Polyfunctional Activity of Metal Complexes Containing 2,6-Di-*tert*-butylphenol in Catalytic Oxidation

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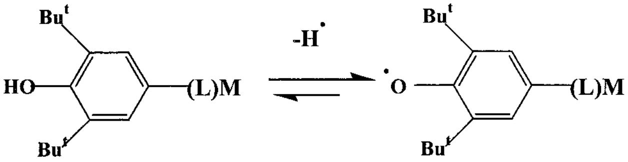
Summary: The results of the investigations of metal complexes containing 2,6-di-*tert*-butilphenol in the ligand environment in catalytic homogeneous oxidation of organic compounds are reviewed. The liquid-phase oxidation of hydrocarbons, olefins, aminophenol and unsaturated fatty acids by molecular oxygen in the presence of phthalocyanines, porphyrins, σ-aryl and π-allyl transition metal complexes is described. The change of the reactivity of organometallic and coordination compounds by oxidation of the redox active phenolic group opens up the possibility to use them as polyfunctional catalytic systems showing positive and/or negative catalytic effects.

Keywords: antioxidant; catalyst; 2,6-di-*tert*-butylphenol; metallocomplexes; phthalocyanines; porphyrins

Introduction

Transition metal complexes of macrocycles – phthalocyanines and porphyrins, are well known catalysts for organic substrates oxidation by molecular oxygen. The mechanism of their action involves electron transfer and dioxygen activation.[1,2] On the other hand sterically hindered 2,6-di-*tert*-butylphenols are widely used as antioxidants. The efficiency of 2,6-di-*tert*-butylphenols as inhibitors of oxidative destruction of hydrocarbons is determined by the nature of the group in *para*-position of the aromatic ring which influences the stability of the corresponding phenoxyl radicals formed in oxidation.[3]

Previously, we have demonstrated[4,5] that the introduction of sterically hindered phenolic fragments into the ligand environment (L) of metal complexes **1** leads to the significant increase of the stability of phenoxyl radicals **1a** due to the interaction of the unpaired electron with the metal center (Scheme 1).



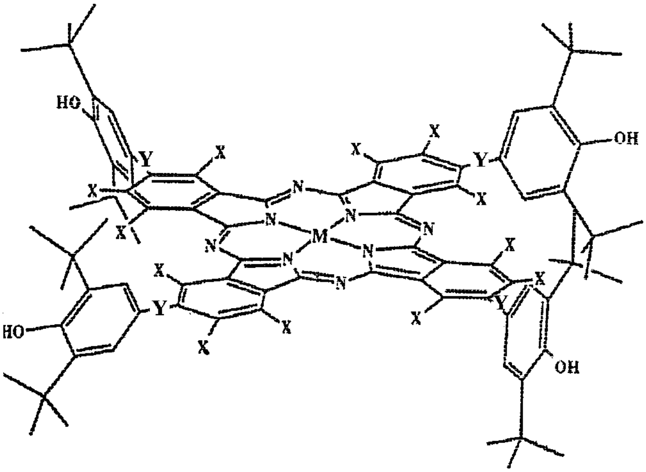
Scheme 1. **1** **1a**

DOI: 10.1002/masy.200351416

Moreover these systems containing redox active groups in the organic ligand and redox active metal atom are capable to induce the intramolecular electron transfer events in redox transformation of metal complexes.[2,5-7] The combination of the antioxidative phenolic fragment and catalytically active metal center in the molecules of metal complexes **1** might be the cause of their dual activity in catalytic oxidation. In this paper we present the results achieved recently by studying the behavior of phthalocyanines and porphyrines containing 2,6-di-*tert*-butylphenols and their low molecular analogous in oxidation of various organic compounds by molecular oxygen.

Phtalocyanines

Metallophtalocyanines (PcM) are well-known catalysts for oxidation of organic substrates. The substituents on the periphery of the phtalocyanine ring determine the solubility of these complexes in polar or nonpolar media, and therefore, open up the possibility of using PcM's as homogenious catalysts for both organic and inorganic substrates. Metallophthalocyanines containing the 2,6-di-*tert*-butylphenol fragments in the macrocyclic ring (R_4PcH_2, R_4PcM, where R = 3,5-di-*tert*-butyl-4-hydroxyphenyl) (**3**) act as either catalysts or inhibitors of oxidation depending on the nature of the metal atom M, the solvent, pH, and the concentration of the catalyst.



