Physical Chemistry

Free radical formation during ethylbenzene oxidation catalyzed by cetyltrimethylammonium bromide

L. M. Pisarenko and O. T. Kasaikina★

N. N. Semehov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (095) 938 2156. E-mail: kasaikina@chph.ras.ru

The dimer of 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione] and α-tocopherol were used as free radical acceptors in a study of the kinetic regularities of free radical formation during ethylbenzene oxidation by molecular oxygen at 60 °C. The reaction initiated by the α-phenylethyl hydroperoxide—cetyltrimethylammonium bromide (CTAB) catalytic system, which generates free radicals. The oxidation kinetics was analyzed using computer simulation.

Key words: 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione], cetyltrimethylammonium bromide, ethylbenzene oxidation, catalysis, free radicals.

The kinetics of hydrocarbon (RH) oxidation by O_2 is determined to a great extent by the rate of chain initiation and its change during oxidation.[1] Chain initiation in autooxidation processes is associated, as a rule, with reactions of hydroperoxides (ROOH), *viz*., primary products of RH oxidation.

Studies of the recent decade[2—7] show that surfactant (Surf) additives can substantially affect the rate and mechanism of hydrocarbon oxidation. In a nonpolar hydrocarbon medium, surfactants form associates (microaggregates) in which polar oxidation products (water, alcohols, hydroperoxides, *etc*.) are concentrated. The effects observed depend on the nature of the surfactant and oxidized hydrocarbon.[2—5] Many data on the influence of different surfactants (cationic, anionic, nonionic) on the rate of O_2 absorption during the oxidation of tetralin, cumene, and cyclohexene are presented in Ref. 6. In the presence of most cationic surfactants, the rate of O_2 absorption increases. Anionic surfactants in the form of acids enhance the oxidation rate, whereas their sodium salts inhibit it. The presence of ROOH was found to be substantial for hydrocarbon oxidation in the presence of surfactants. It is assumed[6] that the cationic and anionic surfactants react with the more nucleophilic (internal) and more electrophilic (external) oxygen atