

DECOMPOSITION KINETICS OF COBALT COMPLEXES
OF PHENOXY RADICALS STUDIED BY EPR METHOD*

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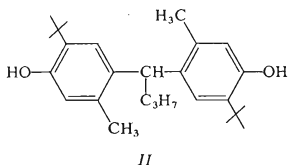
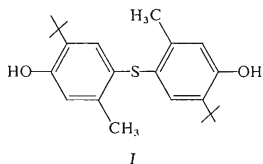
In bimolecular homolytic substitution reactions type S_H2 between coordinated peroxy radicals $[Co(III)]RO_2\cdot$ and partially hindered bisphenol 4,4'-thiobis-(3-methyl-6-tert-butylphenol) (an antioxidant with commercial name Santonox R) in non-polar medium at room temperature an equilibrium is established between free and $Co(III)$ -coordinated phenoxy radicals. Increasing temperature shifts the equilibrium in favour of the decomplexed free radicals. The complexation-decomplexation process of phenoxy radicals is practically reversible up to $90^\circ C$. Polar coordinating solvents (methanol, H_2O , diethyl ether, tetrahydrofuran) displace irreversibly the radicals from the complexes. From their decomposition kinetics at various temperatures activation energy of decomplexation by methanol has been determined ($110 \pm 8 \text{ kJ mol}^{-1}$). The displaced free partially hindered phenoxy radicals are not sufficiently stable and undergo subsequent radical transformations (dimerization, intramolecular and intermolecular H-transfer) with effective activation energy about 67 kJ mol^{-1} .

As activation energy of coordination of phenoxy radicals to $Co(III)$ is substantially lower than that of the subsequent radical transformations, the latter are sufficiently rapid only if the cobalt coordination sphere is blocked by methanol. On the basis of EPR spectra the degree of mesomerism is also discussed as well as the stability of the partially hindered phenoxy radicals with the presumption that the sulphur bridge between the phenyl nuclei is substituted by butylidene bridge (4,4'-butylidenebis-(3-methyl-6-tert-butylphenol) — an antioxidant with commercial name Santowhite Powder).

It was found¹⁻⁴ that in the absence of oxygen stable phenoxy radicals are formed by abstraction of hydrogen (by peroxy radicals) from sterically hindered phenols and bisphenols having bulky tert-butyl groups in *ortho* position and substituted *para* position (in non-polar media as benzene, hexane, CCl_4), whereas from unhindered phenols (H or CH_3 in one or both *ortho* positions) radical complexes with $Co(III)$ are formed. The complexes give characteristic octet EPR signals ($I_{Co} = 7/2$) with splitting constant $a_{Co} = 1.0 \text{ mT}$ and with $g = 1.998$. Introduction of sulphur atom or butylidene bridge between two benzene rings of bisphenols violates this rule,

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and, in the case of commercial partially hindered antioxidants Santonox R (*I*) and Santowhite Powder (*II*), it is possible to prepare, by adjusting the solvent polarity at room temperature, either the coordinated phenoxy radicals, or free phenoxy radicals, or the both forms side by side in dynamical equilibrium. As radical transformations between coordinatively bound and free phenoxy radicals (or the subsequent radical reactions) proceed within the temperature interval 20 to 50°C at measurable rates, EPR spectroscopy can provide kinetical characteristics in studies of stability of radical complexes with transition metals.



EXPERIMENTAL

The published methods^{5,6} were partially modified for preparation of the coordinated [Co(III)]. $\text{RO}_2\cdot$ radicals used for abstraction of hydrogen from OH group of bisfenols.

Method I. Preparation of the initiation $\text{RO}_2\cdot$ radicals for generation of predominantly coordinated phenoxy radicals. The bisfenol (1 to 3 mol excess) is dissolved in $5 \cdot 10^{-2}\text{M}$ solution $\text{Co}(\text{acac})_2$ in benzene or CCl_4 with intensive stirring (magnetic stirrer), and concentrated tert-butylhydroperoxide (BuOOH) is added drop by drop under inert atmosphere of N_2 in a thermostatted reaction vessel (20–50°C), so that molar ratio is $\text{BuOOH}:\text{Co}(\text{acac})_2 = 10$ at the end of the reaction. The system with the complexed phenoxy radicals can be purified by removal of volatile reaction components (BuOOH , BuOH) by vacuum distillation and subsequent dissolution of the obtained paramagnetic powder in non-polar solvent. This procedure is repeated twice.

