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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Inhibiting Effect of Phenolic Compounds in Initiated Oxidation of Tridecane

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Abstract—Initiated oxidation of tridecane in chlorobenzene solution with molecular oxygen in the presence of a series of phenol derivatives was studied by chemiluminescence and gas-volumetric methods. The kinetic parameters of the antiradical and antioxidant activity of the compounds were determined.

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Search for environmentally safe inhibitors of oxidation of polymeric materials contacting with food remains a topical problem. Unshielded natural phenols show promise for this purpose. A solution of tridecane in chlorobenzene can be a primary model system for choosing antioxidants, which is due to similarity of the kinetic relationships of free-radical oxidation with molecular oxygen of long-chain hydrocarbons and polymers [1] having certain specific features. It should be primarily noted that the oxidizability parameter $k_2(2k_6)^{-0.5}$ for these systems is lower by an order of magnitude compared to ethylbenzene and cumene, in agreement with lower susceptibility to oxidation of secondary C–H bonds of the substrate, compared to tertiary C–H bonds. As a result, at comparable rates, the oxidation of saturated C_{12}–C_{13} compounds occurs with shorter reaction chains [1, 2]. The oxidation kinetics is affected by isomerization of peroxy radicals. As a result, the oxidation products are not only monohydroperoxides, but also appreciable amounts of bifunctional hydroperoxides (e.g., >20% with *n*-decane [3]) and other compounds [4]. The kinetic relationships of inhibited oxidation of long-chain hydrocarbons are studied poorly.

In this study we examined the specific features of the inhibiting effect of certain natural unshielded phenols in comparison with synthetic sterically shielded Ionol and its derivatives in oxidation of tridecane (TD) in chlorobenzene, initiated with azobis(isobutyronitrile) (AIBN). An important parameter of the inhibited oxidation in this system is the rate constant of recombination of tridecane peroxy radicals k_6, which was determined using the oxygen aftereffect method [5] from the expression

$$t = \frac{2.3}{2\sqrt{W_i k_6}} \log \frac{\sqrt{I_0} + \sqrt{I}}{\sqrt{I_0} - \sqrt{I}}\ , \tag{1}$$

where t is the time (s); W_i is the initiation rate (mol l^{-1} s^{-1}); I and I_0 in this experiment are the emission intensities at successive bubbling of the reaction mixture with argon and molecular oxygen, respectively (mV).

From the data obtained, we plotted the kinetic curves of chemiluminescence in TD oxidation (Fig. 1a), and from the slope of the linear dependences (Fig. 1b) we calculated the rate constant of the recombination of peroxy radicals: $k_6 = (1.87 \pm 0.04) \times 10^6$ l mol^{-1} s^{-1} at 353 K.

The chemiluminescence observed in the reaction is the emission I_0 arising in events of recombination of peroxy radicals in the course of oxidation of organic substances with molecular oxygen. The main step of the inhibition process is the reaction of a phenolic antioxidant (PhOH) with tridecane peroxy radical:

