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Review

Organic oxidative reactions mediated by copper

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Abstract

Copper containing enzymes are indispensable for their ability to act as oxygen carrier and oxidation reactions of different substrates. The recent developments on various copper catalysed as well as stoichiometric organic oxidative reactions involving copper complexes are discussed. The emphasis is put on the state of art on the role of copper complexes to delineate structure reactivity correlation to perform selective oxidative transformations.

Keywords: Copper complexes; Oxidation reactions; Reaction mechanism

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1. Introduction

The elimination of hydrogen from inorganic or organic substrate(s), replacement of hydrogen atom from a C–H bond with a more electronegative element in a chemical reaction is referred as oxidation reaction [1]. The oxidation reactions are those which involve loss of electron(s). The substrate losing the electron(s) gets oxidised and the reagent causing oxidation is called an oxidant or an oxidising agent. The transition metal complexes [2] can act as catalysts in organic oxidation reactions. The first row transition metal catalysts are of great utility in the oxidation chemistry because of their high reactivity and general utility [3]. Among the first row transition metal complexes, the copper complexes have occupied a major place in oxidation chemistry due to their relevance to abundance and biological chemistry [4–8]. These articles show the multitude of mechanism involved in copper catalysed reactions. This leaves a gap to bring a correlation between the structure and reactivity. The present article discerns the various types of organic reactions that are carried out with the help of copper complexes in recent days with an aim to delineate a rationalistic approach for synthetic paths. The role of copper in oxidative reactions are either through direct involvement of the metal centre in the oxidative reactions or by preformed copper complexes that participate in the organic reactions. The oxygen and hydrogen peroxides are the two most commonly used oxidants with copper(II) complexes for organic oxidation reactions.

2. Oxidations involving copper(III)

The oxidation reaction involving metal centre usually involves copper(II)–copper(I) couple and such aspects are detailed in different reviews [9,10]. In contrast to the +1 and +2 oxidation state of copper, there are only few examples of copper(III) complexes isolated and their reactivities are studied to a very less extent [11,12]. Thus, the utility of copper(III)–copper(II)

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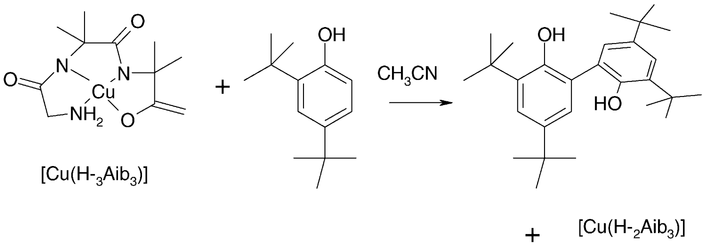
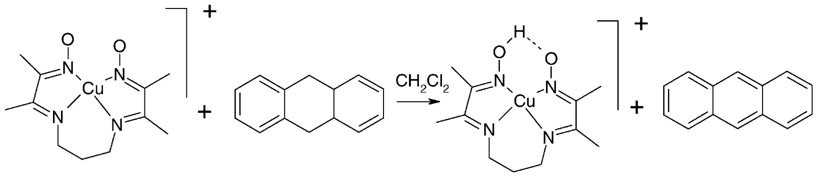
redox couple in oxidation reactions is uncommon. One electron oxidation by preformed copper(III) complexes are demonstrated (Eqs. (1) and (2)) with the well-characterised copper(III) complexes recently [77]. The copper complexes studied are capable of oxidatively dimerising di-tertiarybutyl derivative of phenols as well as dehydrogenation of anthracene derivatives. The theoretical calculation on correlation of reactivity of copper(III) with the thermodynamic parameters are complicated because of co-ordination of axial ligands are involved on reduction of square planar d^8 Cu(III) complexes. This is because copper(II) being a d^9 system prefers Jahn-Teller distorted octahedral environment. The driving force of the reaction is largely effected by the nature of the axial ligand(s).

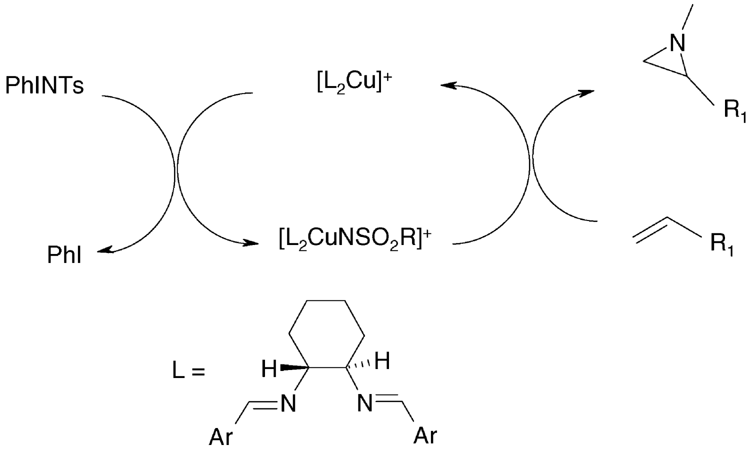


(1)



(2)

Another important reaction in which a copper(II) catalyst can involve in Cu(I)/Cu(III) cycle is the aziridination reaction of alkenes [13] (Scheme 1). In



Scheme 1.

this reaction, copper(II) complexes are used along with [*N*-(*p*-tolunesulfonyl)amino]-phenyliodoinane (PHINTs) as the source of nitrene intermediate. Feasibilities of various intermediate copper complexes were evaluated from theoretical calculations to establish the reaction mechanism that was also supported by kinetic study.

