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Oxidation of 2,6-di-*tert*-butylphenols to diphenoquinones catalysed by Schiff base-Cu(II) systems immobilized on polymer support

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Benzoquinone, diphenoquinones and its derivatives are important intermediates for industrial synthesis of a wide variety of special chemicals, such as pharmaceuticals, dyes and agricultural chemicals. The useful catalyst were obtained by aminolysis of vinylbenzyl chloride/divinylbenzene copolymer with ethylenediamine (1) or urotropine (2) and then modification by salicylaldehyde (1A, 2A) or picolinaldehyde (1B, 2B). The catalytic activity of Cu(II) complexes with Schiff base immobilized on the synthesized supports were tested in the oxidation reaction of 2,6-di-*tert*-butylphenol (DTBP) to diphenoquinone (PQ) with *tert*-butylhydroperoxide. The best oxidation degree of DTBP (60-70%) and the selectivity towards PQ (80%) is revealed by Cu(II) complexes with long Schiff base ligands derived from salicylaldimine (1A), which have CuL structure (EPR measurement).

1. Introduction

The catalytic oxidation of organic compounds is an important industrial technology as well as useful synthesis method. The application of metal complexes of Schiff base immobilized on polymeric carriers as heteregeneous catalysts should be the most interesting for this purpose. Polymer-supported Schiff base ligands and their metal complexes is the subject of extensive review of Leadbeater and Marco [1]. It presents the synthesis methods of Schiff bases by immobilization on supports or by polymerization of salen derivatives as well as the favourable conditions for catalytic process. However, the synthesis by polymerization locates the salen ligands at the end of crosslinks limiting mobility and accessibility of the formed metal complexes. According to Sherrington [2] the highest catalytic activity was reached when metal-Schiff base complexes were isolated and attached to the supports only by one flexible bond what in consequence leads to a small diffusion resistance facilitating the substrate penetration.

The oxidative coupling of 2,6-disubstituted phenols catalysed by polyamine/ Cu(II) complexes is somewhat similar to that for copper-containing proteins, such as laccase and tyrosinase. Depending on the phenols substitution structure, kind of catalysts and reaction conditions, the oxidative coupling leads to the formation of poly(phenylene oxide) (C–O coupling) or phenoquinone (C–C coupling) (figure 1) [3–11]. This type of polymerization discovered by Hay [4] has been studied by many research groups. A simple radical mechanism could not explain the formation of dimethylbenzoquinone or diphenoquinone as products. The polymerization catalysed by copper ions gave poly(2,6-dimethylphenylene oxide) and about 5% of diphenoquinone. Also the oxidation reaction of 2,6-diarylphenols led to the polymers as the main products [4]. Only with phenols giving stable radicals e.g. 2,6-di-*tert*-butylphenols (DTBP), the polymers did not appear. In this case the mixture of benzoquinone (di-*tert*-butylbenzoquinone – DTBQ) and di-*tert*-butylphenoquinone (3,3′, 5,5′-tetra-*tert*-butyldiquinone) called also phenoquinone (PQ) (figure 1) was formed [4,11].

Rockcliffe and Martell [12,13] described the oxidation of substituted phenols by dioxygen in the presence of Schiff base catalysts (obtained from pyridine 2,6-dicarboxaldehyde and triazononane) giving both products DTBQ and PQ with molar ratio depending on the reaction conditions. The oxidation degree of DTBP catalysed by Cu(II) ions reached about 54%.

The oxidation of DTBP to DTBQ and PQ by *tert*-butylhydroperoxide (TBHP) in acetonitrile using polymer (Amberlite XAD-4) with anchored salicylaldoxime complexes of molybdenum and vanadium was presented by Pathak and Rao [14]. DTBP was selectively oxidized by changing the catalyst structure, solvents and temperature. The use of vanadium Schiff base complex as catalyst yielded much more PQ than DTBQ. About 6 h reaction of DTBP in CH_2Cl_2 solution in the presence of binuclear copper(I) complex with amino substituted m-xylyl based ligands gave 85% yield of PQ. The catalytic properties of the specified systems are similar to those observed for tyrosinase [8].