$$RO_2^{\cdot} + PhOH \xrightarrow{k_7} ROOH + PhO^{\cdot}. \tag{2}$$

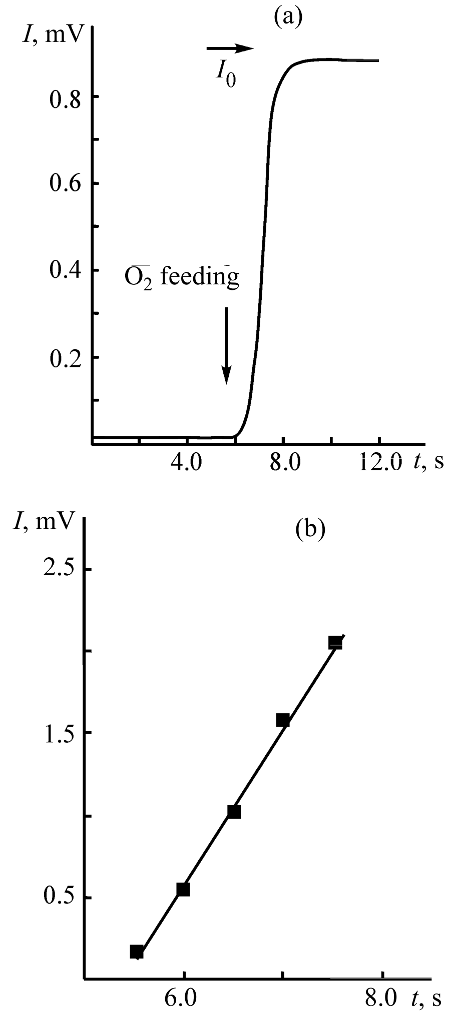


Fig. 1. Variation with time t of the (a) emission intensity I and (b) logarithm of the chemiluminescence intensity ratio according to Eq. (1). $A = \log[(\sqrt{I_0} + \sqrt{I})/(\sqrt{I_0} - \sqrt{I})]$.

Therefore, on introducing an inhibitor the chemiluminescence intensity I drastically decreases, and with an increase in the concentration the inhibiting effect is enhanced (Fig. 2).

To determine the rate constant k_7 of reaction (2), we used expression [5] relating this constant to the concentration of peroxy radicals and, correspondingly, to the chemiluminescence intensity:

$$\frac{[RO_2^{\cdot}]_0}{[RO_2^{\cdot}]} = \left(\frac{I_0}{I}\right)^{1/2} = 1 + 1.1\,\frac{k_7}{\sqrt{k_6 W_i}}\,[\mathrm{InH}], \qquad (3)$$

where $[RO_2^{\cdot}]_0$ and $[RO_2^{\cdot}]$ are the concentrations of peroxy radicals in the absence and in the presence of oxidation inhibitors, and [InH] is the inhibitor concentration.

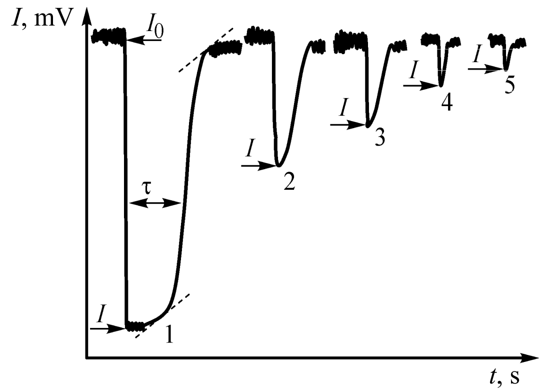


Fig. 2. Variation with time t of the emission intensity I in initiated oxidation of tridecane at various concentrations of syringic acid c. $T = 353$ K; [TD] = 0.82, [AIBN] = 3.04×10^{-2} M; the same for Fig. 3. c, M: (*1*) 1.5×10^{-3}, (*2*) 5.0×10^{-4}, (*3*) 2.5×10^{-4}, (*4*) 1.0×10^{-4}, and (*5*) 2.5×10^{-5}.

To obtain this dependence experimentally, a series of chemiluminescence curves are recorded at various inhibitor concentrations. For example, Fig. 2 shows the chemiluminescence curves in TD oxidation in the presence of syringic acid. Similar series were obtained with all the phenolic compounds. Using Eq. (3), we calculated the inhibition rate constants k_7, and from the S-shaped dependences (Fig. 2) we determined the induction periods of oxidation τ. With this parameter, using the equation

$$f = (\tau W_i)/[\mathrm{InH}], \qquad (4)$$

we calculated the stoichiometric coefficients of inhibition f in tridecane oxidation. The values obtained are given in Table 1. The constants k_7 and coefficients f are relatively low compared to the other model systems. For example, in AIBN-initiated oxidation of ethylbenzene at 333 K, the rate constants of the reactions of phenols with peroxy radicals are higher by an order of magnitude [6]. In this study we used the same phenols. According to [7, 8], the nature of substituent R in peroxy radical does not affect its reactivity in reaction (2). Most probably, significant difference in the parameters of the antiradical activity of phenols in oxidation of various substrates is due to specific features of oxidation of long-chain hydrocarbons: competition of reaction (2) and isomerization of tridecane peroxy radicals (intramolecular chain transfer). Decreased values of the parameter f may be due to short oxidation chains (termination on primary radicals). The value of f calculated for quercetin and Fenozan-23 is higher, which may be due to the presence of several reaction centers in molecules of these compounds.