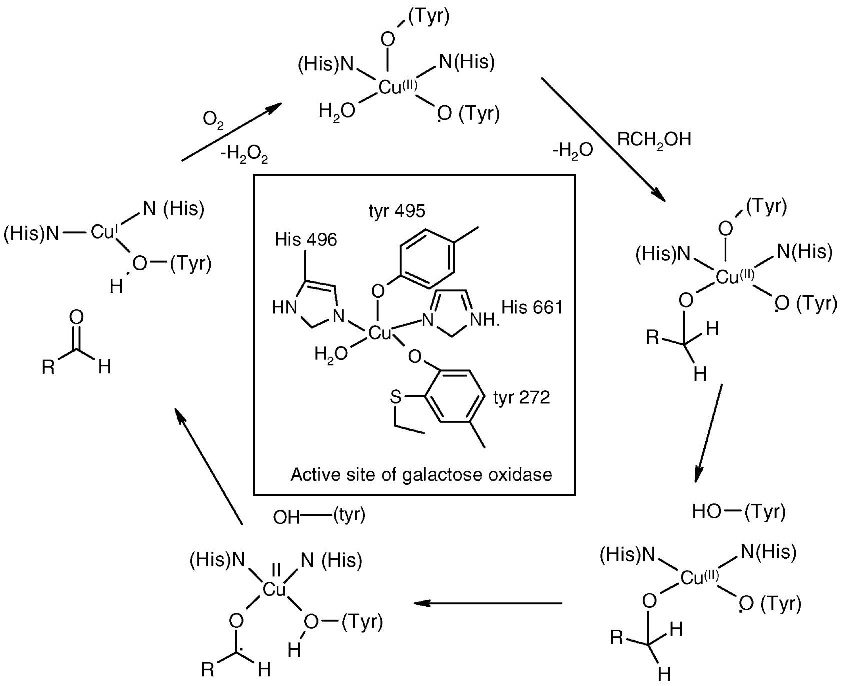
3. Oxidations involving stable radical complexes

Galactose oxidase is a fungal enzyme that contains a mono-copper active site (Scheme 2). It has N_2O_3 type of co-ordination environment around the copper centre in the native state.

This enzyme causes oxidation of primary alcohols to aldehyde [14–19]. In these oxidation reactions, it is demonstrated that an organic free radical proximate to a copper(II) centre is responsible for the oxidation of the organic substrate. The scheme shows one electron oxidation process that occurs via an initial hydrogen abstraction by the tyrosil radical. The authors however do not rule out the two electrons oxidation by molecular oxygen along with one electron oxidation.

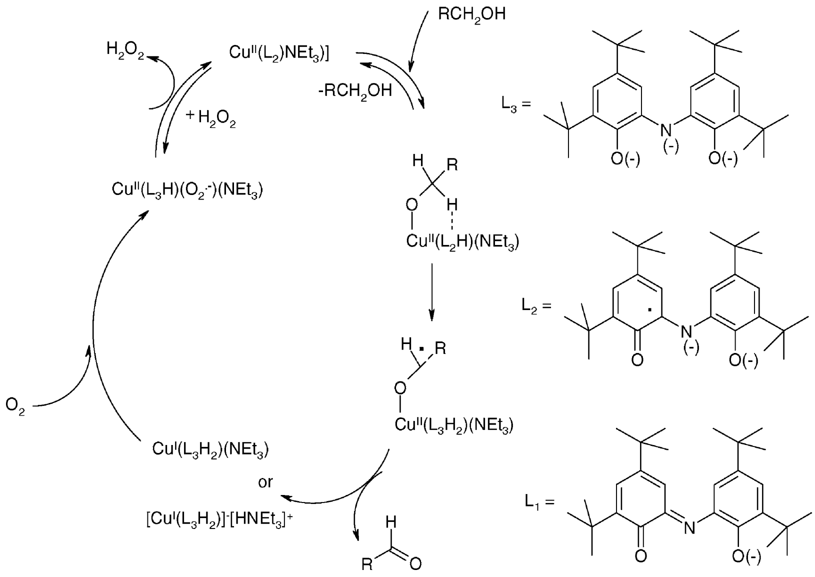
The above reactivities are extended to model compounds from two different angles. Firstly, radical containing copper(II) five co-ordinated (N_3O_2) type complexes were prepared [20]. These copper complexes show the desired reactivity showing that such complexes are responsible for oxidation of 3,5-di-tertiarybutylcatecohol to 3,5-di-tertiarybutyl 1,2-benzoquinone [20]. Secondly, synthons having analogous biological reactivity is also depicted [21] (Scheme 3). The interesting aspect of the reaction sequences is the involvement of radical complexes of copper. The ligand in different forms can have different spin states. This leaves scope for interesting magnetic materials from this class of compounds.

In biological system, aerobic oxidation of primary amines are done by copper containing amine oxidase.



Where tyr = tyrosinase
His = Histidine
Cys = Cystine

Scheme 2.



Scheme 3.

