

# The Radical and Ion-Radical Mechanism of Polymerization of 2,6-Xylenol. II.

## The Reactivity of Aryloxy Radicals with Copper(II) Complexes

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Free tri-*tert*-butyl-phenoxy radical was used as model compound for studying the reactivity of aryloxy radicals with Cu(II)-cyclohexylamine complexes (as homogeneous catalyst of oxidative coupling of 2,6-dimethylphenol). The analysis of the EPR signals leads to the conclusion that electron transfer from the free radical to Cu(II) takes place if Cu(II) is not fully coordinated with cyclohexylamine. In complexes with the copper atom firmly bound in chelate groups (ethylacetylacetonate) no electron transfer occurs. Not only the tri-*tert*-butyl-, but also the polymer phenoxy radicals react very effectively with the catalytic Cu(II)-cyclohexylamine complexes. The polymer phenoxy radical in contrast with the tri-*tert*-butyl radical is not reactive with CuCl<sub>2</sub> molecules.

Assuming that the polymerization of 2,6-xylenol initiated by the copper(II) compounds would exclusively take place by a radical mechanism, a defined concentration level of polymer free radicals measurable by the EPR method, analogically as it was observed in the presence of Ag<sub>2</sub>O [1], could be expected. As it was stated in the previous paper of this series [1], the polymer radicals could be generated at a sufficiently high concentration only after reducing the mobility of the whole system using the technique of the silicon paste on the surface of copper catalyst crystals, while in benzene (or benzene—ethanol) solutions a measurable level of free radicals could not be identified even at the maximum sensitivity of the EPR spectrometer ( $5 \times 10^{11}$  spin/ $\Delta H$ ). These facts pointed at the possibility of consecutive reactions of polymer phenoxy radicals. Therefore attention was paid to the investigation of polymer radical reactivity as well as to the study of the tri-*tert*-butyl-phenoxy radical with different components, considered in the polymerization process. Main attention was paid to the interaction of this type of radicals with CuCl<sub>2</sub> and their complexes with cyclohexylamine.

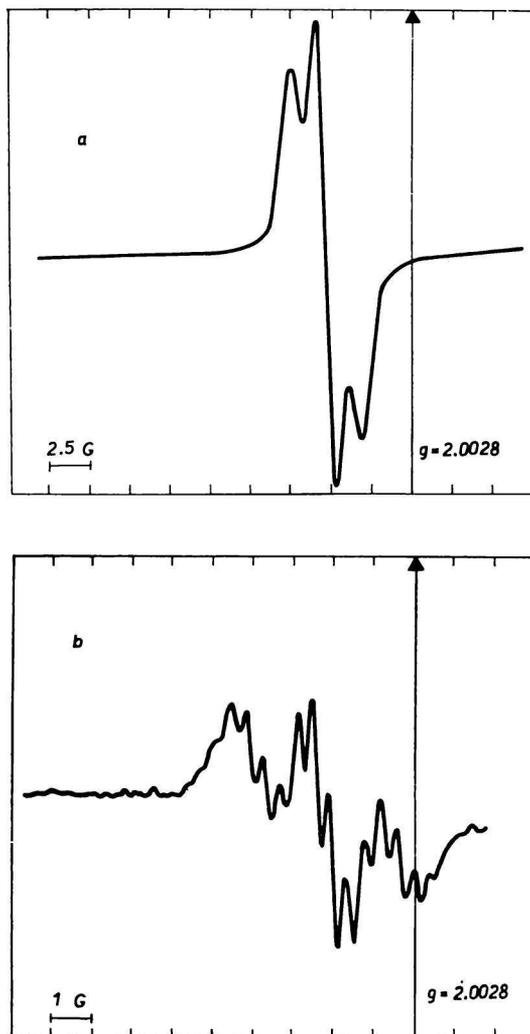
### Experimental

The experimental technique and the chemicals used were dealt with in the previous paper [1]. An X-band EPR spectrometer model Varian E-3 was used.

## Results and Discussion

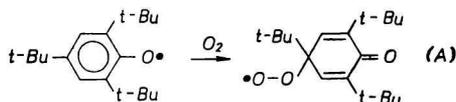
### *Reactions of tri-tert-butyl-phenoxy radical (TTBP)*

For the model studies of reactivity of the primary and secondary phenoxy radicals with copper(II) and its complexes, TTBP radicals were elected. The reactions of this stable free radical were studied in benzene solution and in inert atmosphere by the EPR method.



*Fig. 1.* EPR signal of tri-tert-butyl-phenoxy radical in benzene solutions in an inert atmosphere (a), and after contamination by oxygen traces at temperature of 23°C (b).

