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Relationship between the Electrochemical and Antioxidant Activities of Alkyl-Substituted Phenols

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Abstract—Oxidation potentials and rate constants have been determined for reactions between alkyl-substituted phenols with various structures and the styryl peroxy radical. The overall inhibiting activity of the phenols in the thermal autooxidation of lard has been studied. The interrelation between the structure, physicochemical properties, and antioxidant activity of the phenols is discussed.

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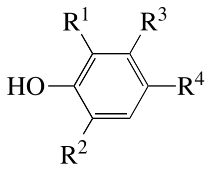
INTRODUCTION

Among the inhibitors of the oxidative destruction of various organic materials (polymers, lubricants, diesel and jet fuels, etc.), alkylated phenols have found the widest commercial use [1–3]. The antioxidant effect of these compounds is due to the ability of the phenolic OH group to deactivate peroxy radicals to form more stable, phenoxyl radicals, which cannot transfer the oxidation chain. The efficiency of the antioxidant effect of phenolic inhibitors is determined, to a great extent, by the reactivity of the phenolic OH group. For this reason, many studies have been aimed at determining the physicochemical parameters that can serve as a measure of the activity of this group.

In particular, there have been several studies [4–9] devoted to the interrelation between the oxidation potential (*E*), structure, and antioxidant activity (AOA) of phenols. However, the attempts to establish an *E*–AOA correlation for phenols have generally been limited to consideration of the overall inhibiting effect in polymer oxidation. No comparison has been made between *E* and the antiradical activity of phenols or any other parameter determining the AOA of these compounds. Therefore, it is unclear whether *E* can serve as a measure of the AOA of phenolic inhibitors.

Here, we report the oxidation potentials of a number of alkyl-substituted phenols (**1**–**11**), the rate constants of the reactions between these phenols and the styryl peroxy radical, and the overall inhibiting effects of these compounds in the thermal autooxidation of lard. For this series of compounds, we studied the relationships between the oxidation potential and several parameters, namely, the O–H bond dissociation energy, the rate constants of phenol–styryl peroxy radical and phenoxyl radical–tetralin reactions, and the overall inhibiting effect.



1, $R^1 = R^2 = R^3 = R^4 = H$
2, $R^1 = R^2 = R^4 = H, R^3 = Me$
3, $R^1 = Me, R^2 = R^3 = R^4 = H$
4, $R^3 = R^4 = H: R^1 = R^2 = Me$
5, $R^1 = R^2 = \text{cyclo-}C_6H_{11}$
6, $R^1 = R^2 = t\text{-Bu}$
7, $R^3 = H, R^4 = Me: R^1 = R^2 = H$
8, $R^1 = H, R^2 = t\text{-Bu}$
9, $R^1 = R^2 = Me$
10, $R^1 = R^2 = \text{cyclo-}C_6H_{11}$
11, $R^1 = R^2 = t\text{-Bu}$

EXPERIMENTAL

Compounds **1**–**3**, **6**, and **7** were received from Russian manufacturers; compounds **4**, **8**, and **11**, from Acros Organics; compound **9**, from Lancaster. Phenols **5** and **10** were synthesized at the Research Institute of Antioxidant Chemistry [10, 11].

Phenols **1**–**11** were electrooxidized on a glassy carbon electrode with a silver/silver chloride reference electrode using an STA voltammetric system (Russia). The following buffer solutions were used as supporting electrolytes: 0.025 M $Na_2B_4O_7$ + 0.5 M NaOH (pH 11), 0.2 M Na_2HPO_4 (pH 8.5), 0.25 M Na_2HPO_4 + 0.25 M KH_2PO_4 (pH 7.0), and $C_8H_5O_4K$ (pH 4.0). The phenol concentration in a sample was 10^{-5} mol/l. The deviation of *E* from its mean value did not exceed 10 mV.

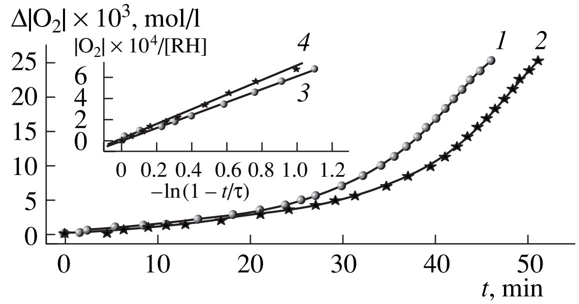


Fig. 1. (*1*, *2*) Oxygen absorption kinetics in the initiated oxidation of styrene at 50°C in the presence of 0.27 mmol of (*1*) **9** and (*2*) **10** and (*3*, *4*) the anamorphoses of curves *1* and *2*, respectively.

