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Determination of the Kinetic Significance of Elementary Steps in the Reaction of Ethylbenzene Oxidation Inhibited by Ionol

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Abstract—The kinetic significance of elementary steps in the liquid-phase reaction of ethylbenzene oxidation inhibited by ionol (2,6-di-*tert*-butyl-4-methylphenol) was determined with the use of the "value" method. The nature of the effectiveness of ionol from the class of *ortho*-substituted phenols was considered. It consists in a ponderable role of the reaction of chain carriers (peroxy radicals) with the inhibitor with a decrease in the contribution of the reverse reaction. In this case, the relatively weak participation of the antioxidant at the step of degenerate chain branching and the high reaction rate constant of the interaction of phenoxy radicals with each other are of considerable importance. The value ranking of steps allowed us to diminish them; this simplified the reaction mechanism under various initial conditions. A satisfactory agreement between base reaction mechanisms, which describe experimental results and the behavior of the inhibited reaction under new reaction conditions, is considered as a reliability criterion for the prediction made.

INTRODUCTION

2,6-Di-*tert*-butyl-4-methylphenol (ionol), which is an *ortho*-substituted alkylphenol (butylated hydroxytoluene (BHT)), and its structural analogs are effective antioxidants. They are widely used for the stabilization of polymers and industrial oils [1–7]. The almost complete absence of toxicity from BHT also allowed it to be used as a food antioxidant. At the same time, BHT and its structural analogs are the active components of currently used antioxidant pharmaceuticals such as dibunol and probucol [8].

Previously [9], we performed a numerical "value" analysis of a kinetic model for the reaction of ethylbenzene oxidation inhibited by *para*-substituted phenols and determined the kinetic "significance" of each individual step. The aim of this work was to perform a detailed analysis of a model for the reaction of ethylbenzene oxidation inhibited by ionol, which is a phenolic antioxidant from the other class of *ortho*-substituted phenols.

A kinetic analysis of models for chain reactions of the oxidation of organic substrates in the presence of BHT would allow us to compare the mechanism of its action with the mechanism of action of sterically hindered phenols and to comprehend more deeply the reason for its effectiveness. Of course, this is useful for the prediction of new structures of effective antioxidants.

CALCULATION OF THE TIME PROFILES OF VALUE QUANTITIES

The kinetic significance of elementary step i was determined by the value quantities of the value (G_i) and the value contribution (h_i) of the step. The value of step i is the ratio of the response of the overall reaction rate (w) at current point t in time to a variation in the rate of the step (w_i) at the initial point t_0 in time. The value and the value contribution of step i are written as follows:

$$G_i(t) = \left.\frac{\partial w[w_1(t), \dots, w_n(t)]}{\partial w_i}\right| w_i = w_i(t_0), \qquad (1)$$
$$h_i(t) = G_i(t)w_i(t), \quad i = 1, 2, \dots, n.$$

Previously [10–14], a mathematical procedure for the numerical calculation of the value quantities G_i and h_i was described. The calculation is based on the Hamiltonian systematization of kinetic models for reaction systems.

EXPERIMENTAL

Experimental Procedure

Experiments on the oxidation of ethylbenzene in the absence and presence of BHT were performed in a thermostated 10-ml glass reactor equipped with a stirrer. In the course of oxidation, the reaction mixture of volume 6 ml was intensely stirred (>10 rps) in an oxygen atmosphere to provide the kinetic regime of the reaction.

The reaction kinetics was monitored using a highly sensitive capillary volumeter at an oxygen pressure of 760 torr. The diameter of the measuring capillary was 0.8 mm.

Materials

Ethylbenzene (Aldrich) was purified according to a published procedure [15]. The initiator 2,2'-azobisisobutyronitrile (AIBN) (Aldrich) was purified by triple recrystallization from absolute ethanol and kept in a vacuum to constant weight. Ionol (Fluka) was purified by triple recrystallization from hexane (Fluka).

REACTION MODEL OF LIQUID-PHASE ETHYLBENZENE OXIDATION INHIBITED BY BHT

The mechanism of the inhibiting action of BHT in the oxidation reactions of organic compounds was studied in detail [1–7]. Table 1 summarizes the kinetic model of the ethylbenzene oxidation reaction inhibited by BHT. In this case, based on the known concepts of the mechanism of the inhibiting action of BHT, we proceeded from an extended kinetic model of the reaction and incorporated reactions with the participation of hydroxyl radicals (steps (VI), (VII), (XV), (XVIII), (XXV), (XXVI), and (XXXI)) and hydroperoxide (steps (VIII), (XII), (XXXIII), and (XXXIV)). The scheme was written for the case of ethylbenzene oxidation at sufficiently high oxygen pressures when the condition $[\mathrm{R}^{\bullet}] \ll [\mathrm{ROO}^{\bullet}]$ is met.