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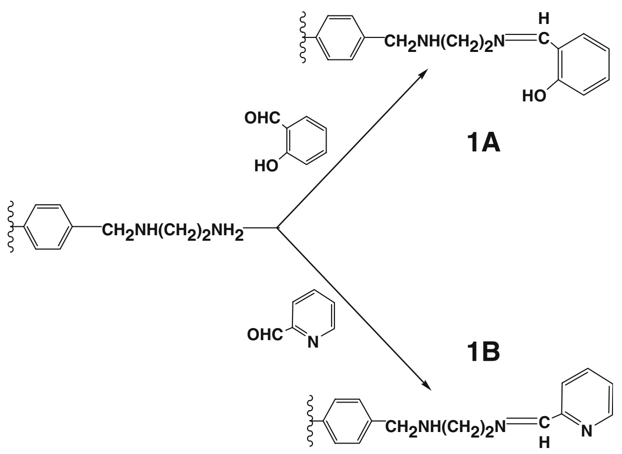

Figure 1. Oxidation reaction of 2,6 di-*tert*-butylphenols to DTBQ and PQ. DTBQ – 2,6, di-*tert*-butylquinone, PQ – diphenoquinone.

Japanese authors [15,16] reported that liquid-phase catalytic oxidation of DTBP was performed on Cu ion-exchanged Na MCM-41 support. They found that in a basic medium or in the presence of alkali metal, DTBP was easy deprotonated to phenolate anion. The corresponding phenoxy radical was formed via one-electron transfer from the phenolate anion to Cu(II) ions. A dimer arose through C–C coupling of the phenoxy radicals and could be easy rearranged to more stable tautomer with two hydroxyl groups. The PQ was obtained by two consecutive oxidation steps or via dimer oxidation. The selectivity of Cu(II)-supported catalysts is affected by the structure of the support pores (meso- and micropores) changing the product shape but an oxidation degree of DTBP is no more than 50%. Also the kind of solvent influences on the PQ and DTBQ content. It turned out that in the strong acidic solvents the oxidation led to PQ as a main product [17].

The structure of the complexes and ligand properties has a significant effect on oxidation degree of DTBP as well as DTBQ and PQ ratio [18,19]. Kurusu [19] presented the influence of blocked substitutes in binuclear Schiff base with Cu(II) ions immobilized on silica. Catalyst without blocked substitutes carried out oxidation of 2,6-DTBP toward PQ (42%) but with *tert*-butyl α-substitutes only 12% (DTBQ 26 and 40% respectively). Also Takaki *et al.* [20] stated the significant influence of polypyridine catalyst structure on DTBQ and PQ ratio. The degree of DBTP oxidation was almost 100% and PQ yielded 43%.

The transformation yield of DTBP reached 100% and high selectivity towards DTBQ increased when DTBP reacted with oxygen in DMF solution in the presence of Co(II) ions coordinated by tetradentate Schiff base with substituents realising an electron density to the metal ion. High yield of quinone formation is observed in the presence of pyridine in the solution [21].

The influence of amine ligand length coordinated to Co(II) ions on oxidation by oxygen in DMSO solution was investigated by Comuzzi *et al.* [22]. The best oxidation degree of DTBP (65%) and selectivity towards PQ (91%) was obtained using the 1,4,7,10-tetraazadecane/Co(II) complex. Peroxidic intermediate,μ-peroxoquinolato/Co(III) complex from initially appearing phenoxyl radical, was proposed as the precursor of the DTBQ. At the same time PQ dimer was formed due to the competitive reaction – a mutual coupling of the phenoxy radicals [22].

Musie *et al.* [23] carried out the DTBP oxidation at supercritical conditions (dioxygen atmosphere, 27 bar, 70 °C, 21 h) in the reactive mixture containing carbon dioxide and Co(II) complex with Schiff base allowing efficient conversion of all DTBP to PQ. They proved that the reaction has radical character [24].