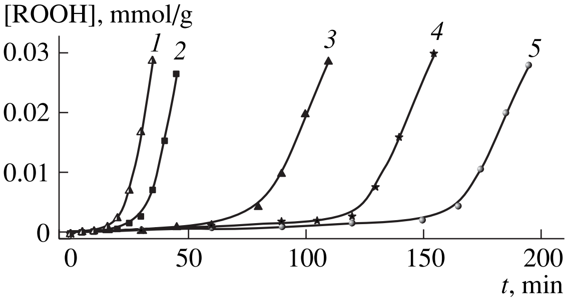


Fig. 2. (*1*) Kinetics of uninhibited lard oxidation. (*2*–*5*) Lard oxidation kinetics in the presence of phenols: (*2*) **7**, (*3*) **9**, (*4*) **10**, and (*5*) **11**.

The rate constants of the reactions of phenols **4**, **5**, and **8**–**11** with the peroxy radical (k_7)[1] were determined in the model reaction of initiated styrene oxidation in chlorobenzene using a procedure described in [13]. Styrene was oxidized at 50°C using azobisisobutyronitrile (Acros Organics, United States) as the initiator, whose concentration in a sample was 0.07–0.12 mol/l. Prior to use, styrene was purified by double vacuum distillation (~170°C, 2–3 Torr). Oxygen absorption kinetics were studied with a high-sensitivity capillary volumeter.

The induction period (τ) was calculated by the integral formula [14]

$$\tau = \int_{\infty}^{0} \{1 - (w/w_0)^2\} \mathrm{d}t,$$

where w_0 is the rate of uninhibited oxidation and w is the average rate of inhibited oxidation in a certain time period.

For this purpose, we plotted $(1 - w/w_0)^2$ versus time and determined the surface area under the resulting curve. This area was equal to the induction period.

The initiation rate w_i was determined by the inhibitor method from induction period data for styrene oxidation in the presence of ionol, for which the stoichiometric inhibition coefficient f (the average number of oxidation chains terminated by one phenoxyl group of an inhibitor molecule) is 2:

$$w_i = \frac{2[\mathrm{PhOH}]_0}{\tau},$$

where $[\mathrm{PhOH}]_0$ is the initial ionol concentration.

The w_i value was determined to be (2.7–4.0) × 10^{-7} mol l^{-1} s^{-1}.

For all of the compounds examined, the initial portion of the kinetic curve of oxygen absorption in styrene oxidation was readily linearizable in the coordinates of the equation

$$\frac{\Delta[O_2]}{[RH]} = -\frac{k_2}{k_7}\ln\left(1 - \frac{t}{\tau}\right), \tag{1}$$

where $\Delta[O_2]$ is the amount of absorbed oxygen per sample volume, k_7 and k_2 are the rate constants of the reactions of the peroxy radical with the antioxidant and with the substrate being oxidized, τ is the induction period, t is time, and [RH] is the substrate concentration in the sample.

This finding indicates that styrene oxidation is inhibited according to a conventional mechanism [12] and k_7 can be determined using Eq. (1). The oxygen absorption curves for styrene oxidation and their anamorphoses in the coordinates of Eq. (1) for phenols **9** and **10** are presented in Fig. 1. The k_2/k_7 ratio was derived from the slopes of these anamorphoses. The absolute values of the rate constant k_7 were calculated under the assumption that, in styrene oxidation, the rate constant of chain propagation is $k_2 = 107.7$ l mol^{-1} s^{-1} [13]. The relative error in k_7 did not exceed 10%.

The overall inhibiting activity of phenols **1**–**11** was studied in the thermal autooxidation of lard (Novosibirsk Meat-Packing Plant, Russia) as a model reaction.

Lard was oxidized with bubbling oxygen at 130°C [15]. The weight of the lard sample to be oxidized was 50 g, and the inhibitor concentration was 1.5 μmol/g. Lard samples (1 g) were taken during the process, and the hydroperoxide concentration was determined iodometrically [16]. These data were represented as kinetic curves, from which the induction period (τ) was determined as the time required for the hydroperoxide concentration to reach 0.004 mmol/g (Fig. 2). The relative error in the induction period did not exceed 5%.

The O–H bond dissociation energies for phenols **1**–**4**, **6**–**9**, and **11**; the rate constants of the reactions of the corresponding phenoxyl radicals with tetralin (k_{10}) at 60°C; and k_7 data for phenols **1**, **3**, **6**, and **7** were taken from a handbook [17].

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[1] Hereafter, we use conventional designations [12].

RESULTS AND DISCUSSION

For the electrooxidation of all phenols, we obtained distinct voltammetric curves with a well-defined wave at positive E values. Since the electrooxidation conditions under which the oxidation potential is measured are of great significance in establishing a correlation between E and the structure of the compound, we studied the dependence of the wave potential on the pH of the supporting electrolyte for phenols **1** and **7**–**11** (Table 1).