Method II. Preparation of the initiation $\text{RO}_2\cdot$ radicals for generation of free and coordinated phenoxy radicals. Methanol in 100–500 molar excess is added to $5 \cdot 10^{-2}\text{M}$ solution of $\text{Co}(\text{acac})_2$ in benzene, the bisfenol is dissolved, and BuOOH is added gradually as in the Method I.

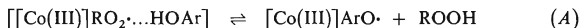
Method III. The initiation system for preparation of only free phenoxy radicals. Concentrated BuOOH (molar excess 1 : 10) is added to $5 \cdot 10^{-2}\text{M}$ benzene solution of $\text{Co}(\text{acac})_2$ and the system is allowed to react under stirring at 20°C 15 min. Then the excess unreacted BuOOH is evaporated from the reaction mixture in vacuum at 10–15°C. After evaporation the paramagnetic solid residue is dissolved in benzene or CCl_4 . The procedure is repeated twice. The system with the stabilized $\text{Co(III)RO}_2\cdot$ radicals is treated with the oxidized reactant along with methanol (ratio methanol: $\text{Co(III)} = 100$).

Chemicals. BuOOH 95% (Fluka, Switzerland) was purified by vacuum distillation in dark under nitrogen and dried over P_2O_5 . Similarly the solvents were dried before use. $\text{Co}(\text{acac})_2$ was recrystallized from methanol and, before use, dried in vacuum 1 Pa at 110°C 2 h. The antioxidants Santonox R and Santowhite Powder (Monsanto) were recrystallized from n-hexane.

Methods and Apparatus. The EPR signals were recorded with a Varian E-3 spectrometer in the range X with 100 kHz modulation. The temperature measurements were carried out with a temperature device Varian Variable Temperature Accessory with accuracy $\pm 1^\circ\text{C}$. The time changes of intensity of primary and secondary radicals were followed in closed cylindrical EPR cells placed in a quartz Dewar vessel located directly in the resonance cavity.

RESULTS AND DISCUSSION

Santonox R. Decomplexation with methanol. In non-polar medium the reaction of $[\text{Co(III)}]\text{RO}_2\cdot$ radicals with Santonox R (ArOH) by the method *I* produces predominantly Co-bound phenoxy radicals (Eq. (A)), whereas in the presence of methanol according to the method *II* partial replacement of phenoxy radicals from the complex with the transition metal takes place according to Eq. (B), and at room temperature the solution contains both the coordinated and free phenoxy radicals.



Ratio of areas of the superposed EPR signals of the coordinated and free phenoxy radicals (Fig. 1) indicates that, in the absence of polar component, the equilibrium (A) in the method *I* is shifted strongly to the right, in favour of the radical complexes with cobalt. In the EPR spectrum the octet signal ($g = 1.998$) is dominating. At lower molar ratios bisphenol: $\text{Co}(\text{acac})_2 < 3$ the octet signal is superimposed with a signal of a free radical at $g = 2.0064$. On the contrary, in oxidation of the partially hindered phenol in the presence of methanol according to the method *II* the EPR spectrum contains as the dominant signal that of free phenoxy radicals ($g = 2.0064$) overlapped, immediately after the reaction, also with the signal of the coordinated phenoxy radicals in the sense of the reaction (A). Splitting constant of the octet signal ($a_{\text{Co}} = 1.0 \text{ mT}$, $I_{\text{Co}} = 7/2$) characterizes the interaction of the nonpaired electron of phenoxy radical with the magnetic moment of cobalt nucleus and indicates an at least 20% spin delocalization of *s*-character to the cobalt nucleus in the complex. Pure EPR spectrum of free phenoxy radical can be obtained by the method *III* or by oxidation with the radicals obtained by thermal decomposition of dibenzoyl peroxide as it was observed by Westfahl^{7,8}. This author assigned the splitting constants $a_0 = 0.513 \text{ mT}$ and $a_m = 0.121 \text{ mT}$ to the *ortho* and *meta* protons, respectively. In our case on the basis of spectral simulation we found for splitting by one *ortho*-proton $a_0 = 0.455 \text{ mT}$ and for that by one *meta*-proton as well as for 3 protons of a methyl group at *meta* position the value $a_m = 0.108 \text{ mT}$. Under the conditions of lowered spectral resolution of the EPR signals (as in Fig. 1) in the superposed spectra of free and coordinated phenoxy radicals individual lines of the basic doublet are not unequivocally split into quintets, whereas, on the contra-

ry, individual lines of the octet are split into doublet $a_0 = 0.33$ mT by interaction of the unpaired electron of the coordinated phenoxo radical with one *ortho*-proton.