The aerobic oxidation of substituted phenols in the presence of poly(2-(acetoacetoxy)ethyl methacrylate)/M (M = Co(II), Cu(II), Pd(II) Mn(III) or Fe(III)) as catalytic systems, has been investigated by Mastrorilli *et al.* [25]. The oxidation degree (after 24 h) of 2,6-di–methylphenol and 2,6-di-*tert* butylphenol was high (92-98%), but the yield of PQ was only 53–70%.

The group of Brasilian authors carried out the kinetic studies on the activity of some new dinuclear Cu(II) complexes with imidazole or pyridine groups. The oxidation of DTBP by molecular dioxygen in the methanol solution of these Cu(II) complexes gave similar yield of PQ to that characteristic for tyrosinase [26,27].

It is possible to conclude that oxidation of DTBP to PQ depends on many parameters, mostly on the complex structure created on Schiff base supports.

The aim of this work is the synthesis and determination of catalytic activity of Cu(II) complexes with Schiff base immobilized on synthetized polymeric supports in the oxidation of 2,6-di-*tert*-butylphenol (DTBP) to diphenoquinone (PQ).

Benzoquinone, diphenoquinones and its derivatives are important intermediates for industrial synthesis of a wide variety of special chemicals, such as pharmaceuticals, dyes and agricultural chemicals [20].

2. Experimental

The starting vinylbenzyl chloride/divinylbenzene (VBC/DVB) expanded copolymer were prepared by suspension polymerization method in the presence of toluene (50% wt% in respect to the monomer mixture, crosslinker 2 wt% DVB). The VBC/DVB copolymers was swollen in dioxane (1:10 v/v) for 24 h and then chloromethyl groups of copolymer were aminolysed with ethylenediamine (ETDA) in dioxane solution (12:1 mol/mol at room temperature for 168 h – anion exchanger 1). Anion exchanger 2 with amino groups was obtained by treatment with urotropine according to [28]. The amino groups were condensated with aldehyde groups of salicylaldehyde (A) or picolinaldehyde (B) in

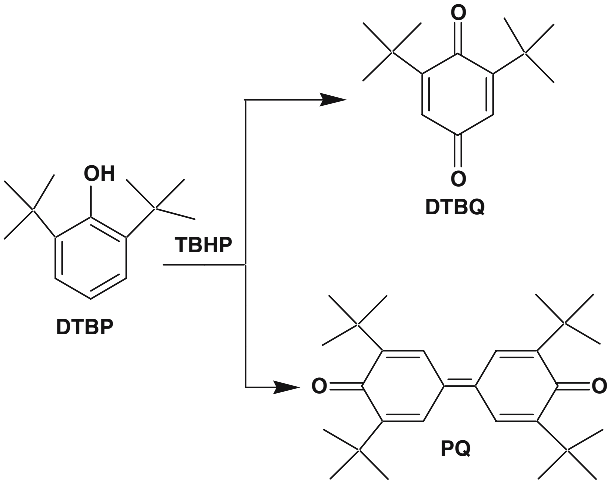

Figure 2. Immobilization of Schiff base ligands onto VBC/DVB copolymer.

dioxane in reflux for 24 h (supports 1A, 1B and 2A, 2B respectively) (figure 2).

Water regain was measured using a centrifugation technique. Nitrogen content was determined by Kjeldahl's method. Anion exchange capacity – Z_c of anion exchanger was analysed according to modified Colella–Siggia method described in [29,30] and used to calculate ligand concentration (Z_L).

Sorption of Cu(II) was performed by bath method from $Cu(NO_3)_2$ solution ($1.10\times^{-2}$–$1.10\times^{-4}$ mol/dm^3) in acetate buffer at pH = 5 to obtain the catalyst with Cu(II) active centres. The concentration of Cu(II) ions in the solution after sorption was determined by atomic absorption spectrophotometry AAS (Perkin Elmer).