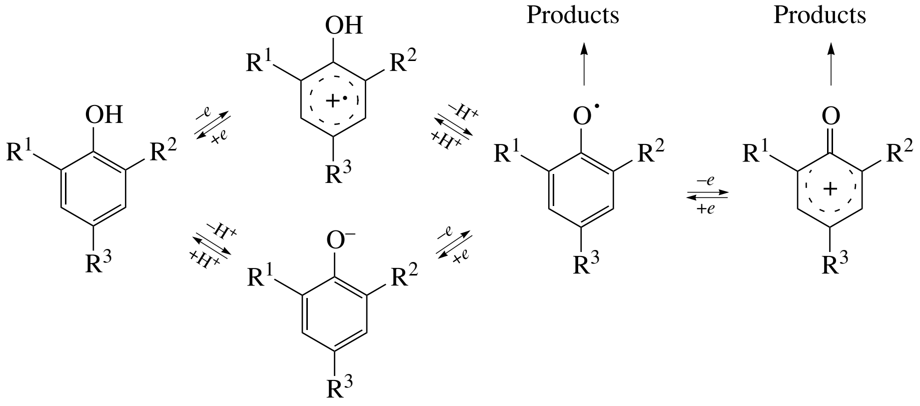
As the pH of the supporting electrolyte is raised, E decreases, because the increasing alkalinity causes an increase in the concentration of phenoxide ions, which are more readily electrooxidized than unionized phenol molecules [8]. At the same time, E depends most strongly on the structure and position of the alkyl substituents in the phenol molecule. For further correlation analysis, we chose the oxidation potentials of phenols **1**–**11** at pH 11 (Table 2).

The observed effect of the alkyl structure on E is in agreement with previous reports [4, 5, 8]. For instance, in the series of *para*-unsubstituted phenols (**1**–**6**) and *para*-substituted phenols (**7**–**11**), E decreases with an increase in the number and donor ability of the *ortho* substituents. Furthermore, all *para*-substituted phenols are characterized by lower E values than their *para*-unsubstituted counterparts.

Table 1. Oxidation potentials of the alkyl-substituted phenols measured at different pH values of the supporting electrolyte

Phenol	E, V			
	pH 11	pH 8.5	pH 7.0	pH 4.0
1	0.59	0.65	0.79	0.93
7	0.46	0.53	0.66	0.82
8	0.30	0.38	0.56	0.69
9	0.28	0.38	0.52	0.66
10	0.18	0.29	0.47	0.61
11	0.10	0.21	0.48	0.69

According to earlier data [18], the phenols are electrooxidized to phenoxyl radicals and their conversion products according to the following scheme:



Based on this phenol electrooxidation mechanism, we can assume that E depends on the formation energy of the phenoxyl radical and is, therefore, determined by its relative stability. For this reason, we compared the observed E values with the energy of homolytic O–H bond cleavage in the phenol molecules.

We found that E decreases with decreasing O–H bond dissociation energy (Fig. 3). The Pearson correlation coefficient was calculated by statistical methods to be 0.94, indicating a strong correlation between the parameters considered. Our experimental data confirm the previous conclusion [19] that the oxidation potential of phenols and the O–H bond energy are tightly correlated.

The inhibiting effect of the phenolic antioxidants is based on their reaction with peroxide radicals,

$$PhOH + RO_2^{\bullet} \xrightarrow{k_7} PhO^{\bullet} + ROOH, \qquad (VII)$$

which replaces reactive peroxy radicals with more stable, phenoxyl radicals [12]. Since phenol electrooxidation also yields phenoxyl radicals, it is possible to analyze the correlation between E and the rate constants of inhibitor–peroxy radical reactions (k_7).

The quantitative calculation of the Pearson coefficient, which appeared to be 0.39, showed that the correlation between E and k_7 is weak. For example, in the series of *para*-unsubstituted (**1**–**6**) and *para*-substituted (**7**–**11**) phenols, the oxidation potential decreases steadily with an increase in the donor ability of the *ortho*-alkyl substituents, while k_7 peaks for the *ortho*-dimethyl- and ortho-dicyclohexyl-substituted compounds and then decreases in passing to the di-*tert*-butyl-substituted phenols (Table 2).

The reactivity of phenols in reaction (VII) is known to depend on the degree of screening of the phenolic

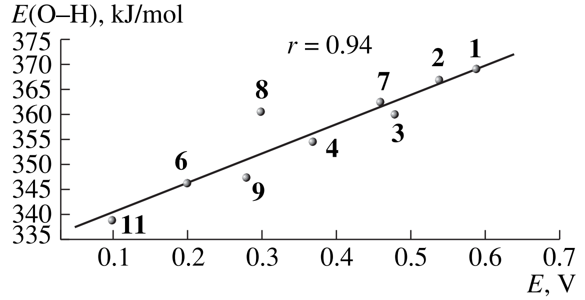


Fig. 3. Correlation between the O–H bond dissociation energy in the phenol molecules and the oxidation potential.

