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The oligomer of 1,6-naphthalenediol as a support in oxidative reactions of *cis*-bisglycinato copper(II) and hydrogenperoxide

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Abstract

Oxidative oligomerization of 1,6-naphthalenediol by *cis*-bisglycinato copper(II)monohydrate with hydrogenperoxide gives C–O bonded oligomer. Further reactivity of this oligomer with hydrogen peroxide and organic substrate shows improvement in the yield of oxidative and hydrolytic reactions. For example the oligomer along with *cis*-bisglycinato copper(II) catalyses hydrolytic reaction of benzamide to benzoic acid. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oligomer; Copper(II); Hydrogenperoxide

1. Introduction

Polyphenolic compounds can recognize guest molecules [1,2], they can have π-cation interactions [3,4] and they have also biological relevance [5–10]. They are commercially important because of their application as rubber [11], resin [12] and in photolithography [13]. Out of several methods for synthesis of polyphenols [14] oxidative polymerization is a suitable method. It requires mild condition and it also resembles few biological reactions. However, the use of polyphenolic compounds as supported reagents in oxidation reactions is less exploited [15,16]. A suitable ligand environment around copper(II) ion enhances catalytic activity [17,18] of many oxidative reactions. In our recent study, we have shown that copper(II) containing oligomers derived from 2-naphthols are reactive for oxidation reaction. Encouraged by this result we have studied few oxidative reactions of copper(II) complexes in the presence of the polymers prepared from the oxidative reaction of 1,6-naphthalenediol [19,20]. This demonstrates the effect of hydrophobic confinement on copper intermediates during oxidative reactions of copper(II) with hydrogen peroxide.

2. Experimental

The TG were recorded on a Mettler-Toledo TGA/SDTA 851[(e)], UV–VIS on a Hitachi U-2001, IR on a Nicolet impact-410, electrochermical studies were performed with a CH instrument. The electrochemical studies were performed by dissolving 2 mg each of the oligomer in acetonitrile (5 ml) with 200 mg of the tetrabutylammonium perchlorate as supporting electrolyte with scan speed 0.1 mV/s. The electrode systems were platinum electrode coupled to Ag/AgCl as reference electrode. The GPC were done with a Water 410 GPC system with RI detector with ultrastyragel[®] column and THF as eluent.

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Table 1
The GPC data of the oligomers of naphthalenediols prepared by catalytic reactions of *cis*-bisglycinato copper(II)monohydrate and hydrogenperoxide

Source of oligomer	1,3-Naphthalenediol	1,5-Naphthalenediol	1,6-Naphthalenediol	2,7-Naphthalenediol
M_n, M_w	3418, 3629	2551, 2790	1079, 1080; 3193, 3306	2551, 2979

2.1. Typical reaction procedure for oligomerization of 1,6-naphthalenediol

The 1,6-naphthalenediol (320 mg, 2 mmol), *cis*-bisglycinato copper(II)monohydrate (4.6 mg, 0.02 mmol) and hydrogen peroxide (30%v/v, 0.5 ml) were reacted together in acetonitrile (2 ml) at room temperature for 2 h. After removal of the solvent under reduced pressure the residue obtained was washed with water (2 ml × 5 ml) which on drying under reduced pressure yielded a black solid (yield: 370 mg) as the oligomer. The ^{1}H NMR (400 MHz, DMSO-d_6) 8.5–6 (m); IR (KBr) 3500 (bs), 1690 (vs), 1400 (s), 1360 (s), 1280 (bs), 840 (m). Elemental anal. Found C, 63.18, H, 3.84 calcd for $(C_{10}H_6O_3 \cdot 0.75H_2O)_n$ C, 63.6, H, 3.98. Copper(II) content estimated was found to be 0.5–1%.

The catalytic reactions were carried out as one pot reaction with the oligomer and the reactants with specified amount as shown in Table 3. The reactions were monitored by gas chromatography with the aid of FID detector and SE-30 capillary column with a Hewlett Packard GC.

3. Results and discussions

It is observed that the various naphthalenediols such as the ones having hydroxyl groups at 1,3-, 1,6-, 2,3-, 2,7-, etc. can be oligomerized to give C–O bonded oligomers at room temperature by the reaction of a catalytic mixture of *cis*-bisglycinato copper(II)monohydrate with hydrogenperoxide. The (M_n, M_w) values of the oligomers are shown in Table 1. In each case the oligomers are obtained as mixture of isomers from unpreferential attack of the naphthaloxy radical produced during oligomerization. Products of one such oligomerization reaction of 1,6-naphthalenediol with *cis*-bisglycinato copper(II)-monohydrate in the presence of hydrogenperoxide