The amine oxidase contains 2,4,5-trihydroxyphenylalaninequinone cofactor which is believed to be responsible for the overall reaction process. Recently, a model for such reactions is studied [22] and it illustrates the involvement of the binding of oxygen to copper co-ordinated to the quinone moiety during oxidation reaction:

$$\mathrm{Cu(II)\ (TOPA)} \rightleftharpoons \mathrm{Cu(I)\ (TPSQ)} \qquad (3)$$

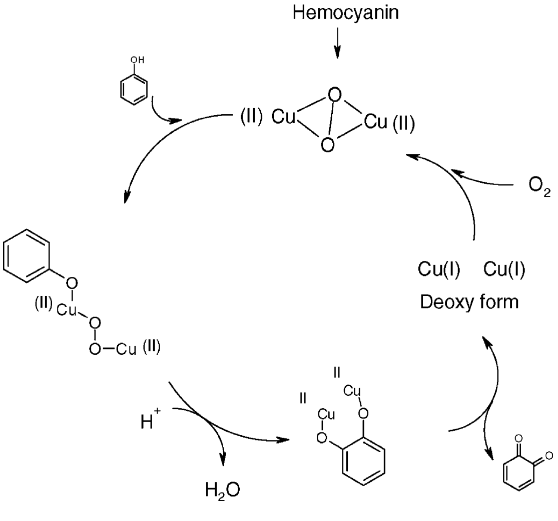
where

TOPA = 2,4,5-trihydroxyphenylaniline
TPSQ = 2,4,5-trihydroxyphenylanilinesemiquinone

The system is believed to involve an electron transfer pathways as shown in Eq. (3). It is also reported that Cu(I)Cl/O_2/pyridine can convert amine to nitrile in excellent yield [23]. The Cu/O_2/acetic acid system has also been successfully used to oxidise primary amine to aldehydes [24].

4. Reactions involving bi-metallic oxo-copper complexes

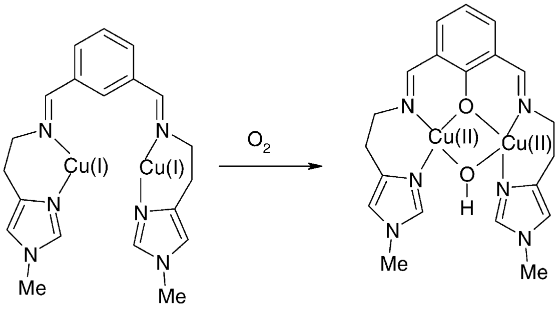
The oxo-species having Cu_2O_2 dimeric cores are involved in many oxidative reactions in biology. Such cores are responsible for many hydroxylations at non-activated C–H bond by biological systems. For example, mono-oxygenases containing the cytochrome P-450 can cause selective hydroxylation of aromatics. The enzyme tyrosinase has a coupled di-nuclear active site of copper(II) and this site is similar to that found in hemocyanins [25]. The interaction of the metal site of tyrosinase with molecular oxygen forms a new species known as oxy-tyrosinase. A phenol molecule could bind to oxy-tyrosinase in an axial



Scheme 4.

fashion and rearrangement of the substrate complex formed through a trigonal bi-pyramidal form results in hydroxylation at the *ortho*-position of the phenol followed by loss of water. Further to this, the hydroxylated di-phenol co-ordinates to the metal centre as shown in Scheme 4. Such catecholate di-copper(II) complex is known in model systems also [26].

In order to have a realistic value of such systems in non-biological chemistry hydroxylation by copper complexes; selective hydroxylation and synthesis of novel copper complexes are envisaged. The important observation is made during copper(I) catalysed oxidative reaction of the reaction [27] shown in Eq. (4), has yielded di-nuclear copper(II) complex. The reaction does not proceed when the *N*-methyl group is replaced by N–H group in the starting complex.



(4)

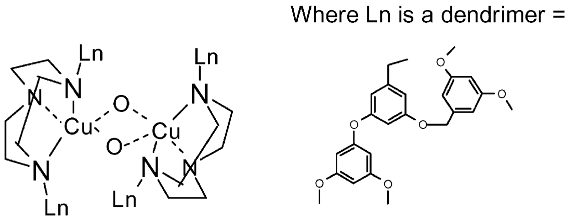
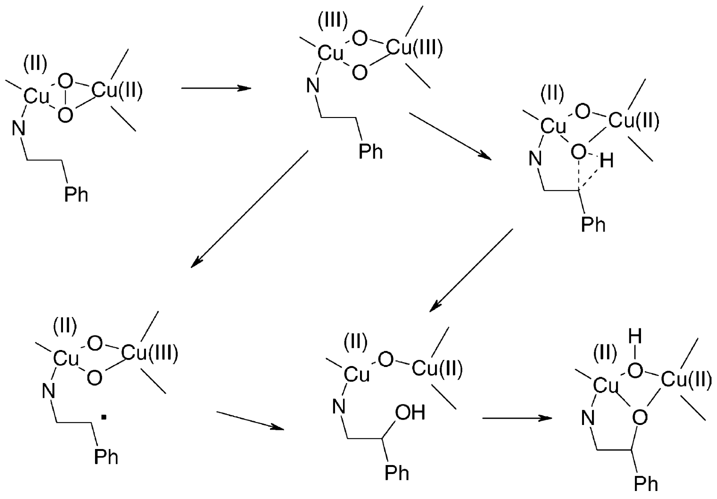


Fig. 1.

Such methodology is extensively used in synthesis of bi-nuclear copper(II) complexes when aromatic ring is hydroxylated provides the neutral bi-nuclear complexes [28]. The hydroxylation of phenol can be carried out by catalytic amount of *cis*-bis glycinato copper(II) mono-hydrate with hydrogen peroxide without selectivity [29].