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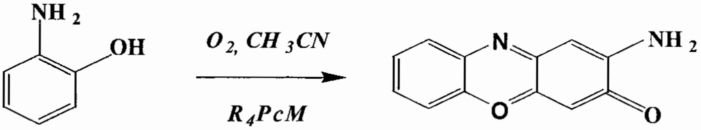
M = HH, Co, Ni, Pd, Pt, Fe, Zn; X = H, Cl; Y = - , CH=N, N=N

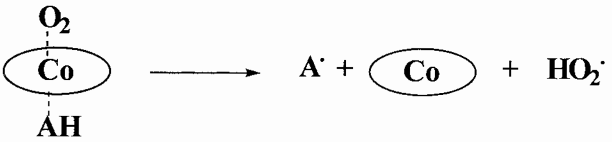
At the same time, their synthetic organic precursors, (3,5-di-*tert*-butyl-4-hydroxyphenyl)phthalonitriles, are efficient inhibitors of the thermooxidative destruction of polyethylene and an oligohexene oil.[8]

The activity of tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)dodecachlorophtalocyanine **3** and it's Co(II), Zn(II), Pt(II) complexes in the oxidation of 2-aminophenol (AP) by O_2 and the mechanism of this catalytic reaction (Scheme 2) was studied in details by kinetic measurements, ESR, UV-vis spectroscopy.[9-11]



Scheme 2.

Kinetic investigation has shown the rate of the formation of 2-aminophenoxazin-3-one to be first-order in [R_4PcCo] in both air and pure O_2. Substrate dependence of the rate has revealed that the kinetic of the catalytic reaction obeys a Michaelis-Menten type rate low. It was concluded that R_4PcCo behaves as other phthalocyanines catalysts and the mechanism involves rate-determing metal ion mediated electron transfer from coordinated 2-aminophenol to coordinated O_2 in the superoxo complex.



⬭ = (3,5-di-*tert*-butyl-4-hydroxyphenyl)dodecachlorophtalocyaninato-dianione

Scheme 3.

The spectrochemical study of the compound **3** behavior in coordinating and non-coordinating solvents in the presence of dioxygen and bases, including 2-aminophenol, indicates the appearance of the anisotropic signal in ESR spectrum attributed to the superoxo complex of R_4PcCo with $g_\perp$ 1.985 and $g_\parallel$ 1.972.[10] The relative intensity of the superoxo signal is time-dependent and decreases with the increase of O_2 content in the air-saturated solution. The UV-vis spectroscopy proves the formation of a new phthalocyanine species with coordinated 2-aminophenol as the axial ligand.[9] These experimental facts confirm the participation of the key intermediate "substrate-catalyst-dioxygen" in the catalytic cycle of 2-aminophenol oxidation.

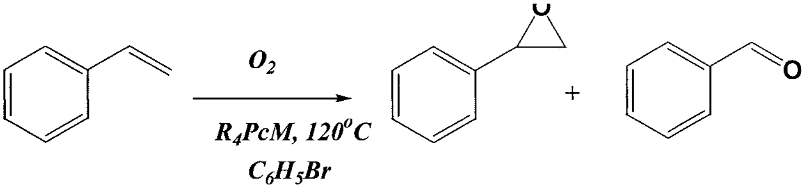
It is to be noted that the rate of 2-aminnophenol oxidation in the presence of free base phthalocyanine R_4PcH_2 and analogous complexes of zinc and platinum decreases, revealing the inhibition of the oxidation by the phenolic groups on the periphery of the phthalocyanine ring (Table 1).

Table 1. Rate constants of 2-aminnophenol oxidation in the presence of phtalocyanines R_4PcM (the concentratiion of 2-aminnophenol $8 \cdot 10^{-2}$ mol·l^{-1} in acetonitrile, the concentration of the additives $8 \cdot 10^{-5}$ mol·l^{-1}).

M in R_4PcM	-	Co(II)	Pt(II)	Zn(II)	HH	2,6-di-*tert*-butyl-4-methylphenol
$w_0 \bullet 10^{-6}$ s^{-1}	28.85	65,45	26,98	25,1	20.04	19,43

Since the formation of superoxo complex is not possible in the case of R_4PcZn, R_4PcPt and R_4PcH_2 the resulting inhibiting effect is attributed to the presence of phenolic fragments which play the same role as the antioxidant 2,6-di-*tert*-butyl-4-methylphenol by H transfer to the substrate radical $A^\bullet$.