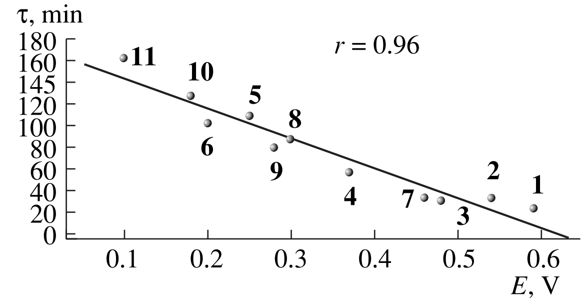


Fig. 4. Correlation between the induction period oxidation potential in phenol-inhibited lard oxidation.

OH group and on the O–H bond dissociation energy [12]. An increase in the donor ability of the *ortho*-alkyl substituents decreases the O–H bond dissociation energy, favoring reaction (VII), and, at the same time, enlarges the steric hindrance for this reaction. It is the interplay of these two factors that is responsible for the fact that k_7 is the greatest for the *ortho*-dimethyl- and ortho-dicyclohexyl-substituted compounds. Apparently, the oxidation potential depends less strongly on the degree of screening of the phenolic OH group. As a consequence, E decreases steadily as the donor ability of the *ortho*-alkyl groups increases and, accordingly, the O–H bond dissociation energy decreases.

The efficiency of phenolic antioxidants is determined by the rate of their reaction with peroxy radicals and by the subsequent transformations of the resulting phenoxyl radicals. For instance, the reaction of the phenoxyl radicals with the oxidized substrate is very significant for the theory of inhibited oxidation:

$$\mathrm{PhO}^{\bullet} + \mathrm{RH} \xrightarrow{k_{10}} \mathrm{PhOH} + \mathrm{R}^{\bullet}. \qquad \text{(X)}$$

This reaction replaces the comparatively inert phenoxyl with an alkyl radical, which regenerates the oxidation chain, thus reducing the AOA of the inhibitor. Since k_{10} is rather difficult to determine experimentally [12], the possibility of estimating this constant from the phenol oxidation potential is of great practical significance.

An analysis of the phenol oxidation potentials and of the rate constants of phenoxyl–tetralin reactions (k_{10}) suggests that these parameters are correlated: k_{10} decreases with decreasing E. The correlation coefficient has a rather high value of 0.85; therefore, the reactivity of a phenoxyl radical in reaction (X) can preliminarily be characterized by the oxidation potential of the parent phenol.

When considering the use of phenolic antioxidants in the stabilization of various organic materials, it is quite necessary to examine their overall inhibiting activity, because this will provide insight into their ability to inhibit oxidation under near-real conditions. In order to see whether the overall inhibiting activity of a phenol in the oxidation of lipid substrates can be preliminarily estimated in terms of the oxidation potential, we correlated the E data with the induction periods measured in the inhibited autooxidation of lard.

It has been demonstrated for lard oxidation (Fig. 4), as well as for the oxidation of polymers [4, 5, 8], that the oxidation potential and the overall inhibiting activ-

Table 2. Physicochemical properties and antioxidant activity characteristics of the phenols

Phenol	E, V (pH 11)	O–H bond dissociation energy, kJ/mol	τ, min	k_7, l mol^{-1} s^{-1}	k_{10}, l mol^{-1} s^{-1}
1	0.59	369.0	22	3.7×10^3	59
2	0.54	366.7	32	–	42
3	0.48	359.9	29	1.9×10^4	15
4	0.37	354.6	55	3.8×10^4	6.9
5	0.25	–	107	3.5×10^4	–
6	0.20	346.4	100	1.1×10^4	2.3×10^{-4}
7	0.46	362.2	32	1.3×10^4	22
8	0.30	360.5	85	4.8×10^4	17
9	0.28	347.5	78	1.7×10^5	2.3
10	0.18	–	125	1.6×10^5	–
11	0.10	339.0	160	2.6×10^4	7.0×10^{-5}

ity of the phenols are interrelated and a decrease in E is accompanied by an increase in the induction period. The high correlation coefficient (0.96) is evidence of a strong correlation between the oxidation potential of the phenols and their ability to inhibit lard oxidation.

As a whole, the results of this study indicate that the oxidation potential of the phenols correlates with the O–H bond energy, with the rate constant of the reaction between the phenoxyl radical and the substrate being oxidized (k_{10}), and with the overall inhibiting activity of the phenols in lard oxidation. Therefore, the oxidation potential can be used in the preliminary comparative evaluation of the above parameters.

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