Products of Prolonged Autoxidation of Simple Dihydric Phenols in the Presence of Copper(II) Ions - An Electron Spin Resonance Study

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ABSTRACT

Electron spin resonance (ESR) spectroscopy was used for characterizing the products obtained by prolonged autoxidation of simple dihydric phenols (hydroquinone, catechol, and 4-methylcatechol) in the presence of copper(II) ions. Room temperature ESR spectra revealed that both paramagnetic copper(II) ions and organic radicals are present in obtained autoxidation products similarly to the humic acid complexed copper(II) ions. The ratio of organic radical signal intensity to the copper(II) ion signal intensity suggests that the smallest amount of copper(II) ions is incorporated in the hydroquinone autoxidation product while the highest amount of copper(II) ions is incorporated in the autoxidation product of catechol. Satisfactory computer simulations of experimental ESR spectra were obtained by considering only one type of copper(II) ion binding site for hydroquinone autoxidation product and two distinct types of copper(II) ion binding sites for catechol and 4-methylcatechol autoxidation products. Parameters obtained by the computer simulation of ESR spectra indicated prevalent ionic bonding of copper(II) ions in polymeric matrices with tetrahedral distortion at copper(II) ion binding sites and negligible exchange interactions between them. Products obtained by the hydroquinone and catechol autoxidation have more similar characteristics in comparison to the product obtained by the 4-methylcatechol autoxidation where more expressed ionic bonding of copper(II) ions, and smaller tetrahedral distortion are present. Due to the dipolar interactions of oxygen-centered organic radicals in autoxidation products with paramagnetic copper(II) ions, their ESR linewidths are larger and *g*-values smaller in comparison to the values found in humic acids from various soil types.

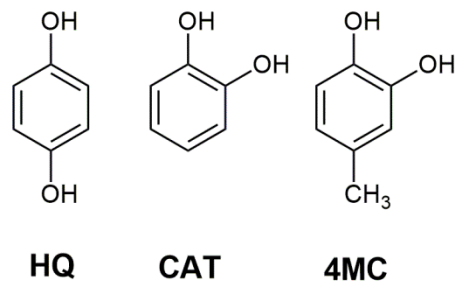*Keywords: Hydroquinone, Catechol, 4-methylcatechol, Autoxidation, Copper(II) ion, ESR*

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Introduction

Many simple phenolic compounds are highly susceptible to oxidation and autoxidation in aqueous solutions, and these processes are strongly influenced by the pH value (Friedman & Jürgens, 2000; Maier et al., 2018) and the presence of metal ions, especially transition metal ions (García et al., 1996; Nkhili et al., 2014; Rinaldi et al., 1995). Prolonged autoxidation (or O_2 oxidation) of polyhydric phenolic compounds or their corresponding quinones in highly alkaline aqueous solutions was employed for obtaining humic-acid like polymers (Barriquello et al., 2010; Doğan et al., 2013; Giannakopoulos et al., 2009; Litvin & Abi Njoh, 2020; Litvin et al., 2015) which have many potential applications. Current research on phenolic polymers covers various fields like antiviral activity (Bianculli et al., 2020), antioxidant properties (Alfieri et al., 2020), and possible uses as electrodes for advanced organic batteries (Patil et al., 2021), humic-like fertilizers (Cha et al., 2017) or for green coloration of textiles (Su et al., 2018). Polymers of phenolic compounds are usually obtained by their enzymatic oxidative polymerization (Alfieri et al., 2020; Dubey et al., 1998; Gamov et al., 2020; Kobayashi & Makino, 2009; Sun et al., 2013), but another viable alternative for their synthesis may be autoxidation in the presence of metal ions (McBride et al., 1988; Oess et al., 1999; Slikboer et al., 2015).