The oxidation reaction was carried out by bath method. To the catalyst, placed in 15 mL of ethanol 0.2 g of 2,6-di-*tert*-butylphenol (DTBP) and 2 mL of *tert*-butylhydroperoxide (TBHP) as 70 wt% solution in water were added. The molar ratio of DTBP to Cu(II) ions in catalyst is 10:1. The reaction mixture was stirred under reflux at 65 °C. The reaction progress was monitored by the UV/VIS spectra of reacting mixture (reaction time: 20, 40, 60, 80, 100 and 120 min.; DTBP at 271 nm, DTBQ at 255 nm and PQ at 418 nm). The mixture composition after 120 min was also analysed by GC.

The EPR spectra were recorded on a Bruker ESP 300E (Bruker, Germany) spectrometer operating at X-band and equipped with the Bruker NMR gaussmeter ER 035M and the Hewlett–Packard microwave frequency counter HP 5350B. EPR parameters were calculated by computer simulation of the experimental spectra using Bruker's WIN-EPR SimFonia Software Version 1.25.

FTIR spectra in KBr pellets were recorded on Perkin–Elmer System 2000 FTIR spectrophotometer.

3. Results

The polymer supports were synthetized from VBC and DVB copolymers (2 wt% DVB) obtained by suspension polymerization from the monomer mixture diluted with toluene. The copolymer was modified using camines: ethylenediamine (1) or urotropine (2) (figure 2). The degree of aminolysis with ethylenediamine in room temperature was about 67% and concentration of ligands 3.2 mmol/g. According to Warshawsky's method [28] the degree of transformation by urotropine was about 97% and concentration of amino groups was 5.9 mmol/g.

Next stage was the reaction between aminogroups of 1 or 2 anion exchangers and aldehyde groups of salicylaldehyde (A) or picolinaldehyde (B) (figure 2). The characteristics of Schiff base supports were presented in table 1. They have the small sorption ability of alcohols and water. Concentration of the ligands was calculated from nitrogen analysis, and was in range 2.3–3.6 mmol/g (table 1).

FTIR spectra of supports 2A and 2B are presented in figure 3. For 2A the most characteristic bands of Schiff base are those for C = N stretching vibration at 1631, 890 and 873 cm^{-1}. The vibrations of C–N bands appear at 1375 and 1329 cm^{-1}. The band at 1279 cm^{-1} is characteristic of bending deformation for salicylaldehyde OH groups whereas at 1150 and 1117 cm^{-1} for stretching vibration of C–O groups. The bands confirming the existence of Schiff base groups, are observed for 2B at 1644 and 888 cm^{-1} as associated with stretching vibration of C = N and at 1358 and 1327 cm^{-1} with C–N groups. The characteristic bands for picolinaldehyde were recorded at 1604, 1587 and 1435 cm^{-1}.

Table 1
Characteristics of Schiff base supports

Symbol	Methanol regain (g/g)	Ethanol regain (g/g)	Water regain (g/g)	Nitrogen content (mmol/g)	Ligands concentration (mmol/g)
1A	0.37	0.29	0.48	6.1	3.1
1B	0.93	0.86	0.54	6.8	2.3
2A	0.10	0.12	0.41	3.6	3.6
2B	0.36	0.24	0.38	5.1	2.6

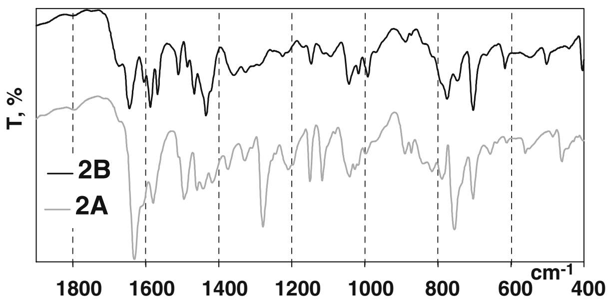

Figure 3. FTIR spectra of 2A and 2B supports.

The bands due to vibration of aromatic rings are seen at about 700–750, 1445, 1565–1570 cm^{-1}.