Table 1. Kinetic parameters of oxidation inhibitors

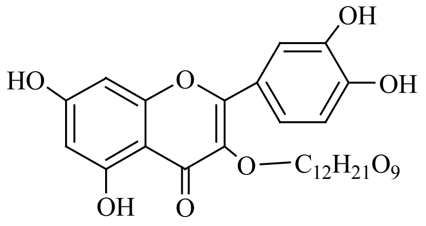
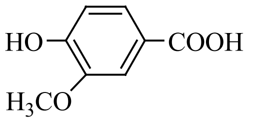
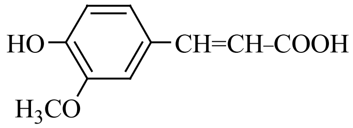
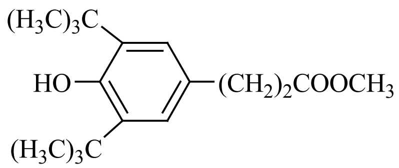
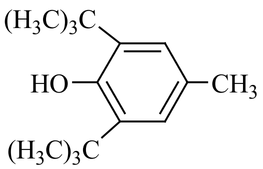
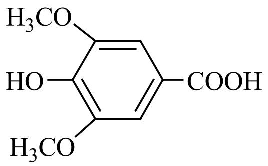
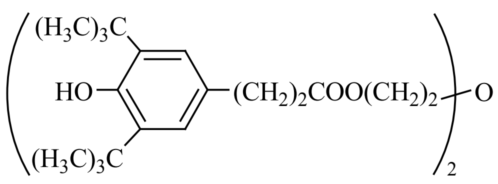
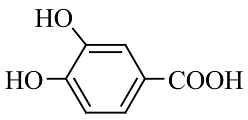
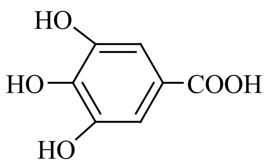
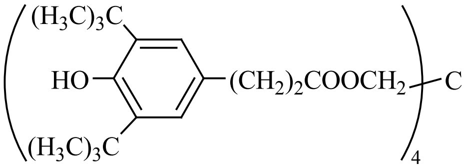
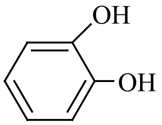
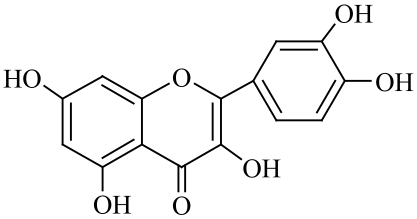
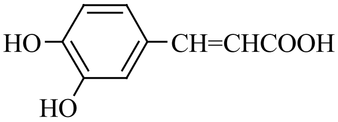
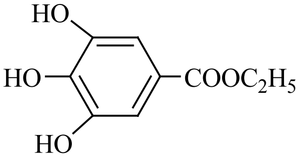
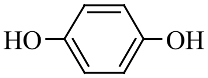
Inhibitor	Formula	f	k_7, l mol^{-1} s^{-1}	IC$_{50\%}$, M
Rutin		–	$(2.17 \pm 0.09) \times 10^2$	–
Vanillic acid		–	$(4.35 \pm 0.10) \times 10^2$	–
Ferulic acid		0.32	$(2.13 \pm 0.08) \times 10^3$	8.5×10^{-5}
Fenozan-1		0.26	$(2.24 \pm 0.09) \times 10^3$	1.4×10^{-4}
Ionol		0.33	$(2.40 \pm 0.10) \times 10^3$	1.4×10^{-4}
Syringic acid		0.20	$(3.80 \pm 0.13) \times 10^3$	1.2×10^{-4}
Fenozan-28		0.38	$(4.18 \pm 0.13) \times 10^3$	9.0×10^{-5}
Protocatechuic acid		0.45	$(7.84 \pm 0.14) \times 10^3$	4.0×10^{-5}
Gallic acid		0.30	$(7.84 \pm 0.21) \times 10^3$	1.6×10^{-5}

