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Determination of the Kinetic Significance of Elementary Steps in the Reaction of Ethylbenzene Oxidation Inhibited by *para*-Substituted Phenols: Choice of an Effective Antioxidant

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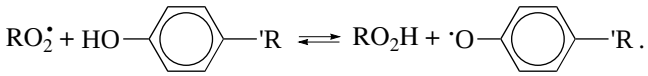
Abstract—A conceivable method ("value" method) for analyzing the reaction kinetics models of inhibited liquid-phase oxidation of organic compounds was considered. A procedure for the numerical calculations of the molecular structure parameters of an inhibitor and an inhibitor concentration that results in a maximum inhibition of the reaction was presented. In the kinetic model of a chain reaction of liquid-phase ethylbenzene oxidation in the presence of a *para*-methylphenol inhibitor, the dynamics of contributions from individual steps was calculated. This allowed us to simplify the reaction mechanism. The inhibition of the oxidation reaction due to reactions with the participation of a phenoxyl radical was found to occur under conditions of the quasi-equilibrium



The molecular structures and initial concentrations of *para*-substituted phenols, which are most effective for the given reaction conditions, were determined.

INTRODUCTION

The kinetic analysis of models for the inhibition of complex (multistep) chemical reactions is a topical problem. It is closely associated with solving an important problem—the nonempirical choice of an effective inhibitor for given conditions of a chemical reaction.

The mechanisms of action of inhibitor antioxidants on the oxidation of organic compounds in a condensed phase were studied in considerable detail, and reactions with the participation of intermediates resulting from inhibitor conversion were examined [1–13]. However, it should be noted that complicated kinetic models of antioxidant action are very difficult to analyze. The main reason consists in the occurrence of great numbers of steps and components in these models.

In the analysis of various mechanisms of inhibited reactions, it is of paramount importance to obtain information on the roles of elementary steps regardless of the complexity of the initial kinetic model. This is also a prerequisite for the characterization of the reactivity of an inhibitor in a multistep chemical transformation. For example, this information is required for determining the contributions of reactions with the participation of an inhibitor and its reaction products in the inhibition of the process. It is also of interest to relate the molecular structure of an inhibitor with reaction characteristics (rate, induction period, etc.).

In this work, we performed the numerical "value" analysis [14–18] of a kinetic model for the inhibition of the autoxidation reaction of ethylbenzene by *para*-substituted phenols and determined the kinetic "significance" of each individual step of the model. We considered the kinetic model of the given reaction as an illustration in some sense; the aim of this study was to demonstrate the capabilities of the numerical analysis of kinetic models of inhibited oxidation by the "value" method.

On the other hand, the value analysis of kinetic models of inhibition provides an opportunity to optimize reaction conditions. This is associated with solving the following kinetic problems: (a) the determination of the molecular structure of an effective inhibitor by modeling in terms of a given kinetic model and under chosen reaction conditions and (b) the determination of an optimum initial concentration of the inhibitor.

THEORETICAL GROUNDS

Calculation of the Time Profiles of Value Quantities

It important to reveal the effects of elementary steps on the overall reaction rate (w) for inhibition processes. In accordance with this, the kinetic significance of an elementary step is determined as the "value" (G) [14–18]—the ratio of a response of the overall reaction rate at the point t in time to a variation in the rate of the

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step at the initial point t_0 in time. The value (G_i) and the value contribution (h_i) of step i are written as follows:

$$G_i(t) = \frac{\partial w[w_1(t), \ldots, w_n(t)]}{\partial w_i}\Bigg| w_i = w_i(t_0),$$
$$h_i(t) = G_i(t)w_i(t), \quad i = 1, 2, \ldots, n, \tag{1}$$

where w_i is the rate of step i.

Previously [14–18], a mathematical procedure for the numerical calculation of the dynamics of value quantities G_i and h_i was described. The calculation is based on the Hamiltonian systematization of kinetic models for reaction systems. The calculation is reduced to simultaneously solving the kinetic and differential equations of ψ_j functions conjugate to component concentrations (C_j)

$$\begin{cases} dC_j/dt = f_j(k, C) = \partial H/\partial \psi_j, \quad j = 1, 2, \ldots, m \\ d\psi_j/dt = -\partial H/\partial C_j \\ G_i = \sum_1^p a_p^i \psi_p^i - \sum_1^l a_l^i \psi_l^i, \quad i = 1, 2, \ldots, n, \end{cases} \tag{2}$$

where m and n are the numbers of components and steps, respectively; $C(t)$ is the m-vector of component concentrations with $C(t_0) = C_0$, k is the n-vector of rate constants; f_j is a function that contains a linear combination of the rates of steps; H is the Hamiltonian of the reaction system, which is equal to

$$H = -w + \sum_1^m \psi_j dC_j/dt = -w + \sum_1^n G_i w_i = \text{const},$$

and a_p^i, a_l^i, ψ_p^i, and ψ_l^i are the stoichiometric coefficients and conjugate functions corresponding to the products (p) and initial substances (l) of the ith individual step.

The quantity ψ_j characterizes the value—the kinetic significance of component j. It is determined as the ratio of the response of the overall reaction rate w at the point t in time to a variation in the buildup rate of component j at the point t_0 in time:

$$\psi_j(t) = \frac{\partial w[f_1(t), \ldots, f_m(t)]}{\partial f_j}\Bigg| f_j = f_j(t_0), \quad j = 1, 2, \ldots, m. \tag{3}$$

Determination of the Molecular Structure of an Effective Reaction Inhibitor

Generally, information contained in the dynamics of value contributions from steps with the participation of an inhibitor and its reaction products can be useful for choosing the molecular structure of an effective inhibitor, which results in the strongest inhibition of the reaction. However, this problem can be rigorously solved by finding optimum reaction conditions with the use of variational calculus [19]. For this purpose, the condition for the objective functional $I(t)$ is written as

$$I(t) = \Delta[\mathrm{RH}]_t = \int_{t_0}^{t} w dt \longrightarrow \min, \quad w = dC_{\mathrm{RH}}/dt, \tag{4}$$

where RH is the substrate.

Condition (4) corresponds to the minimum conversion of the initial substrate ($\Delta[\mathrm{RH}]_t$) at an arbitrary point t in time.

Here, a very important aspect should be emphasized. In choosing an effective (optimum) inhibitor, the parameters of its molecular structure are considered as controlling parameters. For this purpose, the rate constants (k_i) of steps are presented as functions of the molecular structure parameters (D) of the inhibitor. These parameters are chosen so that the reactivity of the intermediates of inhibitor transformations can be described with the use of these parameters.