Although, it is relatively difficult to achieve aliphatic hydroxylation by copper complexes under ambient condition; but such reactions are accomplished in isolated cases. One interesting example for such reaction is the hydroxylation of a preformed copper complex in which hydroxylation at the benzylic position leads to oxo, hydroxo-bridged dimeric copper(II) complex [30] (Scheme 5). In this reaction, bond metathesis as well as radical formation reactions are the possible paths. However, the kinetic studies depict involvement of intramolecular peroxo-bis



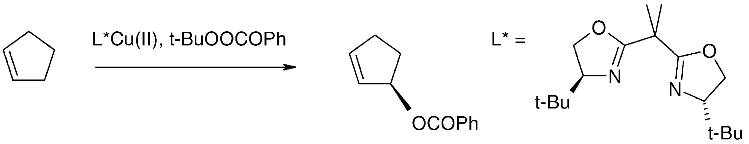
Scheme 5.

(-oxo) isomerisation instead of C–H bond breaking in the rate determining step.

The stability of a reactive intermediate taking part in an oxidation reaction plays a crucial role in achieving better performance in terms of selectivity as well as overall yield. If the reactive intermediate is unstable under ordinary condition, it may be possible to provide confinement by incorporating hydrophobic or hydrophilic groups so as to increase its stability and to reduce possible side reactions. Two such examples in which reactive intermediates are made stable by such confinement are shown in Figs. 1 and 2. Figure 1 shows oxy-bridged Cu_2O_2 core [31] is stabilised and as in Fig. 2 peroxy-bridged Cu_2O_2 [32]. The reactions of the peroxy species shown in Figs. 1 and 2 are tested with different amides and it is found to catalyse hydrolytic cleavage of amide bond to corresponding acid. It is also important to note that the binding with oxygen in this case is reversible and formic acid can be transformed from formamide in such hydrolytic reactions within a second.

5. Optical induction in oxidative copper catalysed reactions

The oxidative reaction of copper complexes having optically active ligand has been successfully used for oxidative benzoylation of olefinic compounds [33] (Eq. (5)). The ligand system as described in the Eq. (5) has great value in homogeneous reactions and may be extended to heterogeneous system by anchoring a polymer chain at carbon bridging the heterocycles. A functional derivative of the ligand system have proved to be excellent in Mukeyama aldol condensation reaction assisted by copper(II) triflet [34].



(5)

The allylic oxidation by bi-nuclear copper(I) complexes having chiral ligand gives cyclohexenylbenzoate [35]. Bis-oxazoline ligand containing copper(I) complexes also causes asymmetric peroxidation of prochiral allylic and benzylic compounds [36].

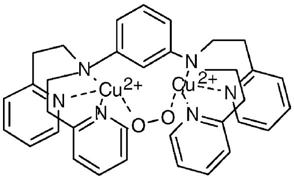
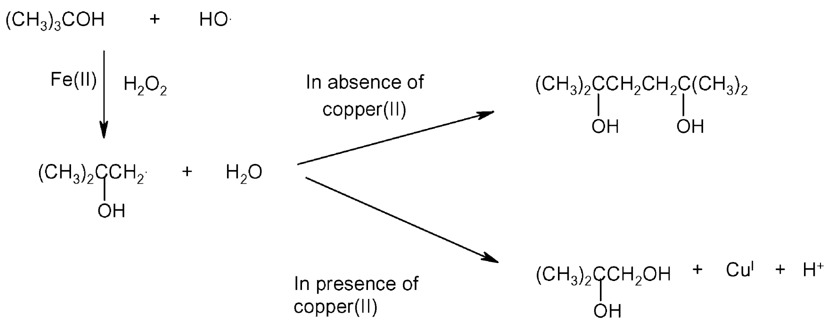


Fig. 2.

6. Oxidative reactions of copper in confined medium

Auto oxidation is another important reaction that can accompany an oxidation reaction. It refers to oxidation of an organic substrate by molecular oxygen via a free radical chain process [37]. Alkoxy and alkylperoxy radicals are the intermediates usually involved in these reactions. When such reactions are carried out in confined medium such as zeolite, they are found to be selective [38]. The selectivities in these reactions are governed by shape selectivity of the confined medium. For example, when confinement is provided by a zeolite; the restricted space in the zeolite channel forbids the formation of certain products or intermediates, minimises overall side product formation. In one such study copper(II)acetate dimer encapsulated in cubic MCM-48 is found to show high catalytic activity for conversion of phenol to catecohol and styrene epoxidation [39]. Hydrated silicon, aluminium gel are used to selectively oxidise 2,3,6-trimethyl-1,4-benzenediol by atmospheric oxygen in the presence of copper catalyst [40]. One electron oxidation by copper(II) complexes of ascorbic acid was observed when copper(II) square planar complex of copper(II) was confined in zeolite [41].



Scheme 6.

7. Oxidative reactions of copper complexes as co-catalyst

There are numerous organo-metallic reactions in which oxygen directly or indirectly participates. Wacker process of oxidation of olefin to aldehyde [42] is promoted by $PdCl_2/CuCl_2$. This reaction affords methyl ketones selectively from terminal olefins. The palladium in such reactions participates in a oxidative addition reaction. The reaction is made catalytic by an additional redox cycle involving copper(I) and copper(II) oxidation states which causes the change in oxidation state of the palladium. Recently, esterification of cyclic carbonyl compounds by a $PdCl_2$ and CO in the presence of cupric chloride [43] is achieved. In a mixture of trifluoroacetic acid and water, a mixture of palladium metal and copper chloride catalyses hydroxylation at remote C–H bond of variety of alcohols, acids and halides [44]. Palladium(0)/copper(I) co-catalysed cross-coupling of the Reformatosky type of reactions are recently studied [45].