Oxidation of styrene by dioxygen (Scheme 4) was investigated in the presence of R_4PcM [(M = Fe(II), Cu(II), Co(II)] and tetra-[N-(3,5-di-*tert*-butil-4-hydroxybenzylidenimine)]-phthalocyaninato cobalt (II).[12]



Scheme 4.

Kinetic data of styrene oxidation (Figure 1) demonstrates the appearance of the induction period in the presence of phthalocyanines under investigation. After that the rate of catalytic oxidation is 2-3.5 times higher in the case of R_4PcFe and R_4PcCo respectively that the rate of the autooxidation; R_4PcCu does not show any catalytic effect.

These data indicate a significant catalytic effect of cobalt phthalocyanine (curve 3) which are in accordance with the previous result of 2-aminophenol oxidation and are explained by the involvement of the key intermediate dioxygen activation step. However cupper phthalocyanine containing four phenolic groups in the macrocyclic ring serves as the effective inhibitor preventing substrate oxidation.

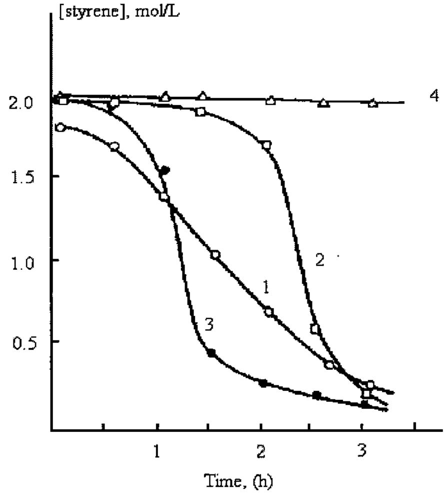
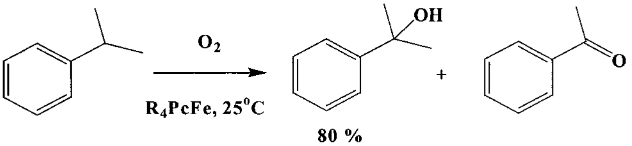


Fig. 1. Kinetic curves of styrene oxidation by O_2: *a*, without additives (1), in the presence of $1.1*10^{-4}$ mol·l^{-1} R_4PcFe (2); $1.6·10^{-4}$ mol·l^{-1} R'_4PcCo (3); $2.6·10^{-4}$ mol·l^{-1} R_4PcCu (4) (PhBr, 120°C).

The oxidation of hydrocarbons (R'H) involves the generation of peroxyl radicals $R'OO^•$ and the corresponding hydroperoxides R'OOH in radical chain process.[13] The role of metal complexes containing 2,6-di-*tert*-butylphenols might be significant in either initiation step of hydroperoxides formation or in their decomposition. Therefore different moieties in the complexes molecules – metal center or phenolic group, can be responsible for the interaction with the active intermediates of substrate oxidation.

The influence of R_4PcM and unsubstituted PcM on the decomposition of cumene (Scheme 5) and α-phenylethyl hydroperoxides (R'OOH) has been investigated in various solvents.[14] The kinetic study confirms the interaction of R_4PcFe with the R'OOH in the rate determing step due to the coordination of hydroperoxide with the metal atom.



Scheme 5.

Figure 2 presents clearly that the rate of cumene hydroperoxide decomposition increases with the R'OOH concentration growth. The second order of the reaction is observed in the region of low R'OOH concentrations which confirms the formation of an intermediate complex between a catalyst and hydroperoxide at the first stage of hydroperoxide decomposition.