Let us represent k_i as

$$k_i = \varphi_i(D), \tag{5}$$

where D is the l-vector of numerical parameters that characterize reactivity.

The quantity D can be bond energy, ionization potential, charges at reaction centers, or another numerical characteristic of the molecular structure of the inhibitor that is commonly used to describe the reactivity of molecules.

Next, the above procedure of finding value quantities with the use of Eq. (2) is reduced to the determination of conditions for Eq. (4). The corresponding rate equations and the Hamiltonian, in which controlling parameters D are distinguished, take the forms

$$dC_j/dt = f_j(C, D), \quad H = -w + \sum_{j=1}^m \psi_j f_j(C, D), \quad j = 1, 2, \ldots, m \tag{6}$$

or

$$w = -H + \sum_{i=1}^n G_i w_i(C, D), \quad i = 1, 2, \ldots, n.$$

We assumed that D varied within the range

$$D_q^{\min} \le D_q \le D_q^{\max}, \quad q = 1, 2, \ldots, l.$$

The procedure for finding optimum solutions allowed us to unambiguously determine molecular structure parameters D^* for an effective inhibitor in accordance with condition (4). According to the princi-

ple of maximum [19], the following equation corresponds to condition (4):

$$\sup H(\psi^*, C^*, D^*) = 0. \quad (7)$$

The optimum value of D^*, at which condition (4) is met, corresponds to the solution of set (2) of kinetic and differential equations of conjugate functions ψ_j and, simultaneously, to maximum condition (7). The principle of maximum also suggests that D^* should be selected from the values of D^{min}, D^{max}, and $D^{(8)}$, where $D^{(8)}$ is the value of D that corresponds to the equation

$$\partial H/\partial D = 0. \quad (8)$$

The condition D^* = const in the course of the reaction significantly simplifies the problem of finding $D^{(8)}$. The value of D^* for the initial point in time corresponds to the parameters of the electronic structure of a reaction inhibitor, which is effective under given reaction conditions. Therefore, using the equalities D = const and H = const, the value of $D^{(8)}$ can be numerically calculated from Eq. (8) even at the initial point in time. The final stage of calculations is the determination of the molecular structure of an effective inhibitor from the value of D.

Determination of an Effective Inhibitor Concentration

It is evident that, because of prooxidant properties of an inhibitor, a situation can occur when a maximum inhibiting effect corresponds to a certain inhibitor concentration from the range $[InH]_{min} \le [InH]_0 \le [InH]_{max}$, where InH is the inhibitor, rather than to the maximal possible initial concentration. The procedure of finding an inhibitor concentration that produces a maximum inhibiting effect is analogous to the above method of finding the molecular structure of an effective inhibitor. In this case, the rate equations and the corresponding Hamiltonian are written in the forms

$$dC_j/dt = f_j\{C, [InH]_0\},$$
$$H = -w + \sum_{j=1}^{m} \psi_j f_j\{C, [InH]_0\}, \quad j = 1, 2, \ldots, m. \quad (9)$$

In this case, the initial inhibitor concentration $[InH]_0$ serves as a controlling parameter. Next, the optimum inhibitor concentration, which meets condition (4), is determined with the use of the above principle of maximum.

EXPERIMENTAL

Experimental Procedure

Experiments on the oxidation of ethylbenzene in the absence and presence of *para*-methylphenol 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 design of the reactor allowed us to take samples for the determination of ethylbenzene hydroperoxide.

The analysis of products was performed using a Chrom-5 chromatograph with a flame-ionization detector. A glass column 80 cm in length with an internal diameter of 0.3 cm was used in the analysis. The column was packed with 10% XE silicone on Gas Chrom S (100/120 mesh) as a solid support. The chromatographic injector, detector, and column temperatures were 80°C. At low hydroperoxide contents, for improving the sensitivity of analysis, the concentration of ethylbenzene hydroperoxide was determined from the methyl phenyl carbinol content after the addition of triphenylphosphine to the sample taken.

Chemically pure ethylbenzene was purified according to a published procedure [20]. The initiator 2,2'-azobisizobutyronitrile (AIBN) (reagent grade) was purified by triple recrystallization from absolute ethanol and kept in a vacuum to constant weight.

Reaction Model of Liquid-Phase Ethylbenzene Oxidation Inhibited by para-Substituted Phenols

The inhibition mechanism of the liquid-phase oxidation of hydrocarbons (RH) by phenols (InH) was repeatedly considered in the literature [1–13]. The kinetic scheme of ethylbenzene oxidation in the presence of *para*-substituted phenol inhibitors is mainly reduced to the set of reactions given in Table 1. The scheme was written for the case of ethylbenzene autoxidation at high oxygen pressures when the condition $[\dot{R}] \ll [R\dot{O}_2]$ is met.

Table 2 summarizes correlation equations for steps (XI)–(XIII), (XVI), and (XVII). These equations describe the dependence of the rate constants of reactions with the participation of a *para*-substituted phenol and a corresponding phenoxyl radical on the OH-bond energy of the *para*-substituted phenol.

Comments on the kinetic parameters summarized in Tables 1 and 2 are given below.

Reaction (I). The value of k_1 was calculated using the Arrhenius equation $\log k = \log k^0 - E/2.303RT$, where k^0 is the preexponential factor, E is the activation energy of the reaction, T is the temperature, and R is the gas constant. According to Denisov [21], $E_1 = -\Delta H_1 + 6 = 122$ kJ/mol. Here, ΔH_1 is the enthalpy change of reaction (I). The value of $\log k_1$ was determined with the use of the values of E_1 and $k_1^0 = 7.51 \times 10^{-10}$ l^2 mol^{-2} s^{-1} at 120°C [22].