Copper(II) salts are extensively used in many organic oxidation reactions as co-oxidant. Molybdenum-(II)–copper(II) catalyst in the presence of oxygen causes oxidation of primary and secondary alcohols [46]; osmium tetroxide and copper(I)chloride catalyst system oxidises benzylic and allylic alcohols [47], copper(II)acetate and bismuth nitrate system oxidises benzoin to benzil [48].

The use of co-catalyst can change the selectivity of product in a reaction. For example, when ferrous sulphate and hydrogen peroxide is used as oxidant of *t*-butylalcohol, it produces 2,5-dimethyl-2,5-hexanediol, while the same reaction in the presence of small amount of copper(II) leads to 2-methyl propanediol through hydroxylation. The role of copper(II) in the later case is to intercept the resulting radical to give hydroxylated products [49,50] (Scheme 6).

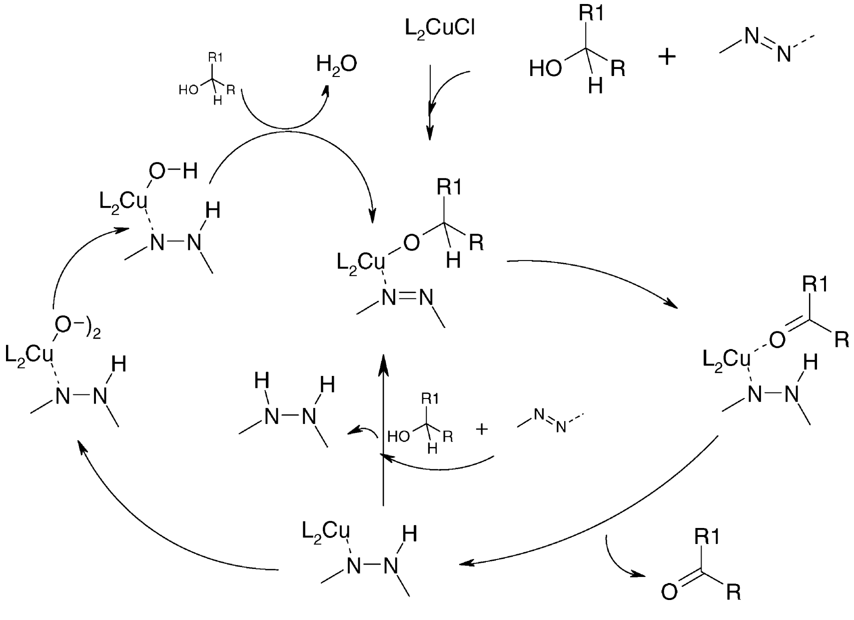
8. Copper catalyst in anaerobic oxidation

The aerobic and anaerobic oxidation reactions of alcohols to carbonyl compound are facilitated by use of azo-compounds [51] (Scheme 7). In these reactions, copper(II) centre can participate through formation of peroxo derivatives that in turn gets converted to hydroxy derivative to oxidise an alcohol. In an alternative path, copper centre captures an azo-compound that abstracts the hydrogen of a C–H bond to form an hydrazine derivative. The hydrazine oxidation by copper(II) has been used for aryl radical generation also. This reaction has been utilised for C–C bond forming reaction [52] (Eq. (6)).

$$ArN_2{}^+Cl^- + CH_2{=}CHZ \overset{Cu(I)}{\rightarrow} ArCH_2CHClZ \qquad (6)$$

9. Copper complexes in oxidative terminal alkyne coupling reactions

Among the oxidative coupling reactions, the reactions of activated aromatic and the alkynes are commonly used reactions. Synthetic transformations of terminal alkynes mostly involve intermolecular and intramolecular homo- and heterocoupling reactions between their sp-carbon centres, leading to butadiyne or acetylinic derivatives. Oxidative homocoupling [53] (Eq. (7)) and heterocoupling reactions



Scheme 7.

of a terminal alkyne with a haloalkyne (Eqs. (8) and (9)) are the two most widely used systems [54].

$$2R{-}{\equiv} \xrightarrow{\mathrm{Cu^+\ or\ Cu^{2+},\ O_2}} R{-}{\equiv}{-}{\equiv}{-}R \qquad (7)$$

$$2R{-}{\equiv} + Br{-}{\equiv}{-}R' \xrightarrow{\mathrm{Cu^+,\ NH_2OH.HCl}} R{-}{\equiv}{-}{\equiv}{-}R \qquad (8)$$