The Cu(II)–Schiff base complexes used as oxidation catalysts were prepared by Cu(II) sorption from aqueous solutions of various concentration and different molecular ratio of Cu(II) to amino groups of the supports (table 2). It is easy to see that 1A and 1B supports exhibited higher Cu(II) sorption than 2A and 2B most likely as a result of different properties connected with flexibility of ligands and nature of the complexes. The sorption from the most concentrated Cu(II) solution is higher leading to the excess of Cu(II) in relation to the ligands. The experiments were performed for the polymer samples with Cu(II) loading in the range 0.23–2.92 mmol/g (table 2).

Table 2
Cu(II) ions loading as a function of different sorption parameters

Carriers	C_{Cu} (M)	Ligand/Cu	S (mg/g)	S (mmol/g)	K
1A	0.1	2	72.65	1.14	46.3
1A	0.1	1	147.54	2.32	98.1
1A	0.1	0.5	165.74	2.61	45.7
1A	0.05	0.5	75.83	1.18	30.1
1A	0.01	0.5	185.67	2.92	572.2
1A	0.005	3.7	49.99	0.78	3124.4
1A	0.001	9.2	48.45	0.76	15.9
1B	0.1	2	78.41	1.23	453.3
1B	0.1	1	132.95	2.09	304.9
1B	0.1	0.2	164.50	2.59	33.8
1B	0.05	0.5	102.61	1.60	49.7
1B	0.01	0.5	152.67	2.40	512.1
1B	0.005	3.2	37.38	0.58	712.0
1B	0.001	3.4	20.72	0.32	627.9
2A	0.1	0.5	53.16	0.84	9.5
2A	0.1	0.2	114.23	1.80	20.0
2A	0.075	0.5	25.29	0.40	5.6
2A	0.05	0.5	37.27	0.59	12.8
2B	0.1	2	14.60	0.23	2.8
2B	0.1	1	31.17	0.49	6.1
2B	0.1	0.2	86.54	1.36	15.2
2B	0.075	0.5	91.92	1.45	22.5
2B	0.05	0.42	16.2	0.25	5.3

C_{Cu} – Cu(II) ions concentration in starting solution.
Ligand/Cu – ligands to Cu(II) ions ratio.
S – sorption of Cu(II) ions.
K – distribution coefficient.

The anisotropic character of the EPR spectra observed for the Cu(II) complexes immobilized by the supports even at room temperature strongly suggests that the stable complexes with the ligands are formed (figure 4). The axial character of the spectral parameters are connected with tetragonally distorted octahedral geometry of the complexes.

In each 1A and 1B ligands there are three donor atoms (two N and O or tree N, respectively) favouring formation of CuL complexes where ligands are tricoordinate. The fourth coordination position in Cu(II) plane may be occupied by solvent molecule or oxygen atom of oxidizing reagent. However, 2A and 2B ligands provide two donor atoms (two N or N and O) and CuL or CuL_2 complexes may be formed. Efficient formation of CuL_2 type complexes attached to the polymers needs an apparent excess of the ligands in relation to metal ions whereas the best catalysts have Schiff bases deficiency. The comparison of EPR parameters (table 3) of the studied catalysts with those observed for model Cu(II) complexes with en, bidentate and tetradentate Schiff bases strongly suggests that CuL type complexes are formed for 1A and 1B. For 2A the parameters are between those for the complex with one and with two ligands. The stability of the complexes with 1A and 1B should be greater than that for 2A and 2B due to a greater length of the ligand fragment derived from ethylenediamine than that from urotropine. Furthermore, tridentate ligands 1A and 1B have stronger chelating effect, similar to that observed by Pui *et al.* [21]. Hence, sorption properties of 1A and 1B towards Cu(II) are stronger as compared to these observed for bidentate 2A and 2B ligands.

The oxidation of DTBP by TBHP in ethanol solution at 65° was used as a model reaction (figure 1) for investigation of the catalytic activity of Cu(II)–Schiff bases complexes immobilized on the supports.