Of the many methods used to characterize natural and synthetic polymers, electron spin resonance (ESR, also known as electron paramagnetic resonance - EPR) spectroscopy proved to be especially useful (Naveed et al., 2018). ESR spectroscopy is also an indispensable tool in transition metal chemistry, given that many transition metal ions, like copper(II) ion, are paramagnetic (Goodman & Raynor, 1970). Having the aforementioned in mind, we applied ESR spectroscopy for the characterization of the products of prolonged autoxidation of frequently used dihydric phenols (hydroquinone, catechol, and 4-methylcatechol) in the presence of copper(II) ions since these results can give valuable information on both copper(II) ion binding environment and organic radical(s) in obtained polymer matrices. Chemical structures of dihydric phenols used in this study are given in Figure 1.

Figure 1. Chemical structures of hydroquinone (HQ), catechol (CAT), and 4-methylcatechol (4MC).

Experimental

Materials

Hydroquinone (HQ), catechol (CAT), and 4-methylcatechol (4MC) were obtained from Sigma-Aldrich (USA), and copper(II) chloride dihydrate ($CuCl_2 \times 2H_2O$) was obtained from Merck (Germany). Buffer compounds, sodium hydroxide, and hydrochloric acid were obtained from a local supplier (Centrochem, Serbia). All the chemicals were of analytical grade and were used without further purification. Demineralized water was used for preparing all aqueous solutions.

Sample preparation

The method used for samples prepared in this work is analogous to the methods used for obtaining phenolic polymers without a catalyst or additional oxidant (Barriquello et al., 2010; Doğan et al., 2013; Giannakopoulos et al., 2009). One gram of a particular phenolic compound (9.1 mmol of hydroquinone and catechol; 8.1 mmol of 4-methylcatechol) was dissolved in 28 mL of phosphate buffer (pH 7.4) in a round-bottom flask. The exact mass of $CuCl_2 \times 2H_2O$ necessary to make the phenol and Cu(II) ion molar ratio of 10 : 1 in solution (0.155 g for hydroquinone and catechol; 0.137 g for 4-methylcatechol) was ultrasonically dispersed in about 2 mL of phosphate buffer and added to stirring phenol solution in small portions. After thorough mixing, a pH value was accurately adjusted to 7.4 by the dropwise addition of 1M NaOH solution. Reaction mixtures were continuously stirred in an open flask for 96 hours at room temperature (22±2 °C) without exposure to direct sunlight. After 96 hours, the pH value was adjusted to ≈2 by adding 1M HCl solution, and mixtures were left for 72 hours without stirring at room temperature for the reaction product to precipitate. Reaction mixtures were then centrifuged at 4000 rpm for 15 minutes and filtered under vacuum. Collected precipitates were rinsed, first with 50 mL of demineralized water

and then 50 mL of 0.01 M HCl solution. Precipitates were dried for 48 hours at 40 °C before ESR measurements.

ESR measurements and spectra handling

An X-band (9.85 GHz nominal frequency) EMX ESR spectrometer (Bruker, Germany) was used for recording ESR spectra of powder samples placed in 2 mm i.d. quartz tube cells at room temperature. Solid DPPH (2,2-diphenyl-1-picrylhydrazyl) was used as a standard (g = 2.0036) for g-value determination of organic radicals, while g-values of copper(II) ion binding sites were determined by computer simulations of ESR spectra. ESR spectra handling and computer simulations were performed on a personal computer by using WinEPR and SimFonia programs (Bruker, Germany).