Comments to Table 1 are given below.

Reactions (I)–(V), (IX)–(XI), (XIII), and (XIV). The rate constants of these steps correspond to the reaction model of ethylbenzene oxidation inhibited by *para*-cresol [9].

Reaction (VI). The rate constant of reaction (VI) was taken to be approximately three times higher than the rate constant of reaction (III).

Reaction (XVIII). The rate constant of reaction (XVIII) was taken to be approximately three times higher than the rate constant of reaction (XVII).

Reactions (XX) and (XXXII). The rate constants of reactions (XX) and (XXXII) were determined using the Arrhenius equation taking into account that $k_{20}/(k_{20} + k_{32}) = 0.27$ [32] and $k_{20} + k_{32} = 3 \times 10^{-4}$ l mol^{-1} s^{-1} at 120°C [31]. We assumed that the activation energies of the reactions are equal to 108.3 kJ/mol, the activation energy of a similar reaction with the participation of 2,4,6-tri-*tert*-butylphenol [39].

Reactions (XXV) and (XXVI). The rate constant of reaction (XXV) was taken to be half the rate constant of reaction (XV), and the rate constant of reaction (XXVI) was approximately twice as high as the rate constant of reaction (XXIV).

Reaction (XXVII). The rate constants of the reaction at 37 and 120°C were found using the Arrhenius equation. The following correlation between $\log k_{27}$ and the Hammett σ constants of *para* substituents in *ortho*-*tert*-butyl-substituted phenols formed the basis for the calculation [36]:

$$\log k_{27} = 0.28 + 2.18\sigma.$$

The value of σ for the methyl group is equal to –0.17. Next, the value of E_{27} can be calculated using the value of $\log k^{\circ}_{27} = 7.2$ l mol^{-1} s^{-1} [20]:

$$E_{27} = 2.303(\log k^{\circ}_{27} - \log k_{27})RT,$$

where k°_{27} and E_{27} are the preexponential factor and the activation energy of the rate constant of reaction (XXVII), respectively; T is the absolute temperature; and R is the gas constant.

Reaction (XXVIII). The rate constant of reaction (XXVIII) was calculated using the following correlation equation taken from [37] and corrected for the participation of the ethylbenzene molecule in the reaction:

$$\log k_{28} = -43.08 + 0.11 D_{\mathrm{OH}} \quad \text{at} \quad T = 60°\mathrm{C},$$

where D_{OH} is the OH-bond energy in phenol, which is equal to 339 kJ/mol in the case of BHT [6, 37]. Next, the reaction rate constants at 37 and 120°C were determined using the Arrhenius equation. In this case, we assumed that $\log k^{\circ}_{28} = 5$ [40].

Reaction (XXIX). We assumed that a *para*-quinolide hydroperoxide decomposed with the formation of free radicals with the same reaction rate constant as in the case of *para*,*para*-quinolide peroxide.

Reactions (XXXIII) and (XXXIV). The rate constants of reactions (XXXIII) and (XXXIV) were taken to be equal to the rate constants of reactions (XXVII) [36] and (XX) [31, 32], respectively.

MATHEMATICAL PROGRAM FOR NUMERICAL CALCULATIONS

The Valkin mathematical computer program, which was developed based on the Hamiltonian systematization of reaction systems, was used for the numerical calculations of the time profiles of the concentrations of reaction components and the value contributions of elementary steps. In this program, the sets of differential equations were solved by the ROW-4A program [41].

RESULTS AND NUMERICAL DESCRIPTION

Data presented in Figs. 1 and 2 indicate that the calculated kinetic curves of oxygen consumption satisfactorily describe experimental data on the reaction of ethylbenzene oxidation with and without inhibition by BHT at 60 and 120°C. The experimental conditions are specified in figure captions. In the simulation of ethylbenzene oxidation initiated by AIBN at 60°C, step (I) was replaced by the reaction of AIBN degradation, which ultimately resulted in the formation of two radicals, with a rate constant of 7.28×10^{-6} s^{-1} (taking into

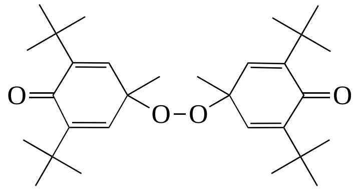
Table 1. Reaction model of the liquid-phase oxidation of ethylbenzene inhibited by BHT