Reaction (IV). The value of k_4 was calculated from the Arrhenius equation, and the constant $k = 1.05 \times 10^6$ l mol^{-1} s^{-1}, which corresponds to the reaction of *tert*-butoxy radical with ethylbenzene at 22°C, and the

Table 1. Reaction model of the liquid-phase oxidation of ethylbenzene inhibited by *para*-substituted phenols

Reaction number	Reaction	Rate constant, l mol^{-1} s^{-1}		References
		T = 60°C	T = 120°C	
(I)*	$2RH + O_2 \longrightarrow 2\dot{R} + H_2O_2$	9.26×10^{-13}	7.70×10^{-10}	[21, 22]
(II)	$\dot{R} + O_2 \longrightarrow R\dot{O}_2$	8.75×10^{8}	1.00×10^{9}	[23]
(III)	$R\dot{O}_2 + RH \longrightarrow RO_2H + \dot{R}$	2.74	20	[24]
(IV)*	$R\dot{O} + RH \longrightarrow ROH + \dot{R}$	2.32×10^{6}	5.85×10^{6}	[25]
(V)	$\dot{O}H + RH \longrightarrow H_2O + \dot{R}$	10^{9}	10^{10}	[26]
(VI)	$RO_2H + RH \longrightarrow R\dot{O} + H_2O + \dot{R}$	1.28×10^{-10}	2.72×10^{-7}	[27]
(VII)	$RO_2H + RH \longrightarrow R'O + H_2O + RH$	3.83×10^{-10}	8.16×10^{-7}	[28]
(VIII)*	$R\dot{O} + RO_2H \longrightarrow ROH + R\dot{O}_2$	4.90×10^{8}	6.43×10^{8}	[25]
(IX)*	$R\dot{O}_2 + R\dot{O}_2 \longrightarrow 2R\dot{O} + O_2$	5.5×10^{6}	1.0×10^{7}	[29–31]
(X)*	$R\dot{O}_2 + R\dot{O}_2 \longrightarrow ROH + R'O + O_2$	1.0×10^{7}	3.5×10^{7}	[29–31]
(XI)	$R\dot{O}_2 + InH \longrightarrow RO_2H + \dot{I}n$	2×10^{4}	8.5×10^{4}	[32]
(XII)*	$R\dot{O} + InH \longrightarrow \dot{I}n + ROH$	2.77×10^{8}	6.80×10^{8}	[33, 34]
(XIII)	$RO_2H + InH \longrightarrow \dot{I}n + R\dot{O} + H_2O$	9.5×10^{-8}	3.4×10^{-5}	[35]
(XIV)	$\dot{I}n + R\dot{O}_2 \longrightarrow In'O + ROH$	7×10^{8}	7×10^{8}	[32]
(XV)	$\dot{I}n + I\dot{n} \longrightarrow InH + In'$	3.5×10^{8}	3.5×10^{8}	[36]
(XVI)*	$\dot{I}n + RH \longrightarrow InH + \dot{R}$	0.31	9.70	Calculated
(XVII)*	$I\dot{n} + RO_2H \longrightarrow InH + RO_2$	5.20×10^{3}	2.29×10^{4}	[32]

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

* Additional comments are given in the text.

average value $\log k_4^0$ = 9 l mol^{-1} s^{-1} [25] were used for calculating E_4.

Reaction (V). It is assumed that the value of k_5 at 120°C is close to the rate constant of a diffusion-controlled reaction.

Reaction (VIII). The value of k_8 was determined using the Arrhenius equation. E_8 = 18 kJ/mol was taken close to the activation energy of reaction (XII). The logarithm $\log k_8^0$ (l mol^{-1} s^{-1}) = 11.2 was calculated using the value $k_8 = 2.5 \times 10^8$ l mol^{-1} s^{-1} at 22°C [25] for the reaction

$$(CH_3)_3\dot{C}O + (CH_3)_3CO_2H \longrightarrow (CH_3)_3COH + (CH_3)_3C\dot{O}_2.$$

Reactions (IX) and (X). The values of k_9 and k_{10} were determined from the values $k_9 + k_{10}$ [29] and k_9/k_{10} [30, 31]. It is believed that the value k_9/k_{10} is independent of temperature, and the yield of radicals formed in reaction (IX) from the solvent cage is close to 1.

Reaction (XI). The equation of $\log k_{11}$ as a function of D_{OH} (Table 2) was derived by a step-by-step calculation technique. The following correlation between $\log k_{11}$ and the Hammett constants σ of *para* substituents in phenol at 60°C formed the basis for the calculation [6, 31]:

$$\log k_{11} = 4.01 - 1.79\sigma. \quad (10)$$

In this case, the constants σ of *para* substituents in phenol are related to D_{OH} by the equation [6]

$$D_{OH} = 368 + 21.7\sigma. \quad (11)$$

From Eqs. (10) and (11), we obtained

$$\log k_{11} = 34.24 - 0.082 D_{OH} \ (T = 60°C).$$

From the average value of the preexponential factor of the rate constant of reaction (XI) $\log k_{11}^0$ (l mol^{-1} s^{-1}) = 7.2 [25], we evaluated E_{11} as

$$E_{11} = 2.303(\log k_{11}^0 - \log k_{11})RT = 0.52D_{OH} - 172.4.$$

Next, the dependence of $\log k_{11}$ on D_{OH} for T = 120°C was found using the Arrhenius equation.

Reaction (XII). The dependence of $\log k_{12}$ on D_{OH} was derived from the equation

$$\log k_{12} = 11 - (0.16D_{OH} - 42)/2.303RT. \quad (12)$$

Mahoney and Weiner [36] derived Eq. (12) from data on the rate constants of the reactions of *tert*-butoxy radical with *para*-substituted phenols [33, 34]. It was also believed that the preexponential factor of the rate constant of reaction (XII) depends only slightly on the molecular structure of phenol. The value of k_{12} was calculated from Eq. (12) for D_{OH} = 364.4 kJ/mol, which corresponds to the OH-bond energy in *para*-methylphenol [6].

Reaction (XIII). The dependence of $\log k_{13}$ on D_{OH} was obtained from the corresponding equation [37]

$$\log k_{13} = 10 - (D_{OH} - 254)/2.303RT.$$

Reaction (XVI). The dependence of $\log k_{16}$ on D_{OH} was derived from the following correlation equation [37] with the use of published data [32]:

$$\log k_{16} = -1.7 - 0.056\Delta H_{16} \ (T = 60°C). \quad (13)$$

Taking into account that the energy of the α-C–H bond in ethylbenzene is equal to 343 kJ/mol [38], we have

$$\Delta H_{16} = 343 - D_{OH}. \quad (14)$$

The dependence of $\log k_{16}$ on D_{OH} at 60°C was found from Eqs. (13) and (14). The equation for $\log k_{16}$ at 120°C was derived by a step-by-step calculation technique, which was used previously for step (XI). In this case, the value $\log k_{16}^0$ (l mol^{-1} s^{-1}) = 9.2 [25] was used.

Reaction (XVII). The dependence of $\log k_{17}$ on D_{OH} was derived from the correlation equation [39]

$$\log k_{17} = 4.1 + 1.56\sigma \ (T = 60°C). \quad (15)$$

The calculation procedure for 120°C was analogous to that used for step (XI) taking into account that $\log k_{17}^0$ (l mol^{-1} s^{-1}) = 7.2.