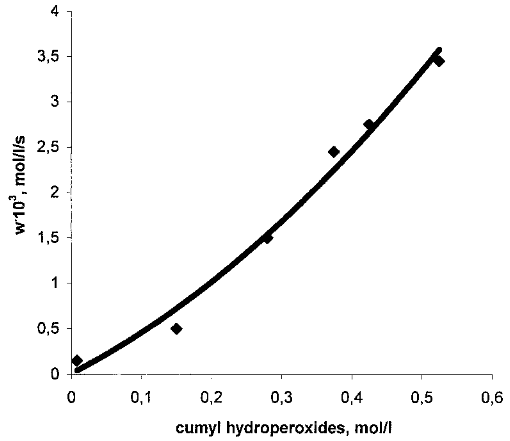
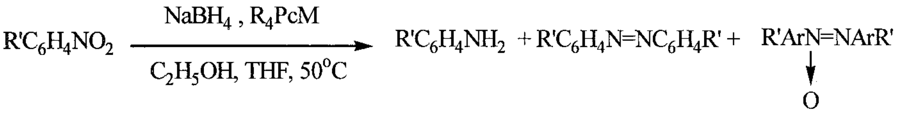


Fig. 2. The dependence of the initial rate of cumene hydroperoxide decomposition on its concentration in the presence of $1.1 \cdot 10^{-4}$ mol/l of R4PcFe in cumene at 25°C in air.

Cumene hydroperoxide decomposition in the presence of R_4PcCo has been studied by means ESR spectroscopy.[15] The formation of different radical species was observed depending on the ratio between the reactants in the solution: phenoxyl radical on the periphery of the macrocyclic ring in Co phthalocyanine,[16] peroxyl radical associated with R_4PcCo and free cumyl peroxide radical at ratio of R'OOH : R_4PcCo equal 3:1, 10:1 and 100:1 respectively.

On the contrary to the oxidation reactions in which metallophtalocyanines serve as electron donors much less attention has been directed to the homogeneous catalytic processes under reducing conditions, when PcM serve as electron acceptors and hydrogen transfer catalysts. Catalytic system for the reduction of aromatic nitrocompounds $R'C_6H_4NO_2$ by $NaBH_4$ or hydrazine were R_4PcM [M = Co(II), Ni(II), Pd(II), Pt(II)](Scheme 6)[17,18]. The principal fragment of the phthalocyanine molecule responsible for the electron transfer to the substrate is the aromatic macrocyclic ring which can be easily reduced to form radical anion in the presence of $NaBH_4$.[16]

The total yield of products, relative yields of aniline, azobenzene, azoxybenzene according to the radical mechanism and the conversion are influenced by the nature of metal and reaction conditions. The transfer hydrogenation of nitrobenzene catalyzed by Ni(II) complex involves the radical anion of Pc ring as key intermediate whereas for Co(II) complex both parts of the molecule are available for electron transfer – the phthalocyanine ring and the metal and therefore the di-negative species serves as intermediate.[18] These data were proved by means of UV-vis spectroscopy, ESR and GLC methods.[17]



$$R'C_6H_4NO_2 \xrightarrow[C_2H_5OH,\ THF,\ 50^{o}C]{NaBH_4\ ,\ R_4PcM} R'C_6H_4NH_2 + R'C_6H_4N{=}NC_6H_4R' + \underset{\displaystyle O}{\underset{\downarrow}{R'ArN{=}NArR'}}$$

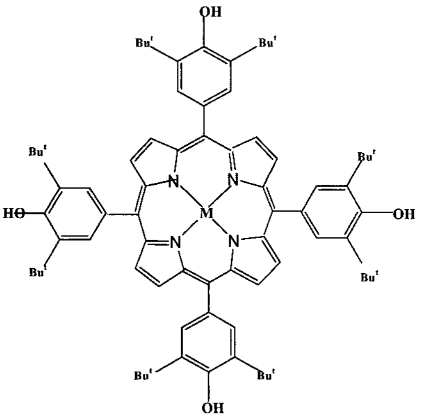
$R' = H$, p-Cl, m-Cl, p-CH_3, p-C_2H_5, p-C_6H_{11}-cyclo; M = Ni(II), Co(II);

Scheme 6.

Porphyrins

Metalloporphyrins are well known effective catalytic agents in reactions of hydrocarbons oxidation by dioxygen.[1] The introduction of 2,6-di-*tert*-butylphenols in *meso*-positions of porphyrine ring might result in the appearance of dual effect of these compounds – the antioxidative one due to the presence of phenolic fragments and the catalytic one due to the presence of porphyrine ring in their molecules.