Reaction number	Reaction	Rate constant, l mol^{-1} s^{-1}			References
		T = 37°C	T = 60°C	T = 120°C	
I	$2RH + O_2 \longrightarrow 2R^\bullet + H_2O_2$	3.52×10^{-14}	9.26×10^{-13}	7.7×10^{-10}	[16, 17]
II	$R^\bullet + O_2 \longrightarrow ROO^\bullet$	8.75×10^{8}	8.75×10^{8}	1×10^{9}	[18]
III	$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet$	0.98	2.74	39	[19]
IV	$RO^\bullet + RH \longrightarrow ROH + R^\bullet$	1.48×10^{6}	2.32×10^{6}	5.85×10^{6}	[20]
V	$HO^\bullet + RH \longrightarrow H_2O + R^\bullet$	10^{9}	10^{9}	10^{9}	[21]
VI*	$HOO^\bullet + RH \longrightarrow H_2O_2 + R^\bullet$	2.94	7.62	60	[20]
VII	$HOO^\bullet + ROOH \longrightarrow H_2O_2 + ROO^\bullet$	6.35×10^{2}	1.05×10^{3}	3×10^{3}	[20]
VIII	$ROO^\bullet + H_2O_2 \longrightarrow ROOH + HOO^\bullet$	1.05×10^{2}	1.68×10^{2}	4.4×10^{2}	[22]
IX	$RO^\bullet + ROOH \longrightarrow ROH + ROO^\bullet$	1.47×10^{8}	4.9×10^{8}	6.43×10^{8}	[20, 39]
X	$ROOH + RH \longrightarrow RO^\bullet + H_2O + R^\bullet$	3.47×10^{-12}	1.28×10^{-10}	2.72×10^{-7}	[23]
XI	$ROOH + RH \longrightarrow R'O + H_2O + RH$	1.04×10^{-11}	3.83×10^{-10}	4.08×10^{-7}	[24]
XII	$H_2O_2 + RH \longrightarrow R^\bullet + H_2O + HO^\bullet$	6.76×10^{-11}	1.06×10^{-10}	1.62×10^{-7}	[25]
XIII	$ROO^\bullet + ROO^\bullet \longrightarrow 2RO^\bullet + O_2$	3.5×10^{6}	5.5×10^{6}	10^{7}	[26–28]
XIV	$ROO^\bullet + ROO^\bullet \longrightarrow ROH + R'O + O_2$	10^{7}	10^{7}	3.5×10^{7}	[26–28]
XV	$ROO^\bullet + HOO^\bullet \longrightarrow ROOH + O_2$	3×10^{8}	3×10^{8}	3×10^{8}	[27]
XVI	$ROO^\bullet + HOO^\bullet \longrightarrow R'O + H_2O + O_2$	1×10^{8}	1×10^{8}	1×10^{8}	[27]
XVII	$ROO^\bullet + InH \longrightarrow ROOH + In^\bullet$	1.3×10^{4}	2.04×10^{4}	6.94×10^{4}	[29]
XVIII*	$HOO^\bullet + InH \longrightarrow H_2O_2 + In^\bullet$	3.9×10^{4}	6.12×10^{4}	2.08×10^{5}	[20]
XIX	$RO^\bullet + InH \longrightarrow ROH + In^\bullet$	2.16×10^{6}	4.54×10^{6}	2.1×10^{7}	[30]
XX	$ROOH + InH \longrightarrow In^\bullet + RO^\bullet + H_2O$	9.25×10^{-9}	1.75×10^{-7}	6.7×10^{-5}	[31, 32]
XXI	$InH + O_2 \longrightarrow In^\bullet + HOO^\bullet$	1.53×10^{-13}	5.8×10^{-12}	8.77×10^{-9}	[33]
XXII	$In^\bullet + In^\bullet \longrightarrow InH + In'$	6.42×10^{3}	1.1×10^{4}	3.3×10^{4}	[34]
XXIII	$In^\bullet + In^\bullet + O_2 \longrightarrow QP_1$	4.9×10^{3}	4.9×10^{3}	4.9×10^{3}	[35]
XXIV	$In^\bullet + ROO^\bullet \longrightarrow QP_2$	3×10^{8}	3×10^{8}	3×10^{8}	[6, 36]
XXV*	$In^\bullet + HOO^\bullet \longrightarrow InH + O_2$	1.5×10^{8}	1.5×10^{8}	1.5×10^{8}	[20]
XXVI*	$In^\bullet + HOO^\bullet \longrightarrow QP_2$	6.5×10^{8}	6.5×10^{8}	6.5×10^{8}	[20]
XXVII	$In^\bullet + ROOH \longrightarrow InH + ROO^\bullet$	0.3	1	15.23	[36]
XXVIII*	$In^\bullet + RH \longrightarrow InH + R^\bullet$	3×10^{-7}	1.91×10^{-6}	6.96×10^{-5}	[37]
XXIX	$QP_2 \longrightarrow 2RO^\bullet$	4.94×10^{-10}	2.09×10^{-8}	4.13×10^{-5}	[6]
XXX	$QP_1 \longrightarrow 2RO^\bullet$	6.3×10^{-9}	2×10^{-7}	4.5×10^{-4}	[6]
XXXI	$HOO^\bullet + HOO^\bullet \longrightarrow H_2O_2 + O_2$	3.5×10^{8}	3.5×10^{8}	3.5×10^{8}	[38]

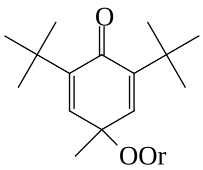
Table 1. (Contd.)