Results and Discussion

ESR spectra of products of prolonged autoxidation of hydroquinone, catechol, and 4-methylcatechol in the presence of copper(II) ions are given in Figure 2.
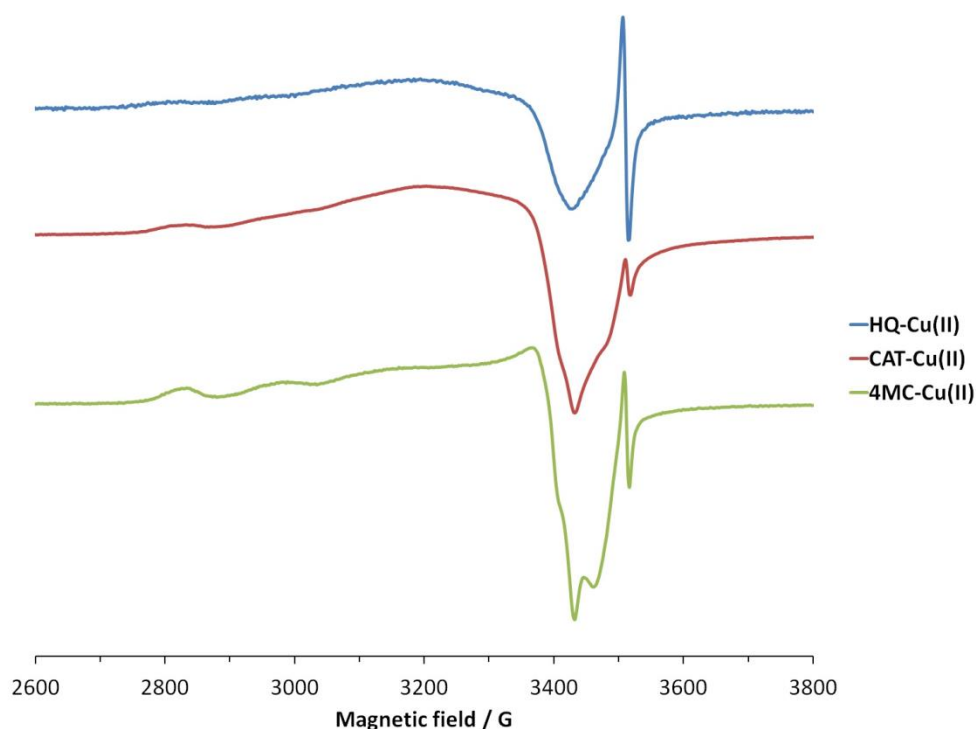
Figure 2. ESR spectra of products of prolonged autoxidation of hydroquinone, catechol, and 4-methylcatechol in the presence of copper(II) ions. Instrumental parameters: attenuation - 25 dB

(microwave power - 0.585 mW), modulation frequency - 100 kHz, modulation amplitude - 2 G, time constant - 0.64 ms, conversion time - 81.92 ms, center field - 3500 G, scan width - 2000 G.

A common characteristic of the ESR spectra shown in Figure 2 is the presence of two distinct spectral contributions: 1) broad resonance lines originating from the presence of copper(II) ions, and 2) one sharp resonance line at higher values of magnetic field originating from the presence of organic radical(s). The overall appearance of these spectra, *i.e.*, the ratio of organic radical signal intensity to the copper(II) ion signal intensity, suggests that the smallest amount of copper(II) ions is incorporated in the hydroquinone autoxidation product while the highest amount of copper(II) ions is incorporated in the autoxidation product of catechol.

Spectral features originating from the presence of copper(II) ions show resemblance to the ESR spectra reported in the literature for copper(II) ions in polymer matrices like polysaccharides (Bartkowiak et al., 1998; Hoffmann et al., 2008; Mitić et al., 2011), starch (Łabanowska et al., 2008) and lignin (Hoffmann et al., 2008; Merdy et al., 2002), where copper(II) ions coordination with only O-donor ligands may be expected. Similar ESR spectra were also reported for copper(II) ions adsorbed on humic acids (Bryukhovetskaya et al., 2016; Cheshire et al., 1977) and synthetic humic acid-like phenolic polymers (Barriquello et al., 2010). The absence of low-field spectral lines in the ESR spectra recorded with enlarged field scale (4000 G scan width, starting from 0 G) eliminates the possibility that binuclear copper(II) binding sites (S = 1) are present in analyzed samples (Etcheverry et al., 2012; Kozlevčar & Šegedin, 2008). Therefore, we assume that our samples contain mononuclear copper(II) centers $(d^9$, S = 1/2), and the general appearance of ESR spectra points towards their axial symmetry with the unpaired electron being placed in a $d_{x^2-y^2}$ ground state. Principal parameters that characterize such bonding sites are parallel and perpendicular hyperfine coupling constants (A‖ and A⊥, respectively) originating from the interaction of the unpaired electron with the magnetic moments of ^{63}Cu and ^{65}Cu nuclei (I = 3/2) and parallel and perpendicular *g*-values (*g*‖ and *g*⊥ respectively). These parameters can be extracted by either measuring directly from the experimental ESR spectra or by computer simulation of spectra. They then may be used to calculate many values useful for the characterization of copper(II) ion binding in systems under study.