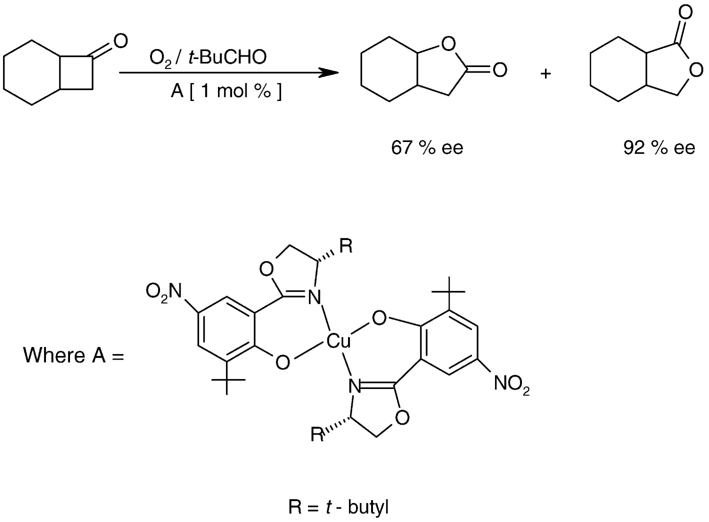
$$2R{-}{\equiv}{-}M + Br{-}{\equiv}{-}R' \xrightarrow{\mathrm{Cu^+,\ NH_2OH.HCl}} R{-}{\equiv}{-}{\equiv}{-}R \qquad (9)$$

The coupling reaction between alkyne Grignard derivatives and 1-haloalkynes using copper(I) salts are well-established [55]. As catalyst organo-copper reagents are found to be most effective for alkynides formation. In these reactions, the generation of alkynylcopper species by transmetalation of an alkynyl group to copper is considered to be a key step. Subsequent oxidative dimerisation of the organic part on the metal-alkenyl complex gives the corresponding 1,3-butadiynes [55]. The [Cu(OH)-TMEDA]Cl_2 (where TMEDA = N,N,N',N'-tetramethylethylenediamine) is a bi-nuclear complex which has very good efficiency in dimerising terminal olefins [56]. It has also good ability to demerise naphthols [57]. The oxidative homocoupling reactions of alkynylsilanes with cuprous chloride in a polar solvent such as di-methylformamide under aerobic condition leads to conjugated diynes and disubstituted ethynes in good yield [58] (Eq. (10)).

$$R{-}{\equiv}{-}SiMe_3 \xrightarrow[\mathrm{DMF\ ,\ 60^0C}]{\mathrm{CuCl\ /\ O_2}} R{-}{\equiv}{-}{\equiv}{-}R \qquad (10)$$

10. Copper complexes in oxygenation reaction

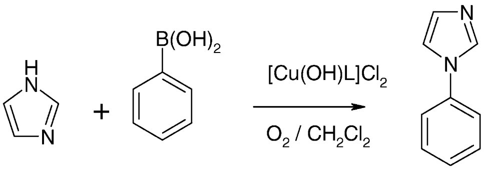
The copper complexes are also capable of oxygenating carbonyl compounds through ring expansion. One of the examples [59] of such a reaction is shown in Eq. (11). The enantioselectivity is one of the added advantages of this reaction.



(11)

11. Oxidative coupling reactions of aromatics by copper complexes

The oxidative coupling reaction of naphthols, napthylamines and aromatic boronic compounds are achieved by using copper catalyst. A recent example leading to C–N bond formation is achieved by copper(II) complexes from aromatic boronic analogue [60] is shown in Eq. (12).



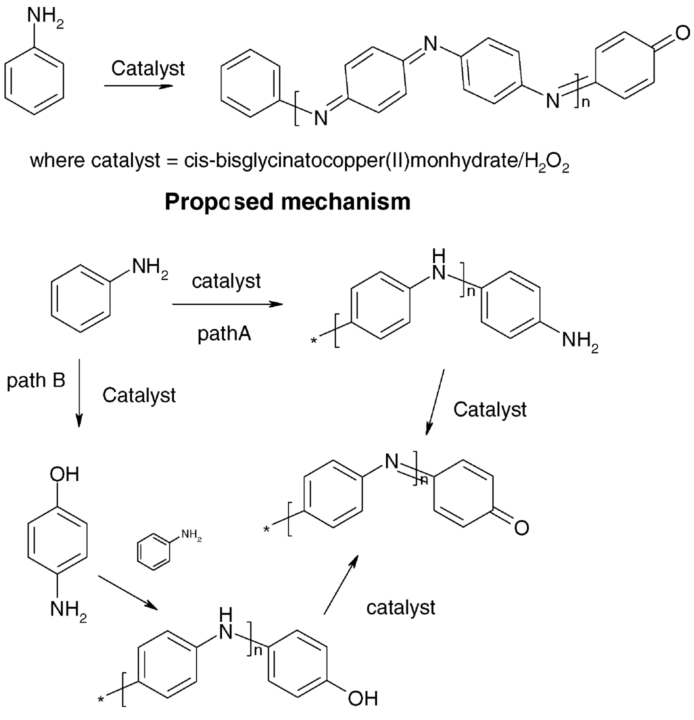
(12)

The copper(II) complexes also participates in thiol coupling reactions to give disulphide [61]. The oxidation of disulphide to sulphonate leads to supramolecular complex of pyridine-2-sulphonato Cu(II) [62].