The comparative study of the activity of the free bases of *meso*-tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin R_4PH_2 and *meso*-tetraphenylporphyrin Ph_4PH_2 and their metallocomplexes of Pt(II) and Co(II) in the substrate oxidation by dioxygen has been performed.[20] The representative of the unsaturated fatty acids – Z-9-octadecenoic acid (oleic acid, R'H) was used as a substrate for this easily oxidazable compound is used for model study of lipids peroxidation.[21]



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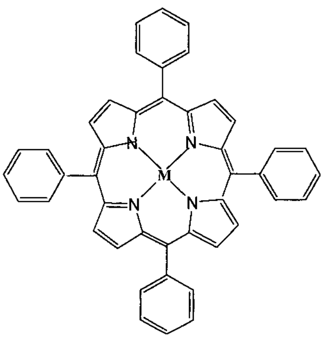

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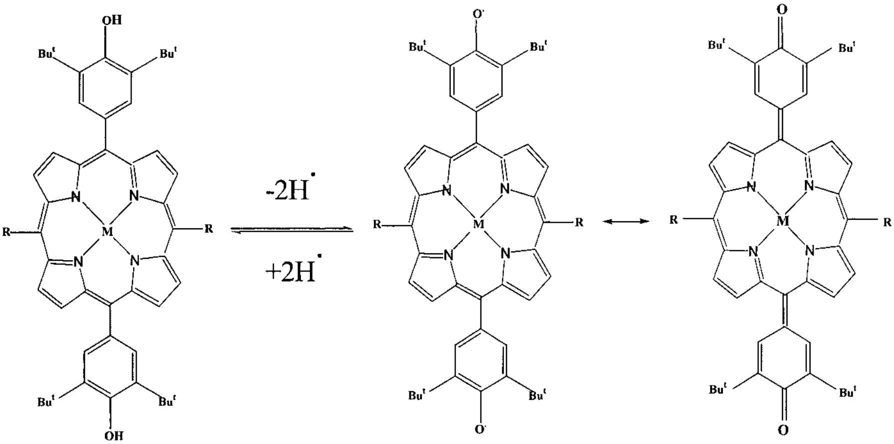
M = HH (a), Pt(II) (b), Co(II) (c)

The monitoring was performed at 65°C by measuring the total concentration of isomeric hydroperoxides R'OOH as a marker of the oxidation.[22] It was found that Ph_4PH_2 **5** and $Ph_4PPt(II)$ **5b** do not influence significantly the peroxidation of oleic acid at 65°C, whereas R_4PH_2 **4a** and $R_4Pt(II)$ **4b** exhibit the antioxidative activity in oleic acid oxidation which is higher than the activity of 2,6-di-*tert*-butylphenol.

The initial rate constants k of the pseudo first order reaction for the R'OOH accumulation without additives and in the presence of 1 mM **4a**, **4b** and 2,6-di-*tert*-butylphenol are 2,74; 1,37; 1,21 and $2{,}29 \cdot 10^{-4}$ s^{-1} respectively. The decrease of k in the presence of **4b** when compared with free base porphyrin **4a** can be interpreted in terms of the phenoxyl radical stability increase due to the incorporation of Pt atom into the porphyrin core.[5] The stabilization of the corresponding radical intermediate **6a**, **6b** responsible for the reversibility of inhibitor's oxidation and therefore of the negative catalytic effect depends on the formation of diamagnetic diquinoporphodimethene structures **7a**, **7b** (Scheme 7).[23,24]



4 **6** **7**

M = HH (a), Pt(II) (b); R = 3,5-di-*tert*-butyl-4-hydroxyphenyl

Scheme 7.

The presence of the redox active metal center makes the compounds **4c** and **5c** efficient catalysts (Figure 3) which is manifested in the increase of the concentration of ROOH compared to that obtained in the control experiment without additives. Despite the presence of the phenolic fragment in R_4PCo molecule the compound **4c** demonstrates the catalytic properties in the initial period of substrate oxidation and the rate constant of R'OOH formation is 1,14 time higher than the corresponding value of the reaction without additives but 1,2 time lower than in the case of Ph_4PCo. After the initial period of oxidation the kinetic curve takes the S-type form characteristic for the chain radical oxidation. This effect can be explained by the known fact that metalloporphyrins have been found to decompose hydroperoxides via both homolytic and heterolytic two-electron mechanisms[1] which is in accordance with the phthalocyanines activities described above.