The results of oxidation reaction are presented in table 4 and figures 5a–d. The composition of the products was determined by two methods: UV/VIS spectrophotometry and gas chromatography (table 4). The spectra unbraiding program was used for the interpretation of UV/VIS spectra [I. Owsik *et al.*, submitted for publication], because of overlapping of two characteristic bands: for DTBP at 271 nm and DTBQ at 255 nm. The band maximum for PQ spectrum is observed at 418 nm. The representative spectra for 2A are presented in figure 6.

UV/VIS method allows to monitor the course of oxidation reaction depending on time (figure 7). Oxidation degree of DTBP is a function of reaction time and is nearly straight line for the catalysts with longer ligands from ethylenediamine (the CuL complexes with 1A and 1B). Initial rates of the oxidation reaction are higher for Schiff base catalysts obtained from salicylaldehyde (1A and 2A) then picolinaldehyde (1B). For the catalyst 2B inhibition reaction was observed and oxi-

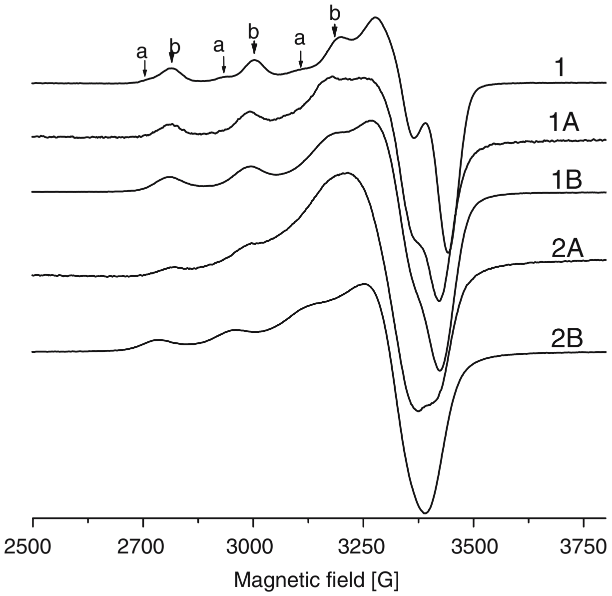

Figure 4. EPR spectra of Cu(II) complexes immobilized on the resins, measured at 77 K (molecular ratios Cu:L for 1A-2B supports are between 1:1 and 5:1).

dation degree after 120 min was smaller (only 35%) than for another catalysts (figure 7).

The oxidation reaction of DTBP carried out under different condition led to DTBQ and PQ mixture (table 4). In general, during the oxidation with the complex CuL, PQ appeared to be predominant product, similarly to the reaction catalysed by Cu(II) ions-amine systems [12,13,15–19,25–27].

Figure 5a–d shows the influence of Cu(II) loading on oxidation degree of DTBP and yield of the products. The function of L_{LDTBP} vs Cu(II) loading for 1A is similar to that observed for 1B, supporting similar coordination mode of the ligands with ethylenediamine structure. Oxidation degree of DTBP reached 60% for the catalysts 1A, 1B and 2A, when sorption degree is about 2 mmol/g, although the content of PQ was different. Only for the 1A catalyst in the examined range

Table 4

Yields of DTBP oxidation reaction catalysed with immobilized Schiff base (CuL complexes)

Symbol	Cu(II) loading (mmol/g)	L_{DTBP} (%)	Y_{DTBQ} (%)	Y_{PQ} (%)
		58.2	28.8	71.2
1A	2.61	62.2*	22.0*	78.0*
		58.7	23.6	76.4
1B	2.09	52.1*	–	–
		60.2	19.8	80.2
2A	1.80	74.7*	–	–
		35.3	27.6	75.4
2B	1.45	34.6*	12.0*	88.0*

L_{DTBP} – oxidation degree of DTBP, Y_{DTBP} – yield of DTBQ, Y_{PQ} – yield of PQ.
*Determined by GC.