Reaction number	Reaction	Rate constant, l mol^{-1} s^{-1}			References
		T = 37°C	T = 60°C	T = 120°C	
XXXII	$ROOH + InH \longrightarrow P + H_2O$	2.5×10^{-8}	4.73×10^{-7}	1.8×10^{-4}	[31, 32]
XXXIII*	$In^{\bullet} + H_2O_2 \longrightarrow InH + HOO^{\bullet}$	0.3	1	15.23	[36, 20]
XXXIV*	$InH + H_2O_2 \longrightarrow In^{\bullet} + HO^{\bullet} + H_2O$	9.25×10^{-9}	1.75×10^{-7}	6.7×10^{-5}	–

Note: The rate constant of reaction (I) is given in l^2 mol^{-2} s^{-1}. R' = R – H, and In' = In – H.
QP_1 is the symmetric *para*,*para*-quinolide peroxide



QP_2 is the asymmetric quinolide *p*-peroxide or hydroperoxide



r = H, R.
P denotes nonradical products.
* Additional comments on kinetic parameters are given in the text.

account the parameter $e = 0.7$, which characterizes the yield of radicals from the solvent cage).

Time Profiles of the Value Contributions of Individual Steps

The numerical calculation of the dynamics of the reduced value contributions of steps was performed under the following initial conditions: $[RH]_0$ = 8.02, 7.83, and 7.35 mol/l for T = 37, 60, and 120°C, respectively; $[RO_2H]_0 = 10^{-5}$ mol/l; and $[O_2] = 10^{-2}$ mol/l. Based on an analysis of the calculated time profiles of the reduces contributions ($\bar{h}_i = (h_i/(\sum_1^n h_i^2)^{1/2})$) of steps in the induction period of the inhibited reaction of ethylbenzene oxidation (Figs. 3, 4), the following special features of the reaction can be distinguished:

—A comparison of data presented in Figs. 3 and 4 clearly indicates that the accumulation of phenoxy radicals was symbatic with the dynamics of contribution from quadratic steps with the participation of these radicals (steps (XXIV) and (XXII)). Here, an increase in the negative effect of steps (XXVII), (XXIX), and (X) at a ponderable consumption of the inhibitor can also be observed, when ethylbenzene hydroperoxide and quinolide peroxides were accumulated in the reaction system.

—Along with step (X) of degenerate chain branching, the main negative contribution was made by the radical decomposition reaction of an asymmetric quinolide peroxide (step (XXIX)) and the exchange of phenoxy radicals for peroxy radicals (step (XXVII)). The

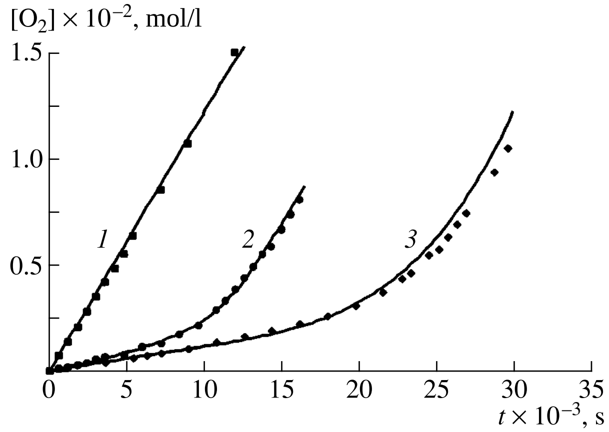


Fig. 1. Kinetic curves of oxygen consumption in the ethylbenzene oxidation reaction initiated by AIBN (*1*) in the absence and in the presence of BHT: $[BHT]_0$ = (*2*) 3.3×10^{-4} and (*3*) 6.4×10^{-4} mol/l. T = 60°C; [AIBN] = 4×10^{-3} mol/l; points and curves indicate experimental and calculated data, respectively.