The geometrical parameter G is a measure of the exchange interaction between the copper centers (Procter et al., 1968) and is calculated by the following equation:

$$G = \frac{g_\parallel - g_e}{g_\perp - g_e}$$

where g_e is the *g*-value of the free electron ($g_e = 2.0023$). Exchange interaction is negligible if G > 4, and considerable exchange interaction is indicated if G < 4.

The in-plane σ bonding parameter α^2 is a covalency parameter (Kivelson & Neiman, 1961) and can be calculated by the following equation:

$$\alpha^2 = \frac{\left|A_\parallel\right|}{P} + \left(g_\parallel - g_e\right) + \frac{3}{7}(g_\perp - g_e) + 0.04$$

where P presents the direct dipolar term with the value of 360×10^{-4} cm^{-1} (McGarvey, 1967). The value of α^2 is connected with the degree of unpaired electron localization in the copper(II) ion $d_{x^2-y^2}$ orbital and if $\alpha^2 = 1$ the ligand-copper(II) ion bond would be completely ionic, while if $\alpha^2 = 0.5$ the bond would be completely covalent.

The value of *f*, an empirical index of tetrahedral distortion of copper(II) binding sites (Sakaguchi et al., 1979), may be conveniently calculated as:

$$f = \frac{g_\parallel}{\left|A_\parallel\right|}$$

For square-planar structures, *f* values range from ~105 to 135 cm, but values higher than 150 cm are observed for tetrahedrally distorted copper(II) complexes.

Values of parallel and perpendicular hyperfine coupling constants and parallel and perpendicular *g*-values were obtained by the computer simulation of experimental ESR spectra. For example, experimental and computer-simulated ESR spectra of the product of prolonged autoxidation of 4-methylcatechol in the presence of copper(II) ions are shown in Figure 3.

As can be seen, the match between the experimental and simulated ESR spectrum in Figure 3 is not so good in the ~3000 to 3400 G range where high-field parallel and low-field perpendicular spectral components overlap. The same discrepancy is observed between the experimental and simulated ESR spectra of hydroquinone and catechol autoxidation products. The reason for that is the distribution of molecular binding parameters in amorphous and polymeric materials, which restricts the quality of computer simulations since simulation algorithms are usually adjusted for typical polycrystalline solids (Hoffmann et al., 2008). Satisfactory spectral simulation in the case of hydroquinone autoxidation product was obtained by considering one type of copper(II) ion binding site, but for catechol and 4-methylcatechol autoxidation products, reasonably good results