Mathematical Program for Numerical Calculations

The Valkin mathematical computer program 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, the contributions of elementary steps, and the corresponding Hamiltonian. In this program, the sets of differential equations were solved by the ROW-4A program [40].

Table 2. $\log k$ (l mol^{-1} s^{-1}) as functions of the OH-bond energies D_{OH} (kJ/mol) of phenols for elementary steps with the participation of *para*-substituted phenols and corresponding phenoxyl radicals

t, °C	$\log k = \varphi(D_{OH})$
60	$\log k_{11} = 34.24 - 0.082D_{OH}$
120	$\log k_{11} = 30.11 - 0.069D_{OH}$
60	$\log k_{12} = 17.5 - 0.025D_{OH}$
120	$\log k_{12} = 16.58 - 0.0212D_{OH}$
60	$\log k_{13} = 50.1 - 0.157D_{OH}$
120	$\log k_{13} = 44.01 - 0.133D_{OH}$
60	$\log k_{16} = -25.2 + 0.066D_{OH}$
120	$\log k_{16} = -16.30 + 0.0474D_{OH}$
60	$\log k_{17} = -22.24 + 0.072D_{OH}$
120	$\log k_{17} = -17.90 + 0.061D_{OH}$

Note: The subscripts at k correspond to the step numbers in Table 1.

RESULTS AND DISCUSSION

As mentioned above, the reaction model chosen for the liquid-phase ethylbenzene oxidation inhibited by *para*-substituted phenols has been well studied, and it describes the available experimental data with sufficient accuracy. Nevertheless, we performed additional experiments (experimental conditions are specified in Figs. 1 and 2).

To calculate data for the experiments performed at 60°C under conditions of ethylbenzene oxidation initiated by AIBN, step (I) in Table 1 was replaced by the following reactions:

$$\text{AIBN} \xrightarrow{O_2} 2\text{rO}_2^\bullet, \quad ek_1' = 7.28 \times 10^{-6} \text{ s}^{-1},$$

$$\text{rO}_2^\bullet + \text{RH} \longrightarrow \text{rO}_2\text{H} + \text{R}^\bullet, \quad k_1'' = 2.74 \text{ mol}^{-1}\text{ l s}^{-1},$$

where k_1' is the rate constant of the step of AIBN degradation [24]; e is the yield of radicals from the solvent cage, which is equal to 0.7; and k_1'' is the rate constant of the radical H-atom abstraction by the cyanoisopropylperoxy radical, which was taken as equal to k_3.

As follows from Figs. 1 and 2, the calculated kinetic curves of ethylbenzene hydroperoxide buildup adequately describe the experimental data for ethylbenzene oxidation with and without inhibition by *para*-methylphenol at 60 and 120°C.

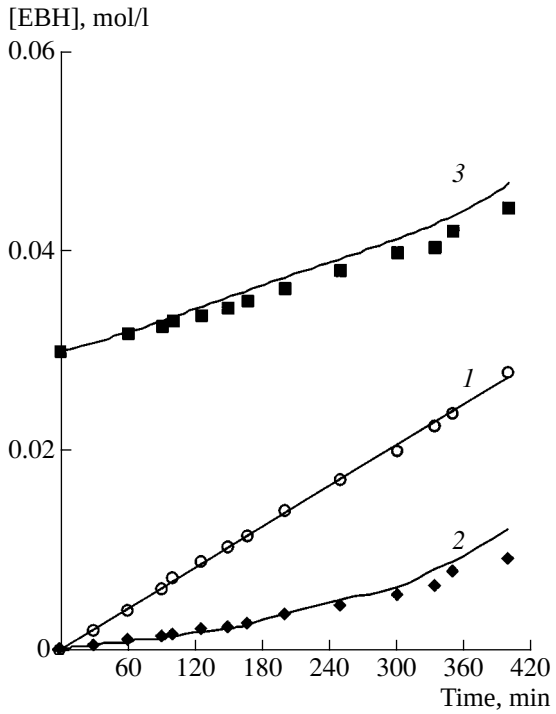


Fig. 1. Buildup of ethylbenzene hydroperoxide (EBH) in the ethylbenzene oxidation reaction initiated by AIBN (*1*) in the absence and (*2*) in the presence of an inhibitor (*para*-methylphenol 6×10^{-4} mol/l) and (*3*) in the simultaneous presence of *para*-methylphenol (6×10^{-4} mol/l) and EBH (0.03 mol/l). [AIBN] = 4×10^{-3} mol/l; $T = 60$°C; points and curves indicate experimental and calculated data, respectively.

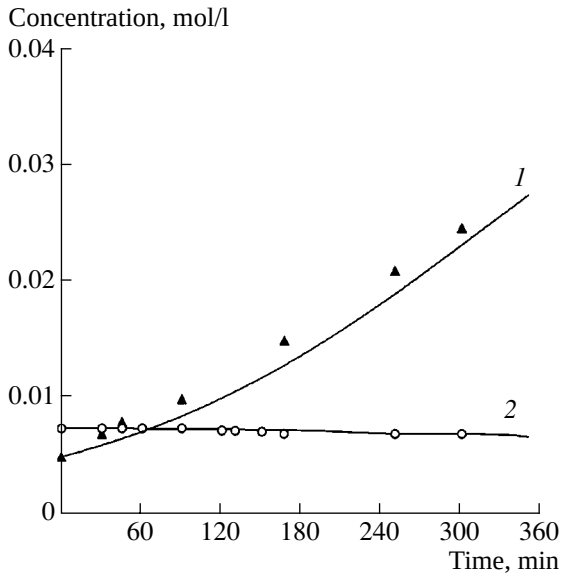


Fig. 2. Kinetic curves of (*1*) ethylbenzene hydroperoxide buildup and (*2*) *para*-methylphenol consumption in the oxidation of ethylbenzene at 120°C. $[EBH]_0 = 5 \times 10^{-3}$ mol/l; [*para*-Methylphenol]$_0 = 7.5 \times 10^{-3}$ mol/l; points and curves indicate experimental and calculated data, respectively.

Time Profiles of the Value Contributions of Individual Steps

The numerical calculation of the dynamics of the reduced value contributions ($h_i^- = h_i/(\sum_1^n h_i^2)^{1/2}$) of steps was performed under the following initial conditions: $[RH]_0 = 7.82$ and 7.35 mol/l for $T = 60$ and 120°C, respectively; $[RO_2H]_0 = 10^{-5}$ mol/l; and $[O_2] = 10^{-2}$ mol/l = const. The special features of the ethylbenzene oxidation reaction inhibited by *para*-substituted phenols distinguished from the time profiles of the contributions of steps (Figs. 3, 4) in the induction period are listed below.