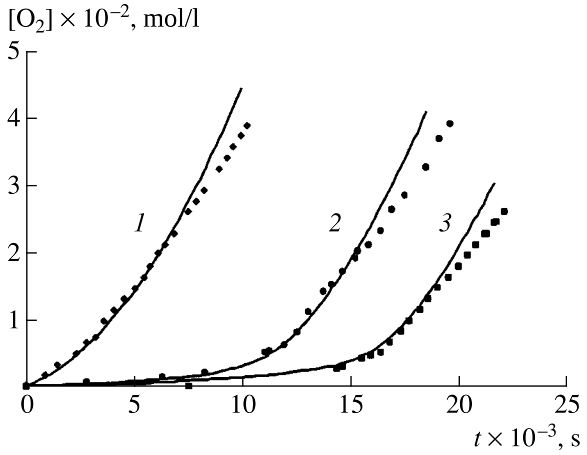


Fig. 2. Kinetic curves of oxygen consumption in the autoxidation reaction of ethylbenzene (*1*) in the absence and in the presence of BHT: $[\mathrm{BHT}]_0$ = (*2*) 6.5×10^{-5} and (*3*) 1×10^{-4} mol/l. $T = 120$°C; initial ethylbenzene hydroperoxide concentration of 1×10^{-3} mol/l; points and curves indicate experimental and calculated data, respectively.

role of these steps in the reaction of ethylbenzene oxidation inhibited by BHT was considerably negative at all of the test temperatures, including 37°C.

—An increase in the temperature considerably increased the contribution of the steps of radical decomposition of a quinolide peroxide. Thus, at 120°C, in some cases, the contribution of this step can be higher than the contribution of the step of radical decomposition of ethylbenzene hydroperoxide.

—The reactions of chain carriers (peroxy radicals) with inhibitor molecules (step (XVII)) and the quadratic decay reactions of phenoxy radicals (steps (XXII) and (XXIV)) played the most significant positive role. At comparatively low concentrations of BHT ($<10^{-3}$ mol/l), the contribution of reaction (XXIV) was greater than the contribution of reaction (XXII), especially, with hydroperoxide and quinolide peroxide accumulation in the reaction medium, when the rate of radical generation and, correspondingly, the concentration of peroxy radicals increased. This resulted in the predominance of the cross decay of phenoxy radicals at step (XXIV). However, with a high inhibitor content ($>10^{-3}$ mol/l) in the reaction system, the contribution of the reaction of phenoxy radicals with one another (XXII) predominated over reaction (XXIV) because of a relative increase in the concentration of phenoxy radicals over peroxy radicals (see Fig. 4).

—An increase in the initial concentration of the inhibitor resulted in a ponderable increase of the negative contribution of step (XX) of degenerate chain branching with the participation of the inhibitor molecule.

—The following regularity was observed: an increase in the negative contribution of reverse reaction (XXVII)