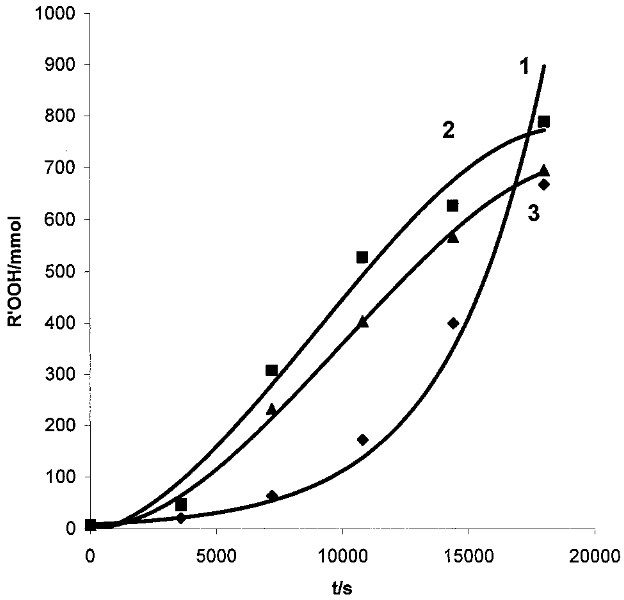


Fig. 3. The kinetic curves of R'OOH formation in oleic acid peroxidation at 65°C without additives (1), in the presence of 1 $mmol{\cdot}l^{-1}$ Ph_4PCo (2) and R_4PCo (3).

The free base porphyrin **4a** attracts much more attention for this compound is capable not only preventing the oxidative destruction of organic substrate but can also serve as a scavenger for metal ions due to the ability to form metal complexes R_4PM. This process might be of a great importance in case when metal-induced lipids peroxidation takes place in cell membranes.[25] One of the heavy metals which promote the peroxidation of unsaturated fatty acids is tin in various oxidation states.[26] The impact of R_4PH_2 on the oxidation of oleic acid by molecular oxygen in the presense of $SnCl_2$ has been studied in order to evaluate the contribution of each part of **4a** molecule - phenolic moiety R (as the antioxidant) and macrocyclic ring PH_2 (as a scavenger) in the effect produced by this compound.

The kinetic curves of R'OOH accumulation over 5 h in the presence of $SnCl_2$, R_4PH_2 and equimolar mixure of $SnCl_2$ and R_4PH_2 are shown in Figure 4. Free base porphyrin **4a** suppress effectively the hydroperoxides formation as it has been discussed above and decrease the rate of hydroperoxides accumulation when compared with the effect of $SnCl_2$ (Scheme 8). Work is in progress on the evaluation of the catalytic properties of other R_4PM.

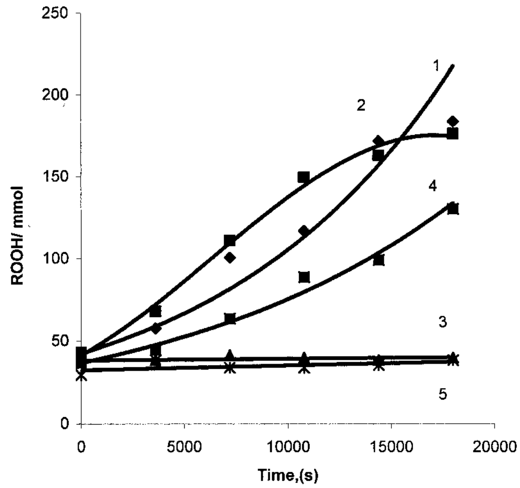
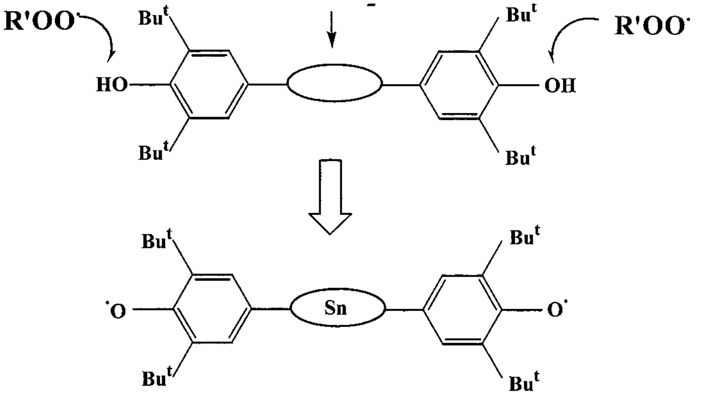