to give C–O bonded oligomer are shown in Eq. (1). The selectivity in isomer being a major issue for pursueing further studies we have done a theoretical calculation on the electron density of 1,6-naphthalenediol. The charge density at each carbon center of the 1,6-dihydroxynaphthalene was calculated. The charge densities in Mulliken scale calculated by AM1 calculation of the 1,6-naphthalenediol are listed in Table 2. Preferential C–O bond formation would occur at a place having higher electron density. The data (Table 2) indicate that the potential sites for such bond formation in the 1,6-naphthalenediol are at C2, C7 positions of the rings. Out of these two, C2 has more electron densities and this is the most probable site for a C–O bond formation through a radical mechanism. The next options for coupling reactions are at C4 and C5. However, the steric factors and the electronic factors are less favorable than the attack at C2 and C7 positions. Thus, the most favorable structures of the oligomer are **A** and **B** which are shown in Eq. (1). The mass spectrum of the oligomer of 1,6-naphthalenediol in the range of 800–2000 (*m/e*) is shown in Fig. 1. The oligomer has the mass fragments corresponding to sequential loss of di- and tri-hydroxynaphthalene units. For example it has mass fragments (*m/e*) at 476 (trimer), 666 (tetramer),

Table 2
Charge densities at different carbon centers of 1,6-naphthalenediol

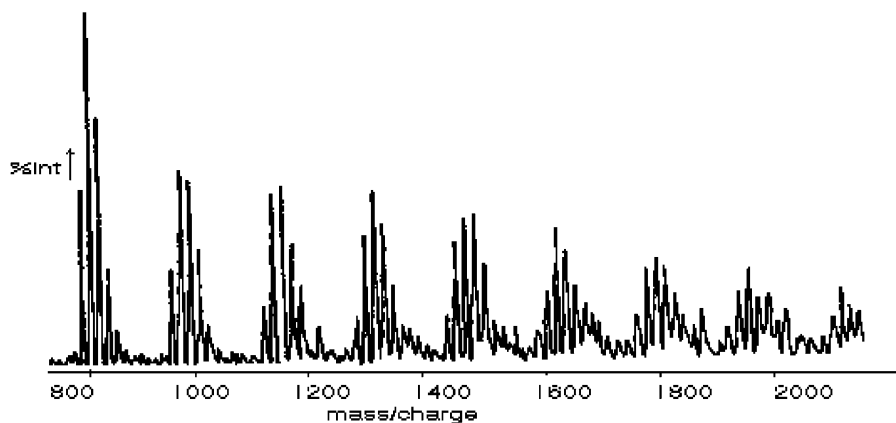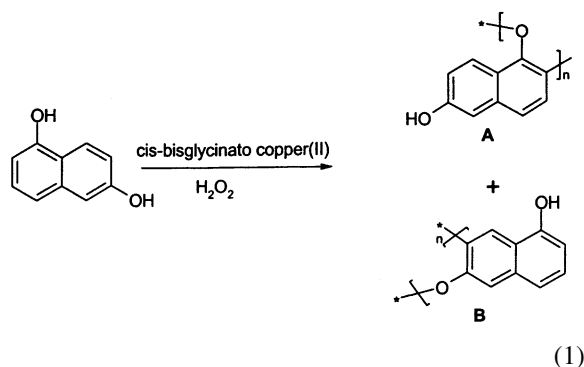| Carbon no.	Charge
1	0.10976
2	−0.29645
3	−0.13611
4	−0.21676
5	−0.21999
6	0.08499
7	−0.27063
8	−0.10706
9	−0.09391
10	0.01503

Fig. 1. MALDI mass spectra of the oligomer of 1,6-napthalenediol.

808 (pentamer), 966 (hexamer), 1108 (heptamer), 1140 (hydroxylated heptamer), 1298 (hydroxylated octamer) and also at 1472, 1646, 1836, etc. for corresponding combination of 9, 10, 11 units, respectively.

(1)

The synthetic methodology used in the above reactions allows the reaction to pass through a radical mechanism [17]. The electron spin resonance study of the oligomer shows that a radical is trapped in it. This radical is stable under ambient conditions. The radical is trapped in the H-bonded network of the oligomer of 1,6-naphthalendiol and it has a sharp ESR signal at 1.93 g (Fig. 2). There is a minor ESR signal adjacent to the above signal and it is assigned to the copper center. Probably a Cu(II)–O radical is trapped inside the polymeric matrix. Such a radical may be due to degradation of Cu_2O_2 core during the oxidative oligomerization reaction. The oligomer has absorption maximum at 334 nm ($e = 16,666\,g^{-1}\,cm^{-4}$). The

material properties of these oligomers are interesting as they are hygroscopic and aggregated through the hydrogen bonding among the hydroxyl groups present in it or through the water molecules in the interstices. The hygroscopicity is reflected in the thermal analysis of the samples as well as in the elemental analysis. The thermogravimetry shows continuous weight loss of the oligomers in the region of 50–600°C. Due to the capability to hold water molecules by the oligomer, it shows interesting electrical properties. The film of the oligomer has resistance profile that increases on heating and has a trend similar to metallic
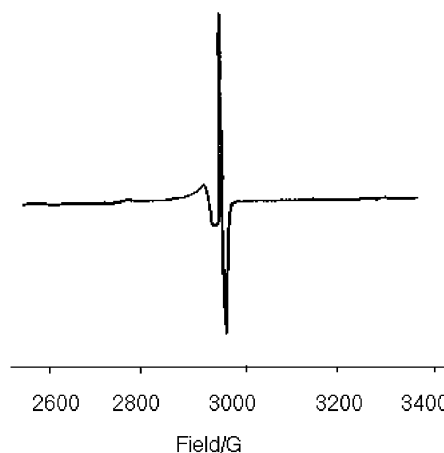