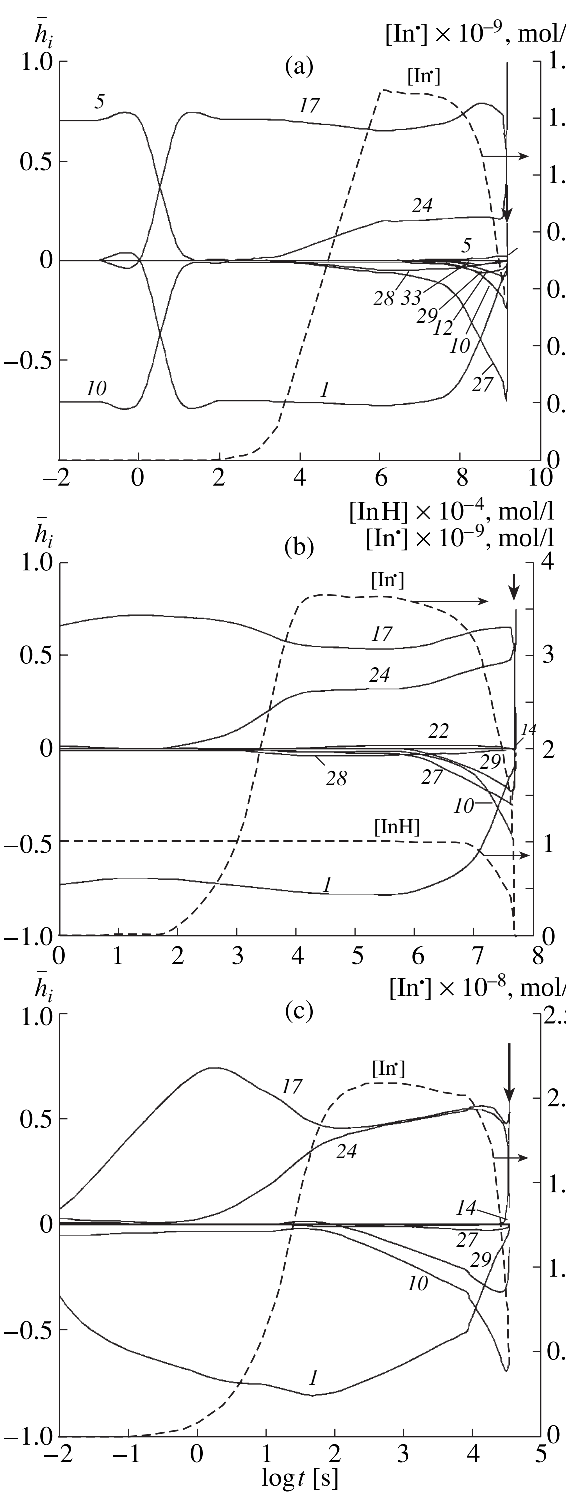


Fig. 3. Dynamics of the reduced value contributions of steps, the buildup of phenoxy radicals ($\mathrm{In}^{\bullet}$), and the consumption of the inhibitor during the induction period of the liquid-phase autoxidation reaction of ethylbenzene inhibited by BHT. T = (a) 37, (b) 60, or (c) 120°C. The initial concentrations of BHT and ethylbenzene hydroperoxide were 10^{-4} and 10^{-5} mol/l, respectively. Curve numbers correspond to the step numbers. A vertical arrow indicates the point in time when the reaction comes out of the induction period.

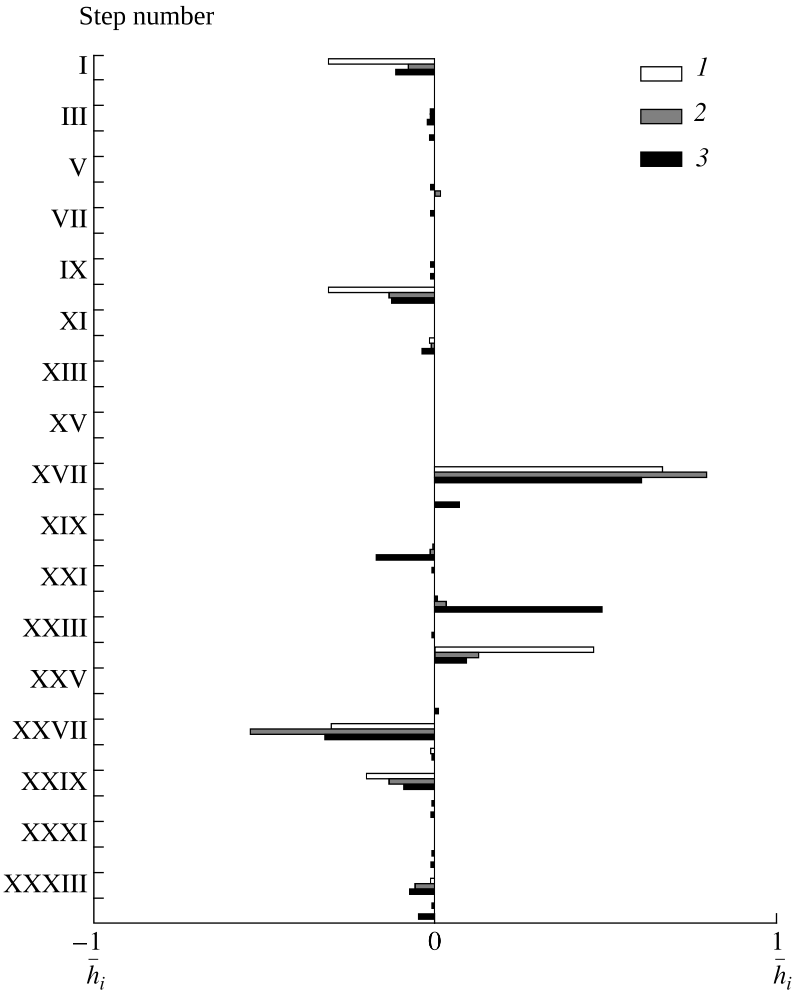


Fig. 4. Reduced "value" contributions of elementary steps in the liquid-phase autoxidation reaction of ethylbenzene during the induction period at $[BHT]_0$ = (*1*) 10^{-4}, (*2*) 10^{-3}, and (*3*) 10^{-2} mol/l and an ethylbenzene hydroperoxide concentration of 10^{-5} mol/l. T = 60°C. The conversion of BHT was 7–10%.

of a phenoxy radical with a hydroperoxide corresponded to an increase in the positive role of step (XVII).