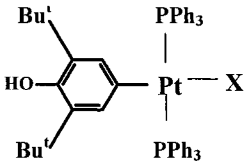
Fig. 4. The kinetic curves of R'OOH formation in oleic acid peroxidation at 50^{o}C without additives (1), in the presence of 1 mmol·l^{-1} $SnCl_2$ (2), R_4PH_2 (3), equimolar mixure of 1 mmol·l^{-1} $SnCl_2$ and 1 mmol·l^{-1} R_4PH_2 (4) and 4 mmol·l^{-1} 2,6-di-*tert*-butylphenol (3).



Scheme 8.

Low Molecular Metal Complexes

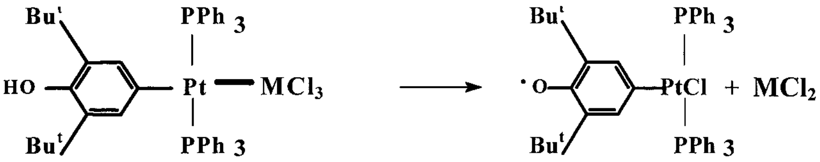
The introduction of transition metal atom in the *para*-position of the phenolic ring is manifested in the significant increase of the corresponding phenoxyl radical stability.[27] The effect of organometallic derivatives of 2,6-di-*tert*-butilphenol **8** on the oxidation of methyl oleate by molecular oxygen has been investigated and compared with 2,6-di-*tert*-butylphenol action.[28]



8

X = Cl (a), Br (b), I (c), $SnCl_3$ (d), $GeCl_3$ (e)

The principal difference between the compounds **8 a-c** and **8d-e** is the appearance of the metal to metal bonds in the molecules in the latter case. The one-electron oxidation of **8 d,e** leads to the corresponding radicals **9 d,e** followed by the elimination of stannylene and germylene molecules (Scheme 9) which are known to promote the oxidation of oleic acid or its methyl ester.[26]



8 **9**

M = Sn (d), Ge (e)

Scheme 9.

Therefore the concurrent processes of the inhibition and promotion of substrate oxidation are the key factors influencing the effect of these compounds. Figure 5 and Table 2 present the results of the kinetic study oriented towards the role of the oxidative destruction of organometallic compounds based on 2,6-di-*tert*-butylphenol in the oxidation of methyl oleate.

Based on these data, compounds **8d,e** containing Pt-Sn and Pt-Ge bonds can be assigned to inhibitors whose activity is lower than that of compound **8a**. The decrease in the inhibiting activity of **8d,e** can be explained not only by the lower stability of radicals **9d,e** but also by the generation of $SnCl_2$ and $GeCl_2$ in the medium as the antioxidants are consumed (Scheme 9). This conclusion was also confirmed by the data obtained with the use of equimolar **8a and** $SnCl_2$ or **8a** and $GeCl_2{\cdot}C_4H_4O_2$ mixtures because in this case the catalytically active salts were added at the beginning of the reaction, which led to the concurrent action of inhibitor **8a** and the catalysts and to the increase in the concentration of hydroperoxides (Table 2).

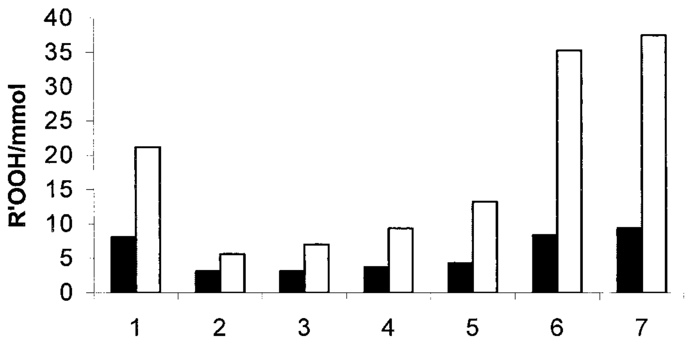


Fig. 5. Accumulation of methyl oleate hydroperoxides without additives (1) and in the presence of 2,6-di-*tert*-butylphenol (2), compound **8a** (3), **8d** (4), **8e** (5), $SnCl_2$ (6), $GeCl_2$ (7); the concentrations of R'OOH after 1 h are shown by hatching, the concentrations after 5 h are not hatched.