(a) Kinetic regimes of the inhibited reaction. According to data given in Figs. 3 and 4, the reaction of liquid-phase ethylbenzene autoxidation inhibited by *para*-methylphenol at 60°C tentatively passes through the following three time stages (the results are given for the initial [*para*-methylphenol]$_0$ concentration equal to 10^{-3} mol/l):

(1) $t < 3 \times 10^2$ s corresponds to the time interval of establishing a quasi-steady-state regime for *para*-methylphenoxy radicals ($In^{\bullet}$). This is supported by the calculated kinetic curves of $In^{\bullet}$ buildup. For this reason, the contribution of reaction (XV) of the disproportionation of phenoxyl radicals is small. This time interval is also characterized by a high positive contribution of step (XI) of the interaction of peroxyl radicals with the inhibitor and by a considerable negative contribution of reaction (XVI) of *para*-methylphenoxy radicals with ethylbenzene.

(2) $3 \times 10^2 < t < 5 \times 10^6$ s corresponds to the nonautoinitiated reaction. In this time interval, the main step of free radical generation is presented by reaction (I). In this case, step (XV) of the disproportionation of phenoxyl radicals is primarily responsible for the inhibition of ethylbenzene oxidation.

(3) $5 \times 10^6 < t < 5 \times 10^7$ s corresponds to the regime of autoinitiation in the induction period of the reaction of ethylbenzene oxidation. Radicals are generated in steps (VI) and (XIII) with the participation of the hydroperoxide formed in the reaction. In this time interval, the contribution of reaction (XIV) of phenoxyl radicals with peroxyl radicals to the inhibition of the process becomes considerable.

Note that at the instant the reaction came out of the induction period the contributions of steps ($\bar{h}_i$) dramatically changed; in particular, $\bar{h}_{10}$ (chain termination by the interaction of peroxyl radicals with each other) increased, whereas $\bar{h}_{14}$ and $\bar{h}_{15}$ (reaction chain termination with the participation of phenoxyl radicals) decreased.

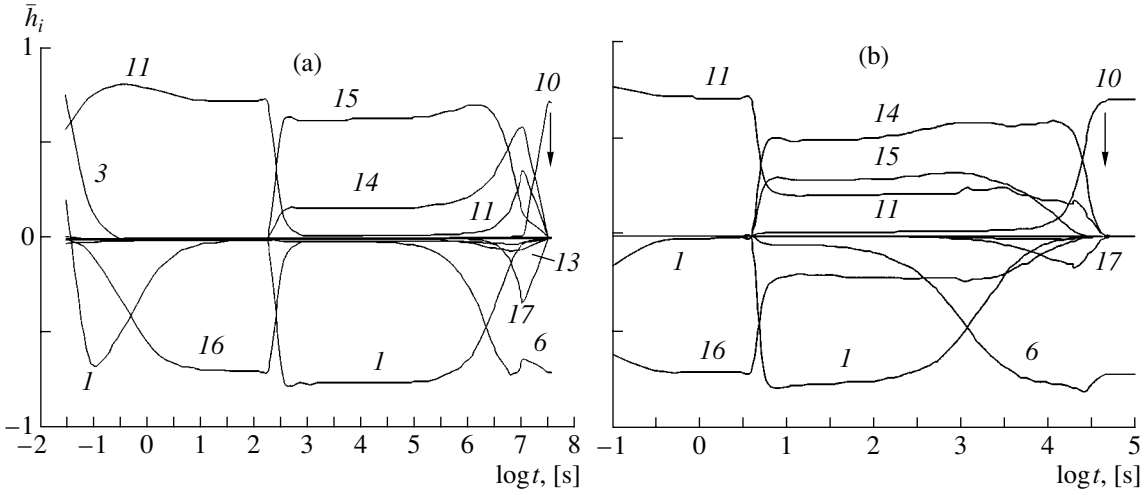


Fig. 3. Dynamics of the reduced value contributions of steps during the induction period in the *para*-methylphenol inhibition of the liquid-phase autoxidation reaction of ethylbenzene. T = (a) 60 or (b) 120°C. [*para*-Methylphenol]$_0 \times 10^{-3}$ mol/l; [EBH]$_0$ = 10^{-5} mol/l. Curve numbers correspond to the step numbers in Table 1. Arrows indicate points in time when the reaction comes out of the induction period.

A similar pattern of the time profiles of value contributions was also observed at the higher temperature of 120°C (Fig. 3b). The following time intervals can be distinguished for the above concentration of *para*-methylphenol (10^{-3} mol/l):

$$1)\ t < 5\ \text{s},\quad 2)\ 5 < t < 4 \times 10^2\ \text{s},$$

$$3)\ 4 \times 10^2 < t < 5 \times 10^4\ \text{s}.$$

However, in contrast to the oxidation reaction at 60°C, the value contribution of step (XIV) prevailed over the contribution of step (XV) for a longer time at 120°C under conditions of equal initial inhibitor concentrations. This is due to the fact that the concentration of peroxyl radicals was higher at 120°C, and this resulted in a relative increase in the kinetic significance of step (XIV), which occurs with the participation of these radicals.

Generally, a change in the initial concentration of *para*-methylphenol had no effect on the general pattern of the time profiles of contributions from steps (for example, see Fig. 4). However, an increase in the inhibitor concentration considerably increased the contribution of step (XIII) with the participation of the inhibitor in the generation of free radicals. This circumstance restricts the applicability of high concentrations of *para*-substituted phenols to the inhibition of chain oxidation reactions. This problem will also be discussed below. Simultaneously, the contribution of step (XV) of the interaction of phenoxyl radicals with each other became increasingly significant in the induction period of the reaction.

(b) Distribution of steps according to their value contributions. The time profiles of contributions from steps also provide an opportunity to reveal steps that have the greatest effect on the inhibition of the reaction. The major portion of the induction period of the reaction of ethylbenzene oxidation corresponds to time regimes (2) and (3) (see above). In this time interval, steps (I), (XIV), and (XIII), which result in the generation of free radicals, make the greatest negative contribution. In contrast, disproportionation steps (X), (XIV), and (XVI) with the participation of peroxyl and phenoxyl radicals positively affect the inhibition of the oxidation reaction.

