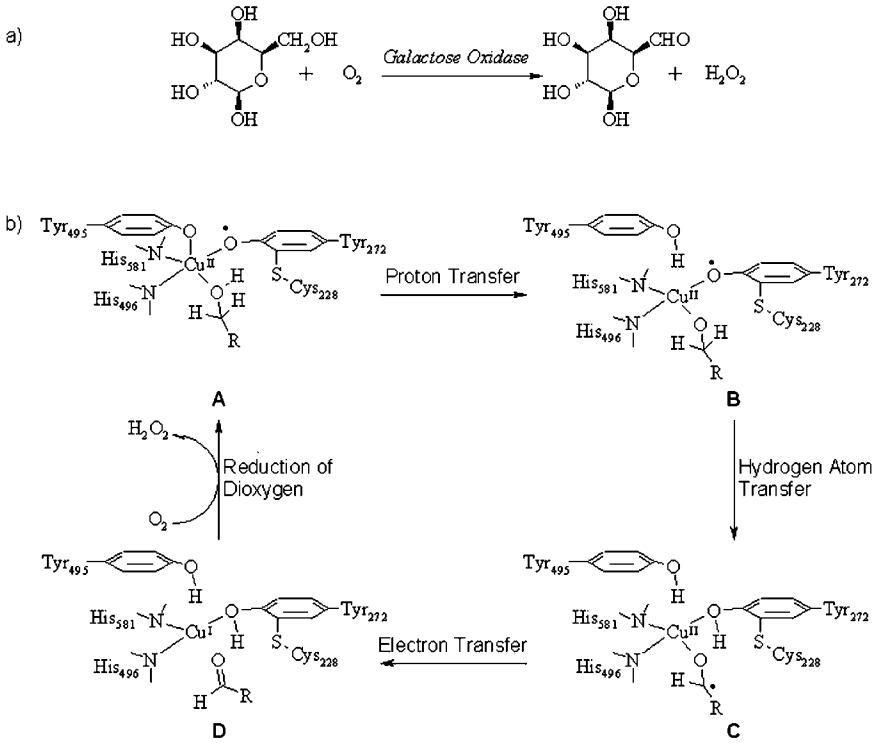

Figure 4. a) Enzymatic oxidation of galactose with the reduction of O_2 to H_2O_2; b) Proposed reaction mechanism for galactose oxidase.[36]

well) were added followed by 112 mg (0.5 mmol) of copper(II) bromide, resulting in a blue-green suspension. 78 mg (0.5 mmol) of 2,2′-bipyridine were then introduced leading to a dark-blue mixture. Finally, 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (78 mg; 0.5 mmol) was added and the reaction suspension immediately turned brown-orange and clear dark-red after 2–3 minutes. Samples (0.5 mL which were extracted with Et_2O/H_2O) of the reaction mixture were taken out regularly to monitor the reaction by GC. The products of the reaction were determined by comparison with the commercially available carbonyl compounds.

Acknowledgements

Financial support from COST Action D21/003/2001 and the Dutch National Research School Combination Catalysis (HRSMC and NIOK) is gratefully acknowledged.

References

[1] R. A. Sheldon, J. K. Kochi, *Metal-Catalysed Oxidations of Organic Compounds*, Academic Press, New York, **1981**.
[2] A. E. J. de Nooy, A. C. Basemer, H. van Bekkum, *Synthesis* **1996**, 1153–1156.
[3] R. A. Sheldon, I. W. C. E. Arends, A. Dijksman, *Catal. Today* **2000**, *57*, 157–166.
[4] T. Mallat, A. Baiker, *Catal Today* **1994**, *19*, 247–283.
[5] M. Musawir, P. N. Davey, G. Kelly, I. V. Kozhevnikov, *Chem. Commun.* **2003**, 1414–1415.
[6] G. Cainelli, G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer, Berlin, **1984**.
[7] W. S. Trahanovsky, *Oxidation in Organic Chemistry*, (Eds.: A. T. Blomquist, H. Wasserman), Academic Press: New York, **1978**.
[8] T. Iwahama, Y. Yoshino, T. Keitoku, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2000**, *65*, 6502–6507.
[9] R. Lenz, S. V. Ley, *J. Chem. Soc. Perkin Trans. 1* **1997**, 3291–3292.
[10] I. E. Marko, P. R. Giles, M. Tsukazaki, I. Chelle-Regnaut, C. J. Urch, S. M. Brown, *J. Am. Chem. Soc.* **1997**, *119*, 12661–12662.
[11] M. J. Schultz, C. C. Park, M. S. Sigman, *Chem. Commun.* **2002**, 3034–3035.
[12] B. Z. Zhan, M. A. White, T. K. Sham, J. A. Pincock, R. J. Doucet, K. V. R. Rao, K. N. Robertson, T. S. Cameron, *J. Am. Chem. Soc.* **2003**, *125*, 2195–2199.
[13] H. B. Ji, T. Mizugaki, K. Ebitani, K. Kaneda, *Tetrahedron Lett.* **2002**, *43*, 7179–7183.
[14] E. Ochiai, *Bioinorganic Chemistry, An Introduction*, Allyn and Bacon, Boston, **1977**.
[15] P. Gamez, P. G. Aubel, W. L. Driessen, J. Reedijk, *Chem. Soc. Rev.* **2001**, *30*, 376–385.
[16] M. F. Semmelhack, C. R. Schmid, D. A. Cortes, C. S. Chou, *J. Am. Chem. Soc.* **1984**, *106*, 3374–3376.
[17] M. F. Semmelhack, C. R. Schmid, D. A. Cortes, *Tetrahedron Lett.* **1986**, *27*, 1119–1122.