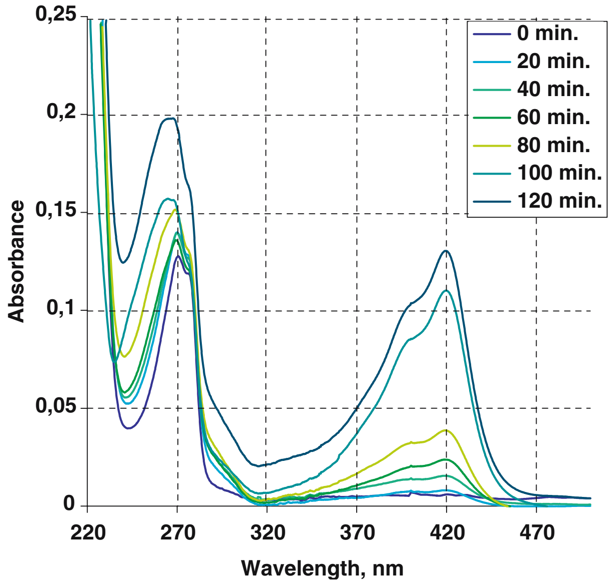

Figure 5. Oxidation degree of DTBP, yield of DTBQ and PQ for the supports with various Cu(II) ions uptake (mmol/g); L_{DTBP} – oxidation degree of DTBP; Y_{DTBQ} – yield of DTBQ; Y_{PQ} – yield of PQ.

Table 3

EPR parameters of the spectra observed for Cu(II)complexes immobilized on polymers

Resin	g_{II}	$g_{\perp}$	A_{II}	$A_{\perp}$	Complex	Donor set around Cu(II) plane
1	2.267	2.060	176	14	CuL (a)	(2N)2O**
	2.210	2.050	191	18	CuL_2(b)	2(2N)
1A	2.222	2.055	183	20	CuL	(2NO)O
1B	2.220	2.060	185	25	CuL	(3N)O
2A	2.227	2.066	176	23	CuL_2	2(NO) or (NO)2O
2B	2.254	2.068	174	20	CuL	(2N)2O
$Cu(N\text{-}R\text{-}sal)_2$*[31]	2.233	2.055	165	15	CuL_2	2(NO)
$Cu(N,N'en\text{-}sal_2)$[32]	2.211	2.055	199	20	CuL	(2N2O)

*R = *n*-Propyl,**in the parenthesis are indicated donor sets of chelating ligands.
(a) and (b) corresponds to two Cu(II) complexes formed with 1, giving rise, respectively, to "a" and "b" lines (from copper hyperfine splitting of parallel orientation) in the EPR spectrum (figure 4).
A parameters in 10^{-4} cm^{-1} units.

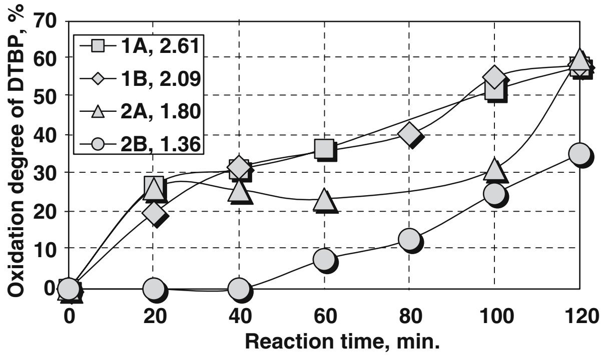

Figure 6. UV/VIS spectra during oxidation reaction catalysed by 2A with 1.8 mmol/g Cu(II) loading.

for Cu(II) uptake resulted in a greater yield of PQ than DTBQ.

The best transformation and selectivity towards PQ was obtained for significant ligand deficiency (tables 2 and 4; figure 5). An excess of Cu(II) ions in relation to the ligands (CuL) favours oxidation reaction yield and selectivity towards PQ (catalyst 1A) whereas when the Cu(II) loading is low the oxidation degree and the PQ selectivity decreased. Both properties of 1B, a weak donor character of its pyridine nitrogen and longer fragment of the ligand derived from ethylenediamine makes difficult molecular dimerization leading to PQ according to the mechanism proposed by Rockcliffe and Martell [13]. Cu(II) ions surrounded by tricoordinating ligands (provided by macrocyclic Schiff bases [12,13] or other tripodal amines [33] were previously reported as effective catalysts). Oxygen atoms of oxidizing agents, dioxygen or hydroperoxide ions occupy fourth coordinating position in the peroxo intermediate. In the former case a second atom of the oxygen is involved in coordination of the next Cu(II) ion surrounded by tricoordinate ligand and dinuclear compound is formed.