The contribution of steps (XVI) and (XVII) is comparatively small, although the rates of these reactions are higher than the rates of steps (I), (VI), and (XIII), in which free radicals are generated. This is likely due to the fact that the inhibitor molecule is formed in these steps along with the transformation of the comparatively inactive phenoxyl radical into the more reactive $\dot{\text{R}}$ and $\text{R}\dot{\text{O}}_2$ radicals. Here, an insignificant difference between the reactivities of $\text{In}^{\bullet}$ and $\text{R}\dot{\text{O}}_2$ radicals in chain-propagation steps, which will be considered below, plays an important role.

Small contributions from steps (VIII), (IX), and (XII) in the course of the inhibition process ($|\bar{h}_i| < 10^{-5}$) allowed us to classify these steps as insignificant. The elimination of these steps from the kinetic scheme had almost no effect (deviation smaller than 5%) on the kinetics of changes in the concentrations of components (RH, InH, RO_2H, $\text{In}^{\bullet}$, and $\text{RO}_2^{\bullet}$) in the induction period of the reaction.

Note that the contribution from step (III) of the chain propagation was relatively small in the steady-state region of the reaction with respect to radicals. However, direct calculations are indicative of a strong effect of k_3 on the

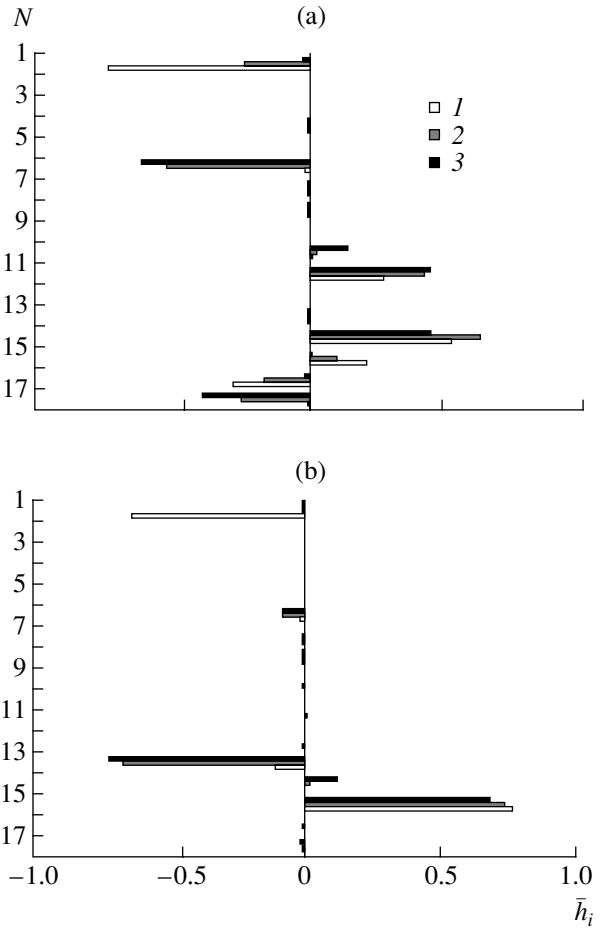


Fig. 4. Reduced value contributions from elementary steps during the induction period in the inhibition of the liquid-phase autoxidation reaction of ethylbenzene at different reaction times. *N* is the step number. The contributions of steps lower than 0.01 are not given. The conversions of RH at times of 3.6×10^6 and 3×10^7 s were 0.25 and 0.76%, respectively. $[para\text{-Methylphenol}]_0$ = (a) 10^{-4} and (b) 0.1 mol/l; $[EBH]_0 = 10^{-5}$ mol/l; T = 60°C. Reaction times, s: (a) (*1*) 1.1×10^{-3}, (*2*) 1.1×10^6, and (*3*) 3.6×10^6; (b) (*1*) 1×10^3, (*2*) 1.1×10^7, and (*3*) 3×10^7.

reaction rate. This is due to the chain nature of oxidation. Thus, according to Eq. (2), the value of step (III) is

$$G_3 = \Psi_{R^\cdot} + \Psi_{RO_2H} + \Psi_{RO_2^\cdot} - \Psi_{RH^\cdot}. \qquad (16)$$

Taking into account Eq. (3), Ψ characterizes the values of reaction system components. It is evident that because of the chain mechanism of the reaction, according to Eq. (3), the values of radicals are much higher than the values of the molecular reaction components RH and RO_2H. In this case, the values of radicals are similar: $\Psi_{R^\cdot} \approx \Psi_{RO_2^\cdot}$. According to Eq. (16), this is responsible for the fact that the value of G_3 is smaller than analogous values for the steps in which free radicals are generated or consumed (for example, steps (I), (VI), and (XIII)–(XV)) by a few (3–6) orders of magnitude. It is likely that objective functionals that are alternative to (4) should be chosen for evaluating the role of step (III) in the inhibited oxidation reaction.

(c) Kinetics of inhibited oxidation. In our opinion, the following fact is of interest: the calculations demonstrated that the reaction of ethylbenzene oxidation comes out of the induction period (at a ~2% conversion of ethylbenzene) under conditions of incomplete inhibitor consumption. This occurred in all cases at 120°C and mainly at comparatively high values of D_{OH} at 60°C (see Table 3). This is associated with the following quasi-equilibrium of reactions (XI) and (XVII):

$$RO_2^\cdot + InH \rightleftharpoons RO_2H + \dot{I}n \quad (w_{11} \approx w_{17}), \qquad (A)$$

in which the inhibitor molecule is restored as a result of the reverse reaction. This equilibrium seemingly becomes more "stable" in the induction period of the reaction with increasing D_{OH} as a consequence of the corresponding increase in the rate constant of reverse step (XVII). In this case, the inhibition effect decreases with increasing D_{OH} and, correspondingly, k_{17}, because the equilibrium is shifted to the formation of a more reactive (at the step of chain propagation) radical.

In essence, *para*-substituted phenols with energies of phenol OH bonds higher than 375 kJ/mol do not inhibit the reaction of ethylbenzene oxidation at 60°C.

The inhibiting effect of phenol under quasi-equilibrium conditions mainly consists in the following:

(a) The phenoxyl radicals $In^\cdot$ are formed in the reaction of the peroxyl radical with the inhibitor molecule (step (XI)); they subsequently participate in the disproportionation (steps (XIV) and (XV)):

$$In^\cdot + In^\cdot \longrightarrow InH + In',$$

$$In^\cdot + RO_2^\cdot \longrightarrow In'O + ROH;$$

Table 3. Inhibitor (InH) conversion after the induction period (τ) of the reaction depending on the OH-bond energy (D_{OH}) in the *para*-methylphenol molecule

Conversion, %	99	47	30	25	7	1	~0.1	~0.1
D_{OH}, kJ/mol	355	360	362	365	370	375	380	382
Induction period $\tau \times 10^3$, h	58.3	41.7	33.0	22.0	8.3	2.8	1.1	1.0

Note: T = 60°C, $[InH]_0$ = 0.01 mol/l; $[ROOH]_0 = 10^{-5}$ mol/l.