[18] I. P. Skibida, A. M. Sakharov, *Catal. Today* **1996**, *27*, 187–193.
[19] I. E. Marko, P. R. Giles, M. Tsukazaki, I. Chelle-Regnaut, A. Gautier, S. M. Brown, C. J. Urch, *J. Org. Chem.* **1999**, *64*, 2433–2439.
[20] I. E. Marko, P. R. Giles, M. Tsukazaki, S. M. Brown, C. J. Urch, *Science* **1996**, *274*, 2044–2046.
[21] Y. Wang, J. L. DuBois, B. Hedman, K. O. Hodgson, T. D. P. Stack, *Science* **1998**, *279*, 537–540.
[22] P. Chaudhuri, M. Hess, U. Florke, K. Wieghardt, *Angew. Chem. Int. Ed.* **1998**, *37*, 2217–2220.
[23] G. Ragagnin, B. Betzemeier, S. Quici, P. Knochel, *Tetrahedron* **2002**, *58*, 3985–3991.
[24] B. Betzemeier, M. Cavazzini, S. Quici, P. Knochel, *Tetrahedron Lett.* **2000**, *41*, 4343–4346.
[25] I. A. Ansari, R. Gree, *Org. Lett.* **2002**, *4*, 1507–1509.
[26] S. Velusamy, T. Punniyamurthy, *Eur. J. Org. Chem.* **2003**, 3913–3915.
[27] P. Gamez, I. W. C. E. Arends, J. Reedijk, R. A. Sheldon, *Chem. Commun.* **2003**, 2414–2415.
[28] A. Dijksman, I. W. C. E. Arends, R. A. Sheldon, *Org. Biomol. Chem.* **2003**, *1*, 3232–3237.
[29] A. Caneschi, A. Grand, J. Laugier, P. Rey, R. Subra, *J. Am. Chem. Soc.* **1988**, *110*, 2307–2309.
[30] J. Laugier, J. M. Latour, A. Caneschi, P. Rey, *Inorg. Chem.* **1991**, *30*, 4474–4477.
[31] P. Gamez, C. Simons, R. Steensma, W. L. Driessen, G. Challa, J. Reedijk, *Eur. Polym. J.* **2001**, *37*, 1293–1296.
[32] J. C. Barnes, T. J. R. Weakley, *Acta Crystallogr. B* **1977**, *33*, 921–923.
[33] R. D. Willett, D. Swank, K. Chang, S. Hawkinson, *Acta Crystallogr. A* **1969**, *A 25*, S175.
[34] A. Dijksman, A. Marino-Gonzalez, A. M. I. Payeras, I. W. C. E. Arends, R. A. Sheldon, *J. Am. Chem. Soc.* **2001**, *123*, 6826–6833.
[35] Y. Wang, T. D. P. Stack, *J. Am. Chem. Soc.* **1996**, *118*, 13097–13098.
[36] M. M. Whittaker, J. W. Whittaker, *Biophys. J.* **1993**, *64*, 762–772.
[37] M. M. Whittaker, Y. Y. Chuang, J. W. Whittaker, *J. Am. Chem. Soc.* **1993**, *115*, 10029–10035.
[38] M. M. Whittaker, V. L. Devito, S. A. Asher, J. W. Whittaker, *J. Biol. Chem.* **1989**, *264*, 7104–7106.