Table 1 (Contd.)

Inhibitor	Formula	f	k_7, l mol^{-1} s^{-1}	IC$_{50\%}$, M
Fenozan-23		1.20	$(1.03 \pm 0.06) \times 10^4$	1.4×10^{-4}
Pyrocatechol		0.37	$(1.83 \pm 0.08) \times 10^4$	8.0×10^{-6}
Quercetin		0.70	$(2.32 \pm 0.09) \times 10^4$	7.5×10^{-6}
Caffeic acid		0.33	$(2.78 \pm 0.10) \times 10^4$	1.2×10^{-5}
Ethyl gallate		0.30	$(3.54 \pm 0.12) \times 10^4$	1.1×10^{-5}
Hydroquinone		0.37	$(5.31 \pm 0.13) \times 10^4$	6.0×0^{-6}

Analysis of the results obtained (Table 1) shows that, in the examined series, hydroquinone and *o*-polyphenol derivatives exhibit the highest antiradical activity toward tridecane peroxy radicals. On the whole, rigorous correlation of k_7 with the energy of the OH bond in the reaction center of these phenols is not observed [6]. At equal bond energies, sterically shielded phenols are less effective than dihydroxybenzene derivatives as inhibitors of tridecane oxidation, in contrast to ethylbenzene oxidation.

To compare the antiradical acitvities of the compounds, we used the parameter IC$_{50\%}$, i.e., the inhibitor concentration at which the chemiluminescence intensity decreases by a factor of 2. The more active the inhibitor, the smaller its amount required to decrease the concentration of peroxy radicals. The values of IC$_{50\%}$ are given in Table 1 and are well consistent with the values of k_7.

In parallel with the chemiluminescence studies in this system, we evaluated the antioxidant activity of some phenolic inhibitors in initiated oxidation of tridecane by the gas-volumetric method and determined the initial rates of the uninhibited reaction and of the reaction in the presence of antioxidants (Table 2). The kinetics of oxygen uptake is shown in Figs. 3a and 3b. The phenols behave as weak inhibitors which only decrease the reaction rate, because induction periods of the oxidation in the kinetic curves are lacking. The curves with saturation (Fig. 3b) show that the oxidation is inhibited by transformation products of ethyl gallate and quercetin. With quercetin and caffeic acid, formation of viscous polymeric products was observed, which complicated the gas-volumetric measurements.

It should also be noted that, to decrease the oxygen uptake volume by a factor of 2, inhibitor concentrations exceeding $IC_{50\%}$ by an order of magnitude are required (Tables 1, 2). This may be due to consumption of phenols in side reactions, detected in gas-volumetric measurements.

The data we obtained (Table 2) show simlar trends with the results of chemiluminescence determinations (Table 1), i.e., the antioxidant acitvity of the compounds is associated with their capability to react with tridecane peroxy radicals.

EXPERIMENTAL

Chlorobenzene and tridecane were purified by distillation, following standard procedures. The oxidation experiments were performed at 353 K, tridecane concentration of 0.82 M, and initiator concentration of 3.04 × 10^{-4} M; the initiation rate was $W_i = 6.6 \times 10^{-7}$ mol l^{-1} s^{-1}.