(b) The fraction of alkylperoxyl radicals, which can more efficiently react with the parent hydrocarbon, decreases in the reaction system.

The intense reaction of the phenoxyl radical with hydroperoxide ($w_{17} > w_6 + w_{13}$) results in the fact that the termination of kinetic chains is determined by steps (XIV) and (XV) of the disproportionation of the phenoxyl radical rather than limited by the reaction of the peroxyl radical with the inhibitor (step (XI)).

Note that, at low inhibitor concentrations ($\leq 10^{-4}$ mol/l), the rate of step (XI) dramatically decreased, and this reaction became a rate-limiting step in the inhibition of ethylbenzene oxidation. As a result, the positive contribution of this step became considerable (see Fig. 4). Simultaneously, the negative contribution of step (XVII), which seemingly counteracts step (XI), increased upon the accumulation of a sufficient amount of hydroperoxide in the reaction system. This behavior is common to the reactions performed at 60 and 120°C.

Both published data [41] and the experimental results of this work suggest the occurrence of equilibrium (A). It follows from Fig. 1 that the rate of oxidation increased with the addition of a hydroperoxide to the reaction mixture under conditions of initiation of the reaction (T = 60°C). Note that under these conditions the rate of hydroperoxide decomposition into radicals is insignificant as compared with the rate of initiation by AIBN. The reason for the increase in the rate of oxidation on the addition of hydroperoxide to the reaction mixture is a shift of equilibrium (A) to the left, which results in an increase in the concentration of the active peroxyl radical.

The experiment performed at 120°C also suggests the occurrence of equilibrium (A) (see Fig. 2). A progressive increase in the hydroperoxide concentration with time was observed at insignificant inhibitor conversions up to a reaction time equal to 400 min. This fact indicates that the inhibitor is regenerated in reaction (XVII).

Numerical Determination of the Molecular Structure of an Effective Inhibitor Based on the Kinetic Model of the Reaction

The molecular structure of a *para*-substituted phenol that exhibits a maximum inhibiting ability in the reaction of ethylbenzene oxidation was determined by the method described above. The OH-bond energy (D_{OH}) of phenols served as a characteristic parameter of the molecular structure of the inhibitor. The reactivity of corresponding phenoxyl radicals can also be described with the use of this parameter (Table 2):

$$355 \leq D_{OH} \leq 382.5 \text{kJ/mol}.$$

Next, we proceeded on the basis of an approach formulated by Denisov [6, 7, 37], which made it possible to characterize the mechanism of action of phenol inhibitors in the oxidation reactions of organic compounds through the OH-bond energies of phenols.

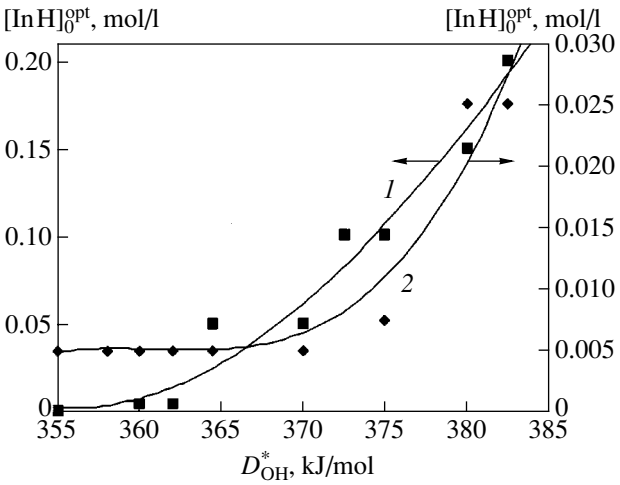
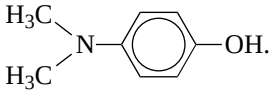


Fig. 5. Dependence of the optimum concentration $[InH]_0^{opt}$, at which the ethylbenzene autoxidation reaction was maximally inhibited, of a *para*-substituted phenol on the OH-bond energy (D^*_{OH}). T = (*1*) 60 and (*2*) 120°C.

We determined the optimum values of D_{OH}, which correspond to an effective inhibitor, using the principle of maximum and considering D^*_{OH} as a controlling parameter. These values were determined for various initial concentrations of the inhibitor. Over a wide range of initial concentrations (10^{-4}–10^{-1} mol/l), D^*_{OH} was equal to a minimally possible value (355 kJ/mol) at both 60 and 120°C. The following molecular structure of a *para*-substituted phenol corresponds to this value:



It was determined from the value σ = –0.6 [42] for a *para* substituent. According to Eq. (11), the value D^*_{OH} = 355 kJ/mol corresponds to the above value of σ for an effective inhibitor.

Determination of an Optimum Concentration of the Initial Inhibitor

An optimum inhibitor concentration $[InH]_{opt}$, that is, a concentration above which the efficiency of inhibition of the autoxidation reaction of ethylbenzene decreases, was found for *para*-substituted phenols. This result is consistent with data obtained in the inhibition of autoxidation (peroxidation) reactions of lipids *in vivo* and *in vitro* by the biogenic inhibitor α-tocopherol [10, 43] and in the antioxidant stabilization of polyethylene with 2,6-di-*tert*-butyl-4-phenylphenol and 4-methyl-6-*tert*-butylphenol [11]. As the concentration of antioxi-

dants was increased, the inhibition efficiency decreased because of the manifestation of prooxidant properties. Note that the optimum concentration of a *para*-substituted phenol increases with D_{OH} (Fig. 5) because of the considerable role played by chain-reaction initiation with the participation of the inhibitor in step (XIII). This provides an opportunity to use a higher concentration of the initial inhibitor most efficiently.

As follows from the results presented in Fig. 5, a considerable increase in the contribution of step (XIII) with temperature explains the observed decrease (by more than one order of magnitude) of $[InH]_0^{opt}$ at a reaction temperature of 120°C, as compared with that at 60°C.