At concentration  $10^{-3}$  mole  $l^{-1}$  the signal gives a singlet according to [2] and a triplet at lower concentration as consequence of the interaction of two hydrogen atoms on the aromatic ring with the free electron (Fig. 1a). When contamination by oxygen occurs, the spectroscopic factor  $g$  varies and a new signal can be observed (Fig. 1b). The lines of the triplet (coupling constant  $a_1 = 2$  gauss) are splitted to quartet ( $a_2 = 0.5$  gauss). The oxidation of the radical takes place according to the following reaction (A):



The EPR signal could be interpreted under the presumption that only one methyl group of the neighbouring tri-*tert*-butyl group is in space-contact interaction with the free electron.

The spectroscopic factor  $g$  for TTBP radical is equal to 2.006, what makes possible quantitatively to follow the concentration changes of radicals after adding  $\text{CuCl}_2$  or its complexes. In this case, another singlet belonging to free  $3d^9$  electron of the  $\text{Cu(II)}$  ion has been observed, for which the  $g$  value is 2.16, that is, the symmetry centre is shifted by 265 gauss to lower fields. By rising the relation TTBP/ $\text{Cu(II)}$ , the signal belonging to the copper ion gradually decreases and after reaching the equilibrium state, a singlet of the non-reacted free phenoxy radicals appears (Fig. 2). By comparing the areas of both signals it is possible qualitatively to express the

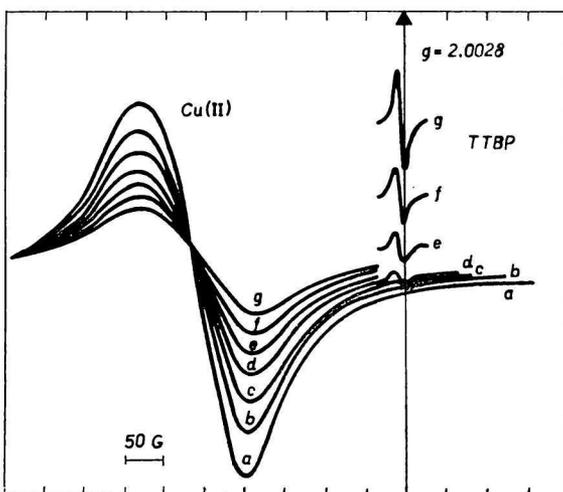


Fig. 2. Variations of EPR signals during the „titration“ of 1 ml of 0.1 mole  $l^{-1}$  ethanol solution of  $\text{CuCl}_2$  by means of TTBP radical (0.3 ml of the reaction mixture in the EPR cell).  $\text{CuCl}_2$  before adding the radical (a); after adding the radical solution in amounts of 0.2 ml (b); 0.4 ml (c); 0.6 ml (d); 0.8 ml (e); 1.0 ml (f); 1.2 ml (g).

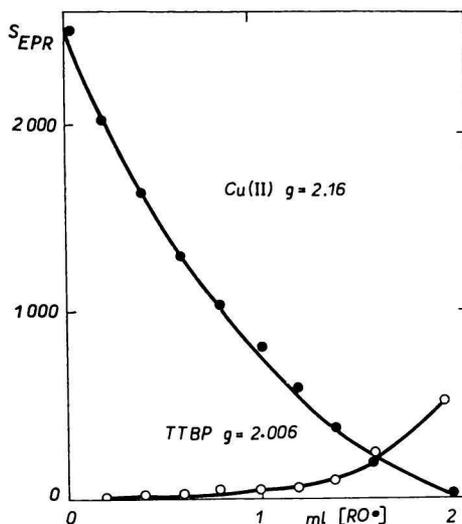
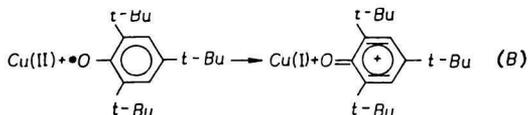


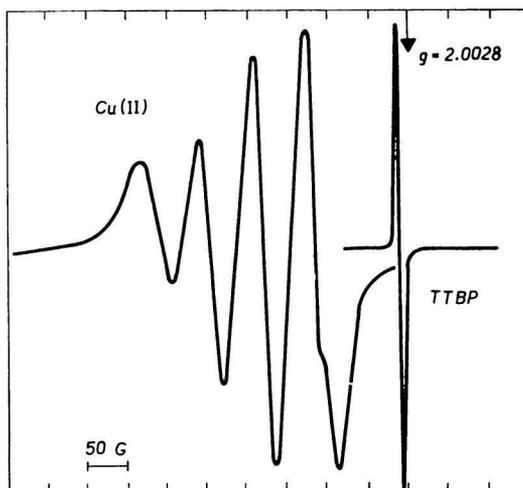
Fig. 3. Change of the intensity of EPR signals expressed by their total area belonging to  $Cu(II)$  ions ( $g = 2.16$ ) and TTBP radicals ( $g = 2.006$ ) during the titration of 1 ml ethanol solution of  $CuCl_2$  ( $0.1 \text{ mole l}^{-1}$ ) by  $0.1 \text{ mole l}^{-1}$  benzene solution of phenoxyl radical at temperature of  $23^\circ C$  (0.3 ml of solution in the EPR cell).