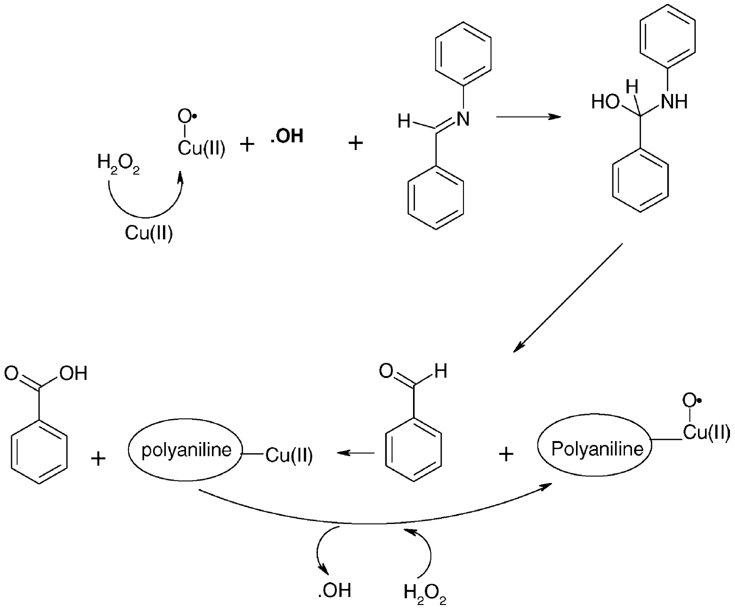
The aromatic amines can be polymerised to polyanilines by copper catalyst. *Cis*-bis glycinato copper(II) mono-hydrate can oligomerise [29] aniline under neutral condition to give polyaniline with end group as C=O. There are two possible paths shown for formation of polyaniline in Scheme 8. But, based on the product isolation and control experiments, the path A is projected as the one (Scheme 8) that actually contributes to the polyaniline formation.

Based on the above results, in situ generation of polyaniline support during the reaction of imine is carried out [63]. In such oxidation reactions, an imine reacts with *cis*-bis glycinato copper(II) mono-hydrate with hydrogen peroxide, leads to carboxylic acid. During the reaction of imines derived from condensation of aniline and aldehyde, leads to the regeneration of aldehyde and aniline. The aniline thus liberated can polymerise to give polyaniline which acts as a support in further oxidative reactions. The reaction mechanism is as follows (Scheme 9).

The copper(II) complexes also leads to C–C bond formation from anilinic compounds. For example, the

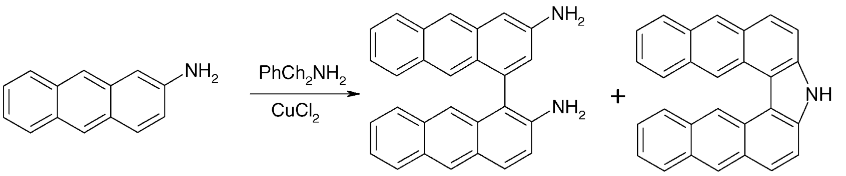


Scheme 8.



Scheme 9.

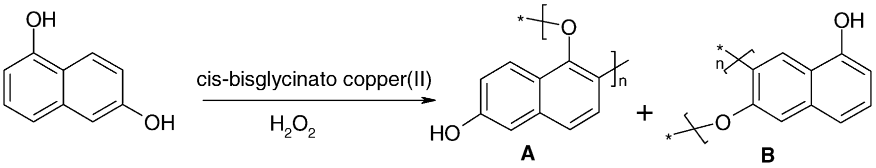
reaction shown in Eq. (13) leads to C–C bond formation [64].



(13)

The oxidative polymerisation of phenol copper has been the reaction that has been discovered in very early days, yet it continues to attract interest for selectivity enhancement as well as for phenylene ether polymer synthesis. Extensive research works both on theoretical and experimental aspect of this reaction are performed. One recent article describing selectivity in such reaction is from the group of Moro-oka [65]. They have selectively prepared and characterised the different polyphenylene ethers from oxidative reactions of few copper complexes containing nitrogen (Scheme 10) on reactions with phenolic compounds. From their study on the selectivity, a reaction mechanism involving oxo-bridged dimeric copper intermediate is proposed.

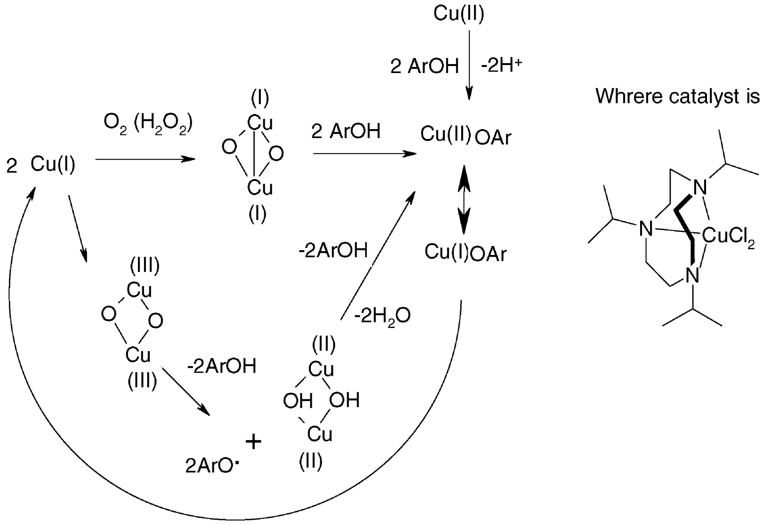
In a more recent work, the selectivity in naphthalenediol oligomerisation on the basis of electronegativity on the ring carbons is discussed. The study also demonstrated a mild oxidative method for oligomerisation of naphthalenic compound [66,67] (Eq. (14)). It is being proposed in the study that the use of naphthols in the oxidation reactions as promoter is to generate supported catalyst.