The catalysts 2A and 2B which have very short ligands are useful in oxidation reaction only for the samples with maximal Cu(II) loading (1.8 and 1.45 mmol/g respectively) (table 4; figure 5).

4. Conclusions

1. The catalysts with the Schiff base on polymer support used in the oxidation reaction of substituted phenols allows to obtain diphenoquinone as a significant reagent in pharmaceutical industry.
2. The best oxidation degree of 2,6-di-*tert*-butylphenol and the selectivity towards diphenoquinone is revealed by Cu(II) complexes with long Schiff base ligands derived from salicylaldimine, which have CuL structure.

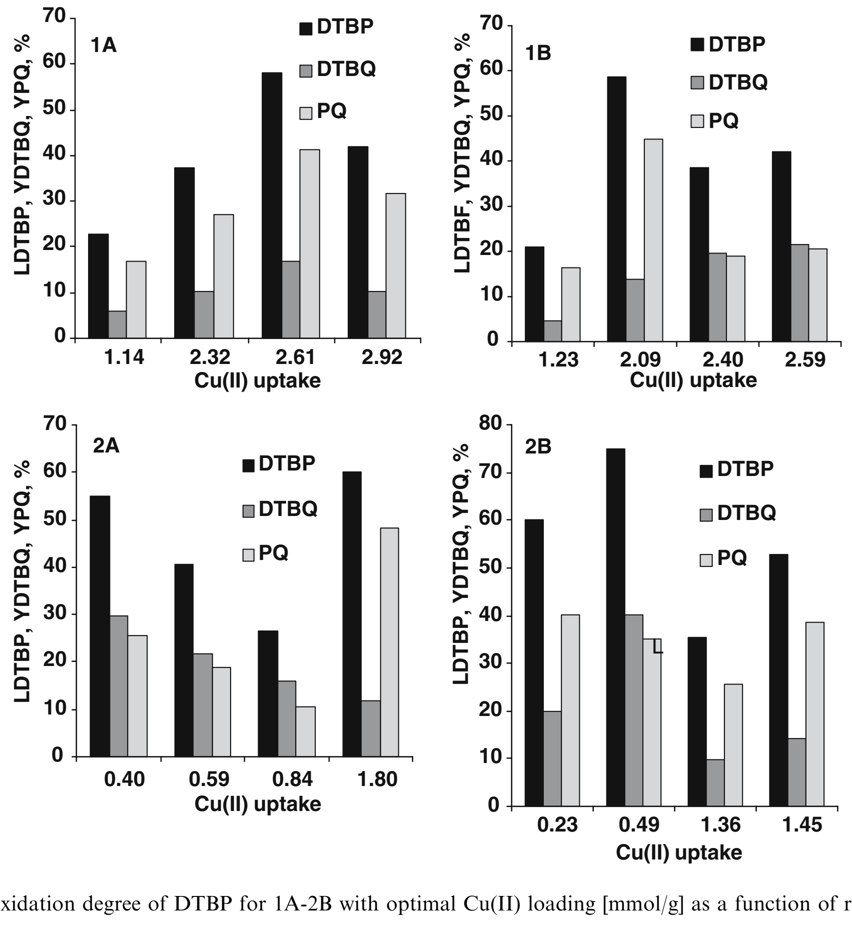

Figure 7. Oxidation degree of DTBP for 1A-2B with optimal Cu(II) loading [mmol/g] as a function of reaction time.

3. The structural properties of ligands and complexes influences on catalytic activity and selectivity and determine the mechanism of oxidation reaction.

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