In principle two mechanisms lower the concentration of the phenoxo radicals coordinated to cobalt at the chosen temperature in the presence of methanol. The primary condition for reactions in the coordination sphere of the transition metal consists in formation of the complex of $\text{Co}(\text{acac})_2$ with the bisphenol, which is partially hindered by the presence of methanol in the system, as it is shown by the dependence of the EPR signal intensity (the last but one line of the octet) of the complexed phenoxo radicals on the ratio $\text{CH}_3\text{OH}:\text{Co}(\text{acac})_2$ (Fig. 2a) in the equilibrium established 2 min after mixing the reactants. Higher bisphenol concentration relative to $\text{Co}(\text{acac})_2$ at constant methanol amount (Fig. 2b) prefers formation of the primary complexes according to Eq. (C)

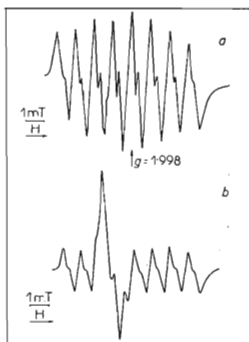
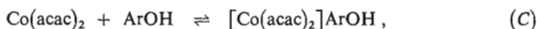


FIG. 1

EPR Signal of Coordinated Phenoxo Radicals Prepared by Method I (a) and of Equilibrium Mixture of Free and Coordinated Phenoxo Radicals Prepared by Method II (b); Benzene Solutions, 23°C

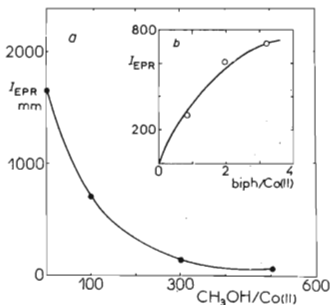
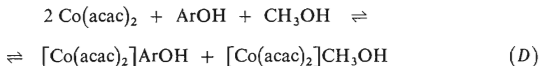


FIG. 2

Dependence of Intensity of the 7th Line of EPR Signal of Coordinated Phenoxo Radicals a) on Ratio $\text{CH}_3\text{OH}:\text{Co}(\text{acac})_2$ at Constant Ratio Santonox R: $\text{Co}(\text{acac})_2 = 3$ at Room Temperature 2 min after Mixing by Method II b) on Ratio Santonox R: $\text{Co}(\text{acac})_2$ at Constant Ratio $\text{CH}_3\text{OH}:\text{Co}(\text{acac})_2 = 100$ at Room Temperature 2 min after Mixing by Method II

which, even in the presence of excess BuOOH, represents a presumption of formation of a higher level of the coordinated phenoxy radicals according to Eq. (A). In fact, the matter is in competition equilibria in the coordination sphere of cobalt according to the overall scheme



From the course of kinetic curves of decomposition of the octet signals with time (Fig. 3a) with excess methanol it can be concluded that the simultaneous increase of the level of the non-coordinated phenoxy radicals (going through a maximum) is due to their displacement from the coordination sphere of the transition metal. The process of disappearance of the octet signals with time obeys kinetic equation of the 1. order (Fig. 4). Decrease of the octet component of the superposed EPR signal with time in the presence of methanol was followed at various temperatures,

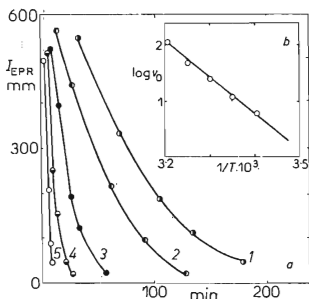


FIG. 3

Dependence of Intensity of the 7th Line of EPR Signal of Coordinated Phenoxy Radicals on Time at Various Temperatures
a) 1 20°C, 2 25°C, 3 30°C, 4 35°C, 5 40°C.

b) determination of activation energy of displacement of phenoxy radicals in the Arrhenium parameters (by method II).