Fig. 2. ESR spectra of the oligomer of 1,6-napthalenediol. Field setting 2500 G central field, 9.04 GHz microwave frequency and 1500 sweep width.

property. Presumably, presence of the radical along with H-bonding in the system imbibes additional conductivity to the film of the oligomer. Thermal energy can cause disruption of H-bonds, which makes the films to loss the proton conductivity present in the system contributing to increase of resistance with temperature.

Copper(II) complexes in basic medium get precipitated as copper(II)hydroxide. This can inhibit the catalytic effect of a copper(II) complex. Such drawback is anticipated to get minimized if a supported reagent can provide some extra stability to a reactive species [15,16] or a hydrophobic confinement [17,18,20,21] on copper can be imparted. In addition to that when two competitive oxidative reactions are performed by the same oxidant it is possible that the formation of one product favors other reaction. As an illustrative example if one considers the one pot competitive

oxidation reaction between benzaldehyde to benzoic acid and polymerization of 1,6-naphthalenediol it is observed that both the reactions proceed simultaneously (Eq. (2)). The presence of 1,6-napthalenediol, slightly improves the yield of benzoic acid. Thus, it is necessary to know whether the effect on enhancement of oxidation of benzaldehyde is by the naphthalenediol or by a supported catalyst formed during polymerization of the napthalenediol. During metal catalyzed oxidative reactions naphthols are added to act as promoter [21]. However, these studies do not discuss the possible role of the promoters as supported reagent. The redox stability of the oligomer is one of the citeria to act as support in an oxidative catalytic reaction. The cyclic voltamogram of the oligomer of 1,6-naphthalenediol has shown two minor oxidation waves at 1019 mV and at 819 mV with a minor reduction peak at 203 mV. There is no significant

Table 3
The catalytic study of oligomer of 1,6-naphthalenediol[a,b]

Entry no.	*Cis*-bisglycinato Cu(II) (mmol)	Amount of oligomer (mg)	Yield (%)
Benzyl alcohol (2 mmol) + H_2O_2 (8.83 mmol) → benzaldehyde + benzoic acid			
1	–	–	14, 0.4
2	0.1	–	9, 0.25
3	–	16	15, nil
4	0.05	16	26, 6
5	0.1	16	16, 8
6	0.05	32	22, 1
Benzaldehyde (2 mmol) + H_2O_2 (4.4 mmol) → benzoic acid			
7	–	–	42
8	0.02	–	49
9	0.05	–	50
10	–	16	45
11	–	32	45
12	0.05	16	80
13	0.05	32	88
Benzamide (2 mmol) + H_2O_2 (8.8 mmol) → benzoic acid			
14	–	–	
15	0.2	–	17
16	0.25	–	18
17	–	40	53
18	–	48	54
19	0.02	40	63
Benzanilide (2 mmol) + H_2O_2 (8.8 mmol) → benzoic acid			
20	0.2	–	32
21	0.2	40	65

[a] All the reactions were carried out at 70°C, for 4 h in acetonitrile (2 ml).
[b] The yields are based on GC data and comparison with authentic samples.

change on these peaks on multiple cycles suggesting it to be stable in potential range of 0–1500 mV. As the oligomer of 1,6-naphthalenediol contains a stable radical and also electrochemically stable it should be useful in initiating further radical reactions. We have utilized the reactivity of this radical in the presence as well as absence of a metal ion/s. The results are summarized in Table 3. It is observed that this oligomer containing a radical can catalyze variety of oxidation reactions such as hydrolysis of benzamide, oxidation of aldehydes, etc. The results suggests that the reactivity of copper(II) complexes is enhanced by the oligomer 1,6-naphthalenediol. The effect may be attributed to a possible stabilization of transient peroxo species by a hydrophobic confinement. We have recently demonstrated [20] that the phenolic oligomer can stabilize Cu_2O_2 core.
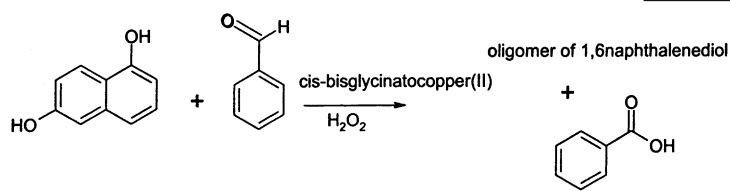
$$(2)$$

In conclusion, this study demonstrates the effect of hydrophobic confinement that can contribute to the reactivity of oxidative reactions of copper complexes where copper–oxo/peroxo species participates. This also demonstrates the possibility of multiple cycle reactions that can occur during competitive oxidation versus oligomerization reactions.

Acknowledgements

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