change of the number of free spins (Fig. 3). The reaction components in equilibrium state reach a concentration level of  $8 \times 10^{17}$  unpaired electrons in 0.3 ml. The gradual decrease of the signal  $Cu(II)$  is caused by the reduction of the bivalent to the non-resonant univalent  $Cu(I)$  ion. It appears necessary to assume the formation of a phenoxonium ion according to the following reaction (B)

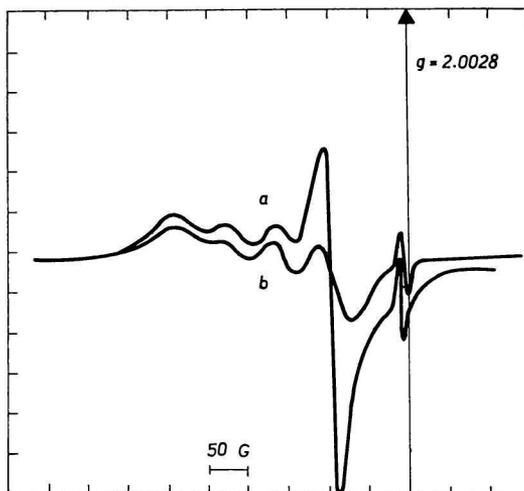


In case the copper ion is closed in a chelate complex, the electron transfer does not take place (Fig. 4). Electron transfer, however, can occur in the course of reaction with the amine complexes of  $CuCl_2$ . This reaction is much more effective in a homogeneous liquid phase, while the reactivity of a heterogeneous system containing insoluble complexes with greater number of coordinated amine ligands decreases (Fig. 5).

The observed decrease of the phenoxyl radical concentration caused by the interaction with  $Cu(II)$  is many times higher than the possible decrease caused by other products in the reaction mixture (ethanol, cyclohexylamine). The effective reaction of these radicals with 2,6-xyleneol has also been confirmed in agreement with observations of Bolon [3].



*Fig. 4.* EPR signal of the mixture of 0.2 ml TTBP radical with 0.2 ml benzene solution of the complex  $\text{Cu}(\text{CH}_3\text{COCHCO} \cdot \text{OCH}_2\text{CH}_3)_2$  ( $1.9 \times 10^{-3}$  mole  $\text{l}^{-1}$ ) at the molar ratio of 1 : 1 in nitrogen atmosphere and at temperature of 23°C.



*Fig. 5.* EPR signal of the mixture of  $\text{CuCl}_2 \cdot 4$  cyclohexylamine (0.2 ml) with TTBP radicals (0.2 ml). a) without elimination of a blue precipitate formed in the solution (the whole heterogeneous system); b) the liquid phase after elimination of the sediment.

#### *Reaction with the polymer radical*

The polymer phenoxy radicals prepared from 2,6-xyleneol by oxidative dehydrogenation using  $\text{Ag}_2\text{O}$  in benzene solution were used for the investigation of their

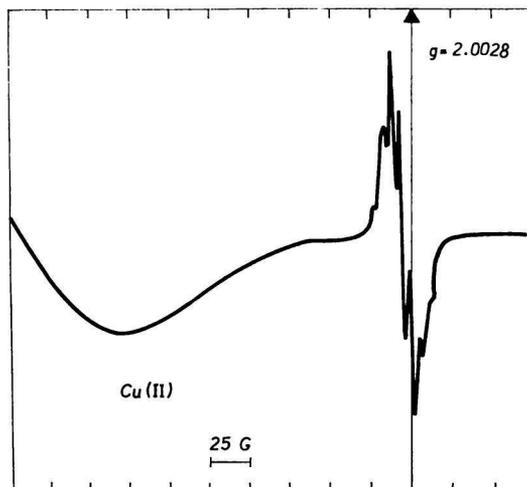


Fig. 6. EPR signal in a mixture of polymer phenoxy radical (generated with  $\text{Ag}_2\text{O}$  from 2,6-xyleneol) in benzene solution with a waterless  $\text{CuCl}_2$  in inert atmosphere (the diagram shows only the second half of the signal belonging to the unpaired electrons of  $\text{Cu(II)}$  ions). 0.1 ml  $\text{CuCl}_2$ -ethanol (concentration  $3.8 \times 10^{-2}$  mole  $\text{l}^{-1}$ ), 0.4 ml of polymer radical, inert atmosphere, temperature  $23^\circ\text{C}$ .

reactivity with compounds of copper(II). The fact that in contrast to the model TTBP radical no electron exchange between  $\text{CuCl}_2$  and the polymer radical occurs, is considered to be important (Fig. 6). On the other hand, the catalytic  $\text{Cu(II)}$ -amine complexes react with the polymer radicals very quickly. It is interesting that even cyclohexylamine reacts with the polymer radicals forming non-paramagnetic products. A hydrogen transfer reaction leading to the inactive products is suggested.

### References

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3. Bolon D. A., *J. Org. Chem.* **32**, 1584 (1967).

Translated by M. Tkáčová