Table 2. Initial rate constants of methyl oleate hydroperoxides formation in the presence of 1 mmol/l of various additives at 50°C.

Additives	$\mathbf{k\bullet10^{-4}/c^{-1}}$
-	1.25±0.12
2,6-di-*tert*-butylphenol	0.25±0.06
8a	0.37±0.09
8b	0.41±0.04
8c	0.44±0.04
8d	0.68±0.03
8e	0.83±0.03
8a + $SnCl_2$[a]	0.81±0.04
8a + $GeCl_2\bullet C_4H_4O_2$ [a]	0.85±0.04
$SnCl_2$	1.53±0.11
$GeCl_2\bullet C_4H_4O_2$	1.59±0.14

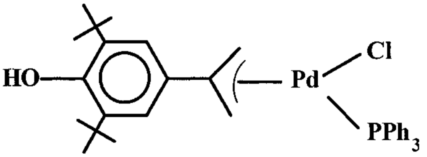
Previously we have demonstrated[27] that the rate of decomposition of radicals **8d,e** was ~10^{-3} s^{-1} and, hence, this was several orders of magnitude higher than the rate of formation of hydroperoxides. In this case, no insertion of MCl_2 at the Pt-Cl bond in radical species **8a** was also observed. Consequently, the high rate of decomposition of radicals **9d,e** is responsible for the rapid appearance of the antioxidant and the catalyst in the reaction mixture. Therefore the impact of compounds **8d,e** would be expected to be comparable with those of mixtures of **8a** with $SnCl_2$ and $GeCl_2{\cdot}C_4H_4O_2$ respectively.

The data presented in Table 2 and in Figure 5 demonstrate that the rate constants of formation of hydroperoxides *(i.e.* the efficiency of the inhibiting activity) are somewhat different for the above mentioned pairs the additives. Thus compounds **8d,e** exhibit higher antioxidating activity than the titled mixtures. Apparently, this difference can be explained by the competition of two processes, *viz.* the promotion of peroxidation of methyl oleate in the presence of MCl_2 (M = Sn or Ge) and the establishment of the equilibrium between the antioxidant and the corresponding phenoxyl radical.

In the case of compounds **8d,e** the additives change the effect from the inhibitory to catalytic one. These organometallic compounds display inhibiting properties during the first hour due to the fact the H atom was readily transferred to the peroxide $R'OO^{\bullet}$ radicals resulting in chain termination. However, further consumption of the functionally active inhibitors **8d,e** was accompanied by the increase in the concentration of the catalyst ($SnCl_2$ or $GeCl_2$) which led to a change in the mechanism of the action of species involved in the process, and, as a consequence, to a change in the overall effect of the compounds.

Thus the results of the study provide evidence that organometallic derivatives of 2,6-di-*tert*-butylphenol are promising non-trivial agents influencing the oxidation of organic substrates which are characterized by the inversion of the inhibitor-catalyst effect.

The effect of π-allyl complexes of palladium **10a,b** containing 2,6-di-*tert*-butylphenol fragment on the oxidation of methyl oleate by molecular oxygen was investigated.[20]



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The values of the initial rate constants k of methyl oleate oxidation without additives and in the presence of **10** are 1,16 and $0{,}38 \cdot 10^{-4}$ ·s respectively that demonstrates the antioxidative activity of π-allyl Pd complexes. However the stability of the corresponding phenoxyl radical formed is significantly lower than the stability of all the complexes described above.[5]

Conclusion

The results described in this review indicate that the introduction of 2,6-di-*tert*-butylphenol in the ligand environment of transition metal complexes leads to the dual activity of these catalytic systems in organic substrates oxidation. The change of the reactivity of organometallic and coordination compounds by oxidation of the redox active phenolic group opens up the possibility to use them as polyfunctional catalytic systems showing positive and/or negative catalytic effects. The macrocyclic metal complexes of phthalocyanines and porphyrins are the most promising systems which are non-trivial agents with changable catalytic effects.

Acknowledgements

Financial support by Russian Foundation for Basic Research (grant N03-03-32938) is gratefully acknowledged.

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