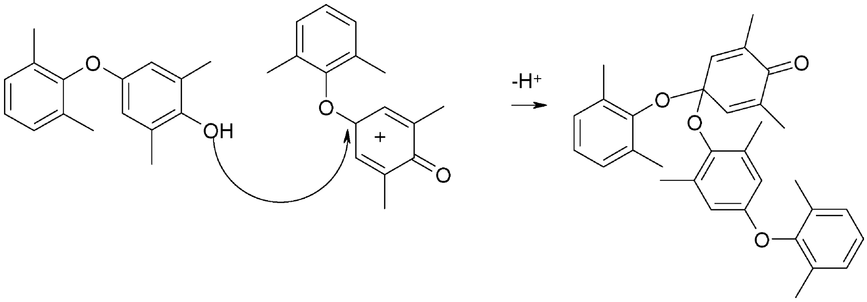
(14)

The above oxidative reactions of phenolic compounds involve C–O bond formation. However, it is observed that the oxidative coupling reaction of hindered phenols leads to bisphenol as well as di-phenoquinone [68] through C–C coupling reactions. On the basis of theoretical calculations, a quinone ketal mechanism involving nucleophilic attack (Scheme 11) of a phenol or phenolate on the *para*-carbon of a phenoxonium cation is put forward for copper catalysed oxidative polymerisation of 2,6-dimethylphenol [69]. The theoretical calculation rules out the other possible electrophilic polymerisation mechanisms as well as charge migration through cationic intermediate. In the reaction, the cation needs to be in the singlet state for attack of a nucleophile. The phenoxonium cation depicted in Scheme 11 are formed by a double one electron transfer within an antiferromagnetically coupled phenoxo-bridged di-nuclear copper(II) complex from the bridging phenolate of two copper(II) ions. The copper mediated *ortho*-oxygenation of phenolate can occur through generation of 6-peroxy-2,4-cyclohexadioenone intermediate. For example, sodium 4-carbethoxy-2,6-di-tertiarybutylphenolate is oxidised by *N*,*N*-bis(*N*-methylbezimidazol-2ethyl) benzylamine gives 4-carbethoxy-2,6-di-tertiarybutyl 1,2-benzoquinone [70], resulting from a 1,2 migration of a tertiary butyl group.

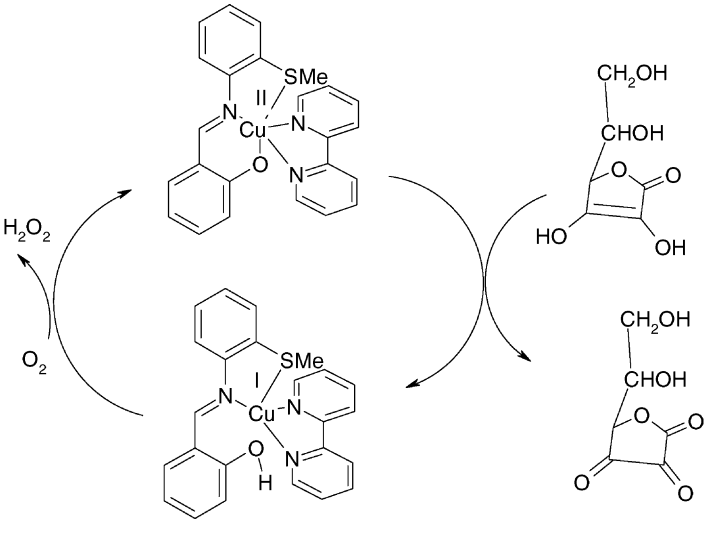
The electro-oxidation of cyanide ions is favoured by modification of carbon electrode with copper oxide [71]. Photochemical oxidation of aryl borane with copper(II) as well as copper(I) salts leads to reduction



Scheme 10.



Scheme 11.



Scheme 12.

of copper salts. During this reaction, the deposition of metallic copper takes place and the bi-aryls are formed [72] from the borane part.

12. Copper complexes in ascorbic acid oxidation

The varieties of reactions discussed earlier are controlled by the redox potential of the metal coupled with the co-ordination environment around copper. Thus, the redox property of the central metal atom is of prime concern in understanding the totality of such a reaction. This is specially the case when the ascorbic acid is used as a mediator in electron transfer [73]. In a recent study, the electrochemical properties of copper(II) complexes having N_3OS co-ordination environment is studied and it is shown that a presence of a quasi reversible redox process occurring involving Cu(I) and Cu(II) can convert oxygen to hydrogen peroxide [74] as depicted in Scheme 12. The catalytic system has similarity to the co-ordination environment of the copper containing glycoprotein such as dopamine-hydroxylase [75,76].

13. Conclusions

The emergence of new and selective copper reagents for oxidative transformations is of great value to improve the existing reactions. The understanding of many naturally occurring oxidation processes have necessitated to design model studies of biologically important molecules and synthesis of model compounds. The oxidation reactions by metal-stabilised radical species that are present in biological systems such as in galactose oxidase, hydrophobic confinement in stabilising the reactive intermediates have drawn the attention of chemists. Other important point of a copper catalysed oxidation reaction is the relevance to biological reactions to synthesis of lignin. Lignin is a wood tissue that comprises major portions of natural plant biopolymer. It plays the crucial role of protection against degradation, water transport in plants. The growth of supramolecular chemistry has made it relatively easier to stabilise reactive intermediates by providing correct environment that in turn can be used for selective transformations. The copper catalysed/mediated oxidation reactions that require clear attention from green chemistry. Any reagent that would lead to non-hazardous degradable product will always be preferred for an oxidation reaction. Nevertheless, the use of catalytic oxidant development from copper complexes will continue to attract attention for stereo and regio-selective transformations.

Acknowledgements

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