were obtained only if the presence of two distinct types of copper(II) ion binding sites (species) was assumed. This may be the consequence of presumably the lowest amount of copper(II) ions being incorporated in the hydroquinone autoxidation product.
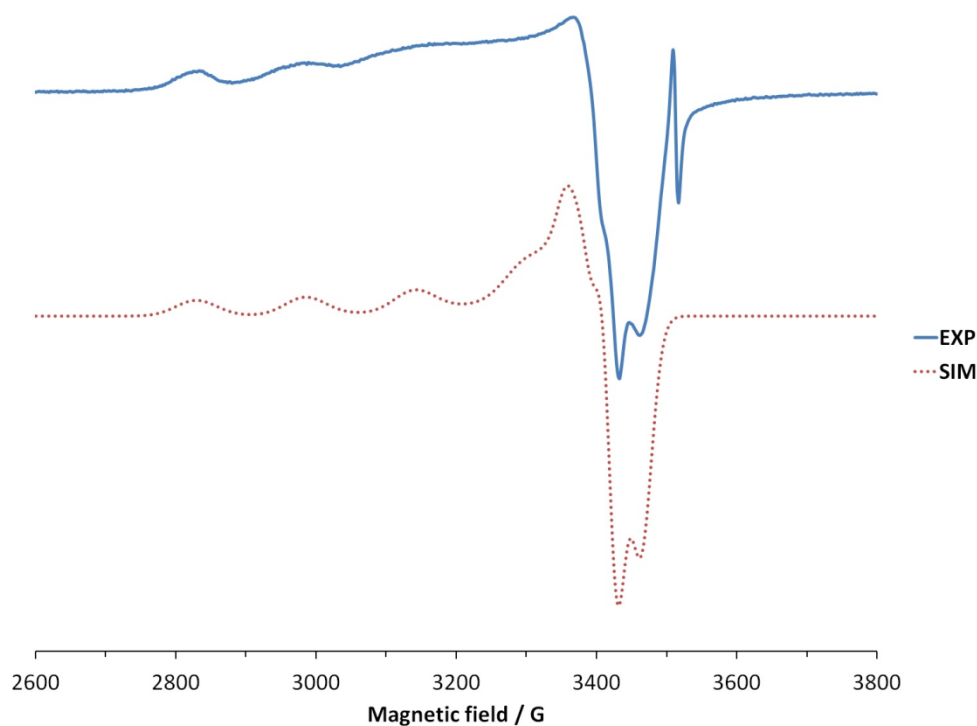
Figure 3. Experimental and computer-simulated ESR spectra of the product of prolonged autoxidation of 4-methylcatechol in the presence of copper(II) ions.

The ESR parameters determined by spectral simulation, together with the calculated values of G, α^2, and f, for the samples analyzed in this work are given in Table 1.

Table 1. ESR spectral parameters of copper(II) ions in analyzed samples.

Sample	Species (fraction)	$g_\parallel$	$g_\perp$	$A_\parallel \times 10^4$ (cm^{-1})	$A_\perp \times 10^4$ (cm^{-1})	G	α^2	f (cm)
HQ-Cu(II)	/	2.341	2.080	145.0	15.0	4.36	0.815	161.45
CAT-Cu(II)	A (0.60)	2.350	2.078	140.0	12.0	4.59	0.809	167.86
	B (0.40)	2.320	2.050	150.0	15.0	6.66	0.795	154.67

4MC-Cu(II)	A (0.41)	2.305	2.085	167.5	8.5	3.66	0.843	137.61
	B (0.59)	2.300	2.064	167.0	7.7	4.82	0.828	137.72

Values of α^2 for our samples indicate predominant ionic bonding of copper(II) ions. The α^2 values for the hydroquinone and catechol autoxidation products are mutually similar and comparable to the values reported for copper(II)-pullulan complexes synthesized at high pH values (Mitić et al., 2011) but are notably smaller than values reported for copper(II) ions introduced as a paramagnetic probe into starch (Łabanowska et al., 2008). Both species found in the autoxidation product of 4-methylcatechol have higher α^2 values, *i.e.*, more expressed copper(II) ionic bonding, than autoxidation products of hydroquinone and catechol. At the same time, according to the *f* values, these two species seem to have the smallest degree of tetrahedral distortion. Except for the specie A in autoxidation product of 4-methylcatechol, the exchange interaction between the copper(II) centers in our samples may be considered negligible.