Let us consider a special feature of the ethylbenzene oxidation reaction inhibited by BHT, which consists in a ponderable role of chain-propagation reaction because of the interaction of phenoxy radicals with hydroperoxide molecules (step (XXVII)). An analysis of the rates of steps allowed us to conclude that, in some cases, the rates of steps (XVII) and (XXVII) are commensurable; that is, the reaction of peroxy radicals with BHT under these conditions is close to equilibrium. With the use of the *ortho*-substituted phenol BHT, as distinct from sterically unhindered phenols considered previously [9], the role of step (XXVII) seemed insignificant because the rate constant of this reaction is relatively low. However, it should be taken into account that in the case of ethylbenzene oxidation inhibited by BHT the concentration of phenoxy radicals is much higher (see Table 2); this fact is responsible for a relative increase in the rate of step (XXVII).

Finally, Roginskii's opinion [6] that the molecular structure of BHT is close to the structure of an optimum inhibitor from this class of compounds seems reasonable. Indeed, phenoxy radicals produced from BHT most intensely react with one another; the role of this reaction is considerable at high concentrations of the inhibitor. Simultaneously, the intense occurrence of this reaction decreases the probability of formation of initiating agents, quinolide peroxides, in the reaction between phenoxy and peroxy radicals. It is also of considerable importance that phenoxy radicals exhibit weak activity in the reaction with a hydroperoxide; this reaction plays a significant role in the inhibited oxidation reaction. It is likely that changes in the molecular structure of the inhibitor, which result in a decrease in the OH-bond energy and, correspondingly, in an increase in the rate constant and a decrease in the degree of reversibility of the reaction of peroxy radicals

Table 2. Calculated concentration ratios $[\mathrm{In}^\bullet]/[\mathrm{ROO}^\bullet]$ in the liquid-phase reaction of ethylbenzene autoxidation inhibited by BHT or *para*-methylphenol depending on initial reaction conditions

T, °C	$[\mathrm{In}^\bullet]/[\mathrm{ROO}^\bullet]$					
	$[\mathrm{BHT}]_0$, mol/l			[*para*-methylphenol]$_0$, mol/l		
	10^{-4}	10^{-3}	10^{-2}	10^{-4}	10^{-3}	10^{-2}
60°C	3.8×10^3	2.4×10^4	4.5×10^5	0.05	0.09	0.94
120°C	10^2	1.8×10^3	2×10^4	0.05	0.26	1.15

Note: The conversion of antioxidants (BHT and *para*-methylphenol) was 9 to 10%.

with the inhibitor, will not give considerable results. Importantly, in this case the negative role of step (XX) of degenerate branching with the participation of the inhibitor molecule considerably increases at inhibitor concentrations that are commonly used in actual practice (10^{-3}–10^{-1} mol/l).

Base Mechanism of the Reaction of Ethylbenzene Oxidation Inhibited by BHT

The value ranking of steps also allowed us to solve the problem of decreasing the number of “excessive” elementary steps in the reaction mechanism of ethylbenzene oxidation inhibited by BHT. As a result, a “base minimum” reaction mechanism was revealed.

As a criterion for the insignificance of a step from chosen steps of little value, a condition was taken according to which changes in the current concentrations of RH, InH, $\mathrm{In}^\bullet$, ROOH, and $\mathrm{ROO}^\bullet$ were no greater than 3.5% if these steps were eliminated from the kinetic model of the reaction. The monitoring was performed at two reaction times that corresponded to 10–20 and 60–70% conversions of BHT. The preliminary distribution of steps in accordance with value contributions was performed in a time interval from 10^{-7} s to τ, where τ is the induction period of the reaction. In this case, steps with small value contributions over the specified time interval ($\bar{h}_i < 10^{-3}$) were chosen as candidates for excluding from the kinetic model. The dominant and most insignificant steps were determined unambiguously. Steps for the base reaction model were chosen among steps with intermediate value contributions (from two to four steps) using the systematic method of excluding them from the reaction scheme. In this case, we were consistent with the above criterion for the insignificance of steps.

Table 3 summarizes the base reaction mechanisms of ethylbenzene oxidation inhibited by BHT determined under various initial conditions, including the conditions of our experiments. Simultaneously, an extended base reaction model is given, which is common to all the reaction conditions of inhibited oxidation.

Data presented in Table 3 suggest that, as the initial concentration of BHT was increased, the corresponding base reaction mechanism somewhat extended. As [BHT] was increased, steps (VI), (XVIII), (XXV), and (XXVI) with the participation of hydroperoxy radicals; the reactions of hydrogen peroxide with BHT and the phenoxy radical (steps (XXXIII) and (XXXIV)); and step (XX) of degenerate branching with the participation of the BHT molecule were included in the base mechanism.