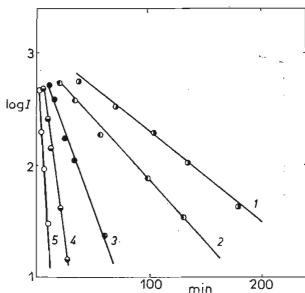


FIG. 4

Dependence of Logarithm of Intensity of the 7th Line of EPR Signal on Time at Various Temperatures (Fig. 3a)

and the effective activation energy of the displacement reaction ($110 \pm 8 \text{ kJ mol}^{-1}$; Fig. 3b) was determined from the initial decomposition rate of the radical complexes in the Arrhenius parameters.

If the phenoxy radicals displaced by methanol from the coordination sphere of the transition metal cannot be complexed back, then they undergo gradual change (Fig. 5). In first minutes of oxidation of Santonox R according to the method II (Fig. 5, 8 min) the octet signal of the radical complex is superposed by the EPR signal of free phenoxy radical, a doublet split into a quintet. Intensity of the lines is continuously changing with time, and, after 10 hours, it comes to rest as a five-line spectrum with binomial intensity ratio. Qualitative difference between spectra of the primary and the final free phenoxy radical consists in elimination of hyperfine interaction of the non-paired electron with one *ortho*-proton ($a_o = 0.455 \text{ mT}$). This fact indicates a proton loss at *ortho* position, so that the resulting signal is only characterized by a quintet due to 4 protons (H and CH_3 at *meta* position, $a_m =$

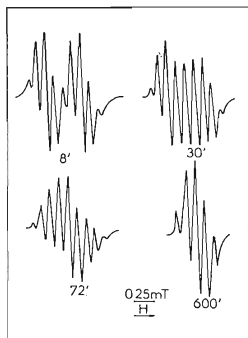


FIG. 5

EPR Spectra in Transformation of Primary Decomplexed Phenoxy Radicals to Final Radical Forms in the System Generated by Method II at Room Temperature in Benzene Solutions

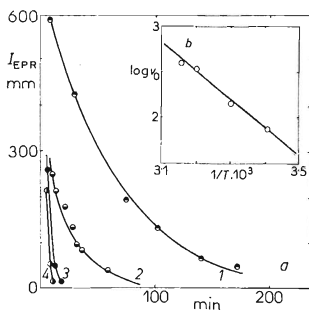
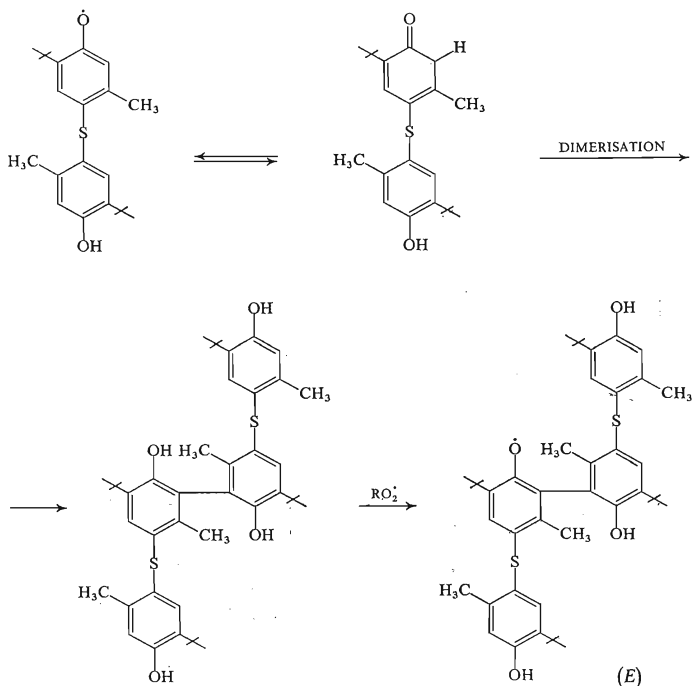


FIG. 6

Decrease of Intensity of EPR Signal of Primary Decomplexed Phenoxy Radicals with Time at Various Temperatures (method II)