ESR signals of organic radicals in our phenolic autoxidation products appear as well separated single lines at the high-field end of the ESR spectra shown in Figure 2. Unlike well resolved ESR spectra of organic radicals obtained during the initial steps of autoxidation of catechol in the presence of Al(III) (McBride & Sikora, 1990) or Mg(II) ions (Nikolić et al., 2019), ESR spectra of organic radicals in phenolic polymers consist of one single broad line (Barriquello et al., 2010; Giannakopoulos et al., 2009; Litvin et al., 2015) with spectral parameters similar to natural humic acids (Watanabe et al., 2005; and references therein). To obtain more accurate values for linewidths and g-values of organic radicals, ESR spectra of investigated samples were recorded under the same conditions listed in the legend of Figure 1, except that scan width was decreased to 200 G to increase spectral resolution. ESR spectral parameters of organic radicals in samples studied in this work are given in Table 2.

Table 2. ESR spectral parameters of organic radicals in investigated samples

Sample	Linewidth / G	*g*-value
HQ-Cu(II)	8.1	2.0027
CAT-Cu(II)	6.6	2.0014
4MC-Cu(II)	7.1	2.0028

Linewidths found in our samples somewhat exceed the usual range of linewidths characteristic for ESR signals of humic acids from a wide range of soil types (Watanabe et al., 2005), and this is probably the consequence of dipolar interactions of oxygen-centered radical species with paramagnetic copper(II) ion binding sites present in polymer matrices. On the other hand, *g*-values for our samples are lower than the values for both natural humic acids and synthesized humic acid-like polymers (Barriquello et al., 2010). The characterization of organic radical ESR signal was not performed for the samples obtained by the polymerization of simple phenols in the presence of copper(II) ions (Oess et al., 1999) or by the adsorption of copper(II) ions on humic acids (Bryukhovetskaya et al., 2016) and synthetic humic acid-like polymers (Barriquello et al., 2010) but there are literature data that even addition of diamagnetic Pb(II) ions to humic acids causes an appreciable decrease of their radicals *g*-values (Giannakopoulos et al., 2005). It is also worth noting that the smallest *g*-value in our samples was measured for the autoxidation product of catechol which was supposed to have the highest amount of copper(II) ion incorporated.

Conclusion

Electron spin resonance (ESR) study of products obtained by the prolonged autoxidation of simple dihydric phenols (hydroquinone, catechol, and 4-methylcatechol) in the presence of copper(II) ions revealed that they contain both paramagnetic copper(II) ions and organic radicals, similarly to the humic acid complexed copper(II) ions. According to the ratio of organic radical ESR signal intensity to the copper(II) ion ESR signal intensity, we concluded that the smallest amount of copper(II) ions was incorporated in the hydroquinone autoxidation product while the highest amount of copper(II) ions was incorporated in the autoxidation product of catechol. Parallel and perpendicular hyperfine splitting constants and *g*-values for copper(II) ions were obtained by computer simulations of experimental ESR spectra under the assumption that only one type of copper(II) ion binding site with axial symmetry exists in hydroquinone autoxidation product while two distinct types of copper(II) ion binding sites with axial symmetry exist in catechol and 4-methylcatechol autoxidation products. Obtained parameters allowed the calculation of values used for estimating exchange interactions between copper(II) ions, the degree of ionic binding of copper(II) ions in polymer matrices, and tetrahedral distortion of copper(II) ion bonding sites. Prevalent ionic bonding of copper(II) ions in polymeric matrices with tetrahedral distortion

at copper(II) ion binding sites and negligible exchange interactions between them was found for all three investigated samples. Products obtained by the hydroquinone and catechol autoxidation have more similar characteristics compared to the product obtained by the 4-methylcatechol autoxidation where more expressed ionic bonding of copper(II) ions and smaller tetrahedral distortion are present. Oxygen-centered organic radicals in autoxidation products have larger ESR linewidths and smaller *g*-values in comparison to the values found in humic acids from various soil types due to the dipolar interactions with paramagnetic copper(II) ions.

Acknowledgment

Conflict-of-Interest Statement

None.

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