It is of considerable importance to compare the base mechanism that describes the experimental results with those used for predicting the behavior of the inhibited reaction under new initial conditions. A satisfactory agreement, particularly, of dominant steps, was observed at 120°C. This agreement of base mechanisms can be considered to some extent as a characteristic of the good prediction ability of the kinetic model. A dramatic difference was observed between the base mechanisms determined for the experimental conditions of initiated oxidation and those used for the prediction of the behavior of the BHT-inhibited oxidation reaction at 60°C. Thus, the value analysis allowed us to make a prediction. Because of this, the design of new experiments can be performed. In the consideration of these experiments, steps responsible for a more reliable prediction of the behavior of the inhibited reaction are revealed in the base mechanism that describes experimental data. For example, we can recommend studying reactions under conditions with lower rates of initiation, lest the prooxidant role of the inhibitor be suppressed, or designing experiments with the additives of hydrogen peroxide, various hydroperoxides, or quinolide peroxides. These additives could reveal a wider set of steps, which are necessary for making an adequate prediction, in the base mechanism. However, based on the results obtained at 120°C and taking into account available reliable kinetic data on the initial reaction mechanism, it is believed that the analysis of the inhibited reaction was reliable at both 60 and 37°C.

Table 3. Base mechanisms of the liquid-phase reaction of ethylbenzene oxidation inhibited by BHT at various initial conditions, including those for numerical calculations (see Figs. 3 and 4) and experimental studies of the reaction (see Figs. 1 and 2)

[BHT]$_0$, mol/l	Reduction of the reaction mechanism of ethylbenzene oxidation inhibited by BHT																																	
	Step number																																	
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	XXIV	XXV	XXVI	XXVII	XXVIII	XXIX	XXX	XXXI	XXXII	XXXIII	XXXIV
120°C																																		
1×10^{-4}	■	■	■	■	■	□	□	□	□	■	■	■	□	□	□	□	■	□	□	□	□	□	□	■	□	□	■	□	■	□	□	□	□	□
3×10^{-4}	■	■	■	■	■	□	□	□	□	■	■	■	□	□	□	□	■	□	□	■	□	■	□	■	□	□	■	■	■	□	□	□	□	□
1×10^{-3}	■	■	■	■	■	■	□	□	□	■	■	■	□	□	□	□	■	□	□	■	□	■	□	■	□	□	■	■	■	□	□	□	■	□
1×10^{-4}*	■	■	■	■	■	□	□	□	□	■	■	□	□	■	□	□	■	□	□	□	□	□	□	■	□	□	■	□	■	□	□	□	□	□
Insignificant steps	□	□	□	□	□	□	▨	▨	▨	□	□	□	▨	□	▨	▨	□	▨	▨	□	▨	□	▨	□	▨	▨	□	□	□	▨	▨	▨	□	▨
Base model	■	■	■	■	■	■	□	□	□	■	■	■	□	■	□	□	■	□	□	■	□	■	□	■	□	□	■	■	■	□	□	□	■	□
60°C																																		
1×10^{-4}	■	■	■	■	■	□	□	□	□	■	□	■	□	□	□	□	■	□	□	■	□	■	□	■	□	□	■	□	■	□	□	■	■	□
1×10^{-3}	■	■	■	■	■	■	□	□	□	■	■	■	□	□	□	□	■	□	□	■	□	■	□	■	□	□	■	□	■	□	□	■	■	□
1×10^{-2}	■	■	■	■	■	■	□	□	■	■	■	■	□	□	□	□	■	■	□	■	□	■	■	■	■	■	■	■	■	■	□	■	■	■
6.5×10^{-4}*	■	■	■	□	□	□	□	□	□	□	□	□	□	■	□	□	■	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□
Insignificant steps	□	□	□	□	□	□	▨	▨	□	□	□	□	▨	□	▨	▨	□	□	▨	□	▨	□	□	□	□	□	□	□	□	□	▨	□	□	□
Base model	■	■	■	■	■	■	□	□	■	■	■	■	□	■	□	□	■	■	□	■	□	■	■	■	■	■	■	■	■	■	□	■	■	■
37°C																																		
1×10^{-4}, Base model	■	■	■	■	■	□	□	□	□	■	■	■	□	□	□	□	■	□	□	■	□	■	□	■	□	□	■	■	■	□	□	■	■	□
37-120°C																																		
Insignificant steps	□	□	□	□	□	□	▨	▨	□	□	□	□	▨	□	▨	▨	□	□	▨	□	▨	□	□	□	□	□	□	□	□	□	▨	□	□	□
General base model	■	■	■	■	■	■	□	□	■	■	■	■	□	■	□	□	■	■	□	■	□	■	■	■	■	■	■	■	■	■	□	■	■	■

Note: □ insignificant steps of the model under given kinetic conditions; ▨ insignificant steps in the model for the chosen range of initial data; ■ steps in the base model.

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