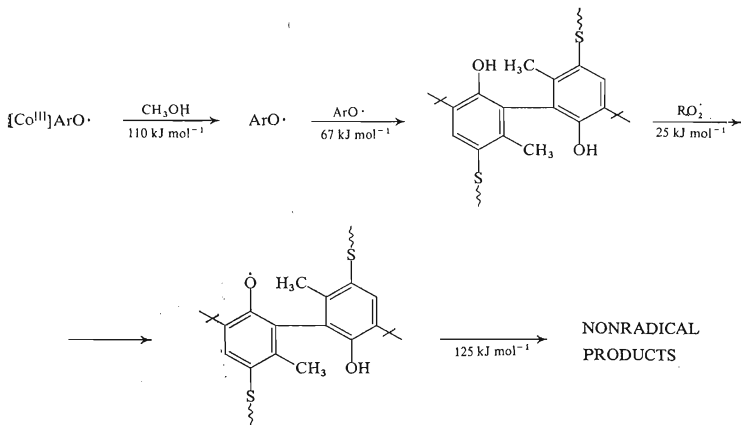
a) 1 20°C , 2 30°C , 3 40°C , 4 45°C ; b) determination of activation energy of the radical transformation in the Arrhenius parameters.

= 0.108 mT). Formation of the secondary radicals is explained by dimerization of the resonance forms of the primary decomplexed phenoxy radicals at their non-hindered *ortho* position accompanied by a proton rearrangement and a further intermolecular H-transfer in the reaction with the $\text{RO}_2\cdot$ radicals according to the following (Eq. (E)).



Dimerization of phenols and parabispheols at *ortho* position was studied by a number of authors^{9,10}. Interaction of the unpaired electron with only 4 protons at *meta* position indicates disturbed coplanarity of the two nuclei bound through *ortho* position in contrast to 2,2'-bispheols⁷ in which a closed mesomeric system is present. The given reaction scheme is confirmed also by the experiment carried

out according to the method *III* where no excess of RO_2^\cdot radicals is available, and, hence, the time change of the doublet-quintet spectrum into quintet is not observed. Figure 6a gives kinetic curves of decomposition of the primary free phenoxy radicals at various temperatures. From initial rate activation energy of the radical change was determined (67 kJ mol^{-1}). This relatively fast transformation of radicals preferred to reversible complexation with cobalt is due to $\text{Co}(\text{acac})_2$ being blocked by methanol according to Eq. (B). Therefrom it follows that coordination of an unhindered phenoxy radical requires a considerably lower activation energy, which stands in accordance with high stability of the radical complexes in the absence of coordination agents. The final radical forms of dimerization must be considered to be hindered polyphenols for which enhanced stability can be expected, which is confirmed by relatively high activation energy of their decomposition (Fig. 7) 125 kJ mol^{-1} .



Santonox R. Decomplexation at enhanced temperature. In non-polar media without methanol the radical complexes are decomposed by increased temperature practically reversibly up to 90°C . Fig. 8 represents transformations of the octet signals of the radical complexes of phenoxy radicals into free phenoxy radicals characterized by EPR signal with basic doublet splitting. It can be seen that at 90°C octet signals are markedly decreased, but reverse temperature decrease to 25°C results in their reappearance. This transformation can be repeated several times, but absolute concentration of the radicals gradually decreases due to subsequent reactions,

as it can be seen from dependence of the EPR signal areas on temperature (Fig. 9). In the absence of methanol the subsequent reactions are relatively slow, as Co(III) is not blocked by polar component, and the reverse formation of the complexes is substantially faster than the subsequent radical reactions. At low temperatures equilibrium is established practically immediately, which makes the kinetic study by EPR spectra impossible and indicates relative low activation energy of this process in the range $20-40 \text{ kJ mol}^{-1}$. Determination of approximate equilibrium constants of decomplexation at two temperatures (30°C , 50°C) made it possible to express the value of $\Delta H = 80-90 \text{ kJ mol}^{-1}$ on the basis of classical thermodynamic relations.