The antiradical activity of phenolic inhibitors was determined with a chemiluminescence installation equipped with an FEU-38 photoelectron multiplier in the presence of an emission activator, 9,10-dibromoanthracene, whose optimal concentration determined in the preliminary experiments was 8.5 × 10^{-5} M.

The antioxidant activity of the compounds was evaluated by the gas-volumetric method from the oxygen uptake and was determined from the ratio of the oxidation rate in the initial step of the reaction in the presence of an inhibitor, $W(O_2)$, to the rate of the uninhibited process, $W(O_2)_0$. To attain the conditions of the kinetic control, the oxidation was performed at the partial oxygen pressure of 600 mm Hg with vigorous stirring with a magnetic stirrer (200–250 rpm).

Table 2. Antioxidant activity of phenolic compounds in initiated oxidation of tridecane. T = 353 K; [InH] = 5.0 × 10^{-3}, [TD] = 0.82, [AIBN] = 3.04 × 10^{-2} M

Inhibitor	$W_{O2} \times 10^3$, M	$W_{O2}/(W_{O2})_0$, %
Quercetin	3.69	30.4
Ethyl gallate	2.27	42.9
Ionol	2.27	44.6
Protocatechuic acid	1.77	66.6
Caffeic acid	0.41	92.7

CONCLUSIONS

(1) Kinetic parameters characterizing the reactivity of a series of phenolic compounds were determined.

(2) Unshielded natural *o*-polyphenols are more effective than Ionol and its derivatives as antioxidants in oxidation of a long-chain hydrocarbon. In this system, rigorous correlation between the antiradical activity and the energy of the O–H bond of the reaction center of phenol was not observed.

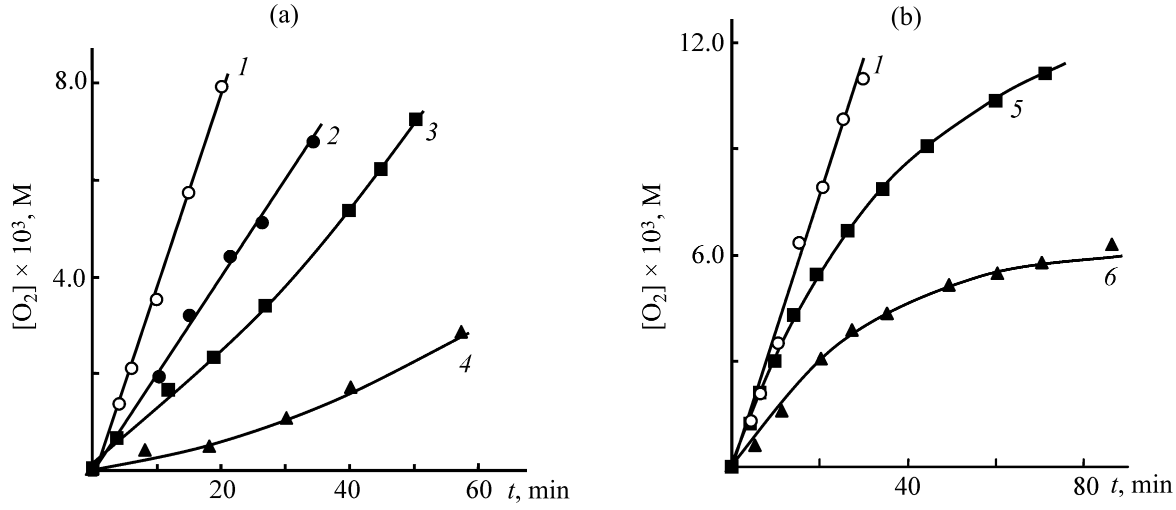


Fig. 3. Kinetic curves of oxygen uptake $[O_2]$ in initiated oxidation of tridecane. Inhibitor ([InH] = 5 × 10^{-3} M): (*1*) none, (*2*) Ionol, (*3*) protocatechuic acid, (*4*) caffeic acid, (*5*) quercetin, and (*6*) ethyl gallate. (*t*) Time.

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