REFERENCES

1. Emanuel', N.M., Denisov, E.T., and Maizus, Z.K., *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* (Chain Reactions of Liquid-Phase Oxidation of Hydrocarbons), Moscow: Nauka, 1965.
2. Scott, J., *Atmospheric Oxidation and Antioxidants*, Amsterdam: Elsevier, 1965.
3. Pospisil, I., *Degradation and Stabilization of Polymers*, Amsterdam: Elsevier, 1983, vol. 4, p. 193.
4. Howard, J.A., *Advances in Free Radical Chemistry*, London: Logos, 1972, vol. 4, p. 173.
5. Emanuel', N.M. and Buchachenko, A.L., *Khimicheskaya fizika molekulyarnogo razrusheniya i stabilizatsii polimerov* (Chemical Physics of Molecular Degradation and Stabilization of Polymers), Moscow: Nauka, 1988.
6. Denisov, E.T., *Oxid. Commun.*, 1984, vol. 6, p. 309.
7. Denisov, E.T. and Azatyan, V.V., *Ingibirovanie tsepnykh reaktsii* (Inhibition of Chain Reactions), Chernogolovka, 1997.
8. Roginskii, V.A., *Fenol'nye antioksidanty. Reaktsionnaya sposobnost' i effektivnost'* (Phenolic Antioxidants: Reactivity and Effectiveness), Moscow: Nauka, 1988.
9. *Autooxidation and Antioxidant*, Lundberg, W.O., Ed., New York: Wiley, 1961, vol. 1, p. 450.
10. *Autooxidation in Food and Biological Systems*, Simic, M.G. and Karel, M.W.O., Eds., New York: Plenum, 1980.
11. Shlyapinikov, Yu.A., Kiryushkin, S.G., and Mar'in, A.P., *Antiokislitel'naya stabilizatsiya polimerov* (Antioxidating Stabilization of Polymers), Moscow: Khimiya, 1986.
12. Kharitonov, V.V., Psikha, B.L., and Zaikov, G.E., *Chem. Phys. Rep.*, 1997, vol. 16, no. 3, p. 416.
13. Pis'menskii, A.V., Psikha, B.L., and Kharitonov, V.V., *Vysokomol. Soedin. A*, 1998, vol. 40, p. 632.
14. Tavadyan, L.A., *Arm. Khim. Zh.*, 1987, vol. 40, no. 2, p. 81.
15. Tavadyan, L.A. and Martoyan, G.A., *Chem. Phys. Rep.*, 1994, vol. 13, no. 5, p. 793.
16. Tavadyan, L.A. and Martoyan, G.A., *Khim. Zh. Arm.*, 1995, vol. 48, nos. 1–3, p. 81.
17. Martoyan, G.A. and Tavadyan, L.A., *Khim. Zh. Arm.*, 1996, vol. 49, no. 4, p. 17.
18. Martoyan, G.A. and Tavadyan, L.A., *Khim. Fiz.*, 2001, vol. 20, no. 2, p. 26.
19. Pontryagin, L.S., Boltyanskii, V.G., Gamkrelidze, R.V., and Mishchenko, E.F., *Matematicheskaya teoriya optimal'nykh protsessov* (Mathematical Theory of Optimal Processes), Moscow: Fizmatgiz, 1961.
20. Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.
21. Denisov, E.T., *Itogi Nauki Tekh., Kinet. Katal.*, Moscow: VINITI, vol. 9, p. 158.
22. Gagarina, A.B., Pisarenko, L.M., and Emanuel', N.M., *Dokl. Akad. Nauk SSSR*, 1973, vol. 21, no. 3, p. 653.
23. Mailard, B., Ingold, K.U., and Scaiano, J.C., *J. Am. Chem. Soc.*, 1983, vol. 105, no. 15, p. 5095.
24. Emanuel', N.M. and Gal, D., *Okislenie etilbenzola. Model'naya reaktsiya* (Oxidation of Ethylbenzene: A Model Reaction), Moscow: Nauka, 1984, p. 208.
25. Landolt-Bornstein, *Numerical Data and Functional Relationships in Science and Technology*, Berlin, 1984, p. 142.
26. Andar, M., Meyerstain, D., and Neta, P., *J. Chem. Soc. A*, 1966, vol. 2, no. 8, p. 742.
27. Gal, D., Blumberg, E.A., Valendo, A.Ya., and Emanuel, N.M., *Magy. Kem. Folyoirat*, 1979, vol. 85, p. 529.
28. Matienko, L.I., Goldina, L.A., Skibida, I.P., and Maizus, Z.K., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, no. 2, p. 287.
29. Tsepalov, V.F. and Shlyapintokh, V.Ya., *Kinet. Katal.*, 1962, vol. 3, p. 870.
30. Tavadyan, L.A., *Khim. Fiz.*, 1986, vol. 5, no. 1, p. 63.
31. Tavadyan, L.A., *Khim. Fiz.*, 1991, vol. 10, no. 5, p. 650.
32. Mahoney, L.R. and Da Rooge, M.A., *J. Am. Chem. Soc.*, 1975, vol. 97, no. 16, p. 4722.
33. Das, P.K., Encinas, M.V., Steenken, S., and Scaiano, J.C., *J. Am. Chem. Soc.*, 1981, vol. 103, no. 14, p. 4162.
34. Encinas, M.V. and Scaiano, J.C., *J. Am. Chem. Soc.*, 1981, vol. 103, no. 21, p. 6393.
35. Martem'yanov, V.S., Denisov, E.T., and Samoilova, L.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, no. 5, p. 1039.
36. Mahoney, L.R. and Weiner, S.A., *J. Am. Chem. Soc.*, 1972, vol. 94, no. 2, p. 585.
37. Denisov, E.T., *Itogi Nauki Tekh., Kinet. Katal.*, Moscow: VINITI, 1987, vol. 17, p. 115.
38. Korcek, S., Cheiner, J.H.B., Howard, J.A., and Ingold, K.U., *Can. J. Chem.*, 1972, vol. 50, no. 14, p. 2285.
39. Rubtsov, V.I., Roginskii, V.A., Miller, V.B., and Zaikov, G.E., *Kinet. Katal.*, 1980, vol. 21, no. 3, p. 612.
40. Gottwald, B.A., *Simulation*, 1981, vol. 33, p. 103.
41. Tomas, J.R., *J. Am. Chem. Soc.*, 1964, vol. 86, no. 22, p. 4807.
42. Hammet, L.P., *Physical Organic Chemistry*, McGraw-Hill, 1970.
43. Khrapova, N.G., *Lipidy. Struktura, biosintez, prevrashcheniya i funktsii* (Lipids: Structure, Biosynthesis, Transformations, and Functions), Burlakova, E.B. and Severin, S.E., Eds., Moscow: Nauka, 1977, p. 157.