Santonwhite Powder. This bisphenol type differs from Santonox R in that the sulphur bridge is replaced by butylidene bridge. This structural change partially lowered stability of the partially-hindered phenoxy radicals and, at the same time increased stability of the radical complexes with cobalt. Obviously, in the case of sulphur the unpaired electron is partially delocalized to the sulphur atom, which enables the existence of relatively stable free phenoxy radicals of Santonox R in spite of that this bisphenol is partially hindered. In the case of Santowhite Powder in the method *I*

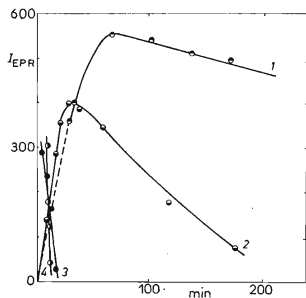


FIG. 7

Kinetic Curves of Generation and Decomposition of Final Radical Forms Produced from Primary Decomplexed Phenoxy Radicals; 1 20°C , 2 30°C , 3 40°C , 4 45°C

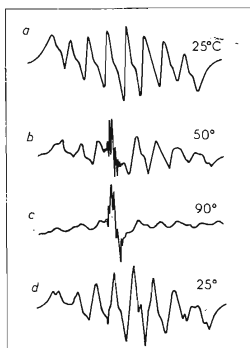


FIG. 8

Change of Superposed EPR Signals of Co-ordinated and Free Phenoxy Radicals with Temperature ($25-90^\circ$) (a-c) and after Cooling to Room Temperature (d)

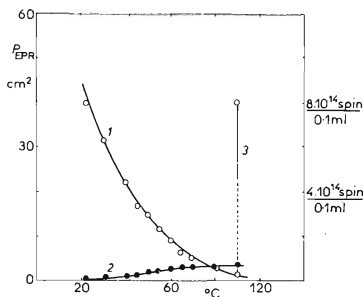


FIG. 9

Dependence of EPR Signal Area and Concentration of Unpaired Electrons (spin/0.1 ml sample) on Temperature

1 Coordinated phenoxy radicals; 2 free phenoxy radicals; 3 increase of intensity of coordinated phenoxy radicals after temperature decrease to 25°C.

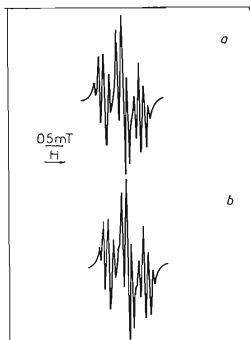


FIG. 10

Experimental (a) and Simulated (b) EPR Spectra of Free 4,4'-Butylidenebis(3-methyl-6-tert-butylphenoxy) Radical Formed by Method III ((1 H) $a_0 = 0.525$ mT, (1 H) $a_p = 0.525$ mT, (4 H) $a_m = 0.145$ mT, $p/p = 0.080$ mT)

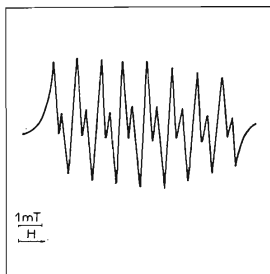


FIG. 11

EPR Spectrum of Coordinated 4,4'-Butylidenebis(3-methyl-6-tert-butylphenoxy) Radicals at Cobalt Prepared by Method I or II

very stable octet signals were generated which were split into doublet, and no free phenoxy radicals were observed in equilibrium. Neither the presence of methanol (method II) brought about marked decomplexation. Free phenoxy radicals of relatively low concentration could be generated by the method III in the presence of methanol or by oxidation of Santowhite Powder by cobalt(III) di- μ -hydroxotetrakis-acetylacetonate (synthesized by the method of Boucher and Herrington¹¹). On the basis of spectral simulation (Fig. 10) it was possible to interpret the electronic structure of phenoxy radical the basic triplet splitting being due to interaction of unpaired electron with two equivalent protons (one in *ortho* position and the other in the butylidene bridge; $a_H = 0.525$ mT). The basic triplet is further split into quintet by four *meta*-protons ($a_m = 0.145$ mT). EPR spectrum of the radical complex of 4,4'-butylidenebis-(3-methyl-6-tert-butyl)phenoxy radicals at cobalt is given in Fig. 11 ($a_{Co} = 1.05$ mT, $a_o = 0.37$ mT).

In the both studied cases of partially hindered bisphenols the second phenyl nucleus is not involved in the mesomerism, the unpaired electron being delocalized to benzene ring with oxygen and partially to the sulphur atom or the butylidene bridge. The group of bisphenols able to produce radical complexes in equilibrium with the relevant free radicals extends the two so far known categories of phenols, *i.e.* the hindered ones giving free phenoxy radicals, and the unhindered ones giving only the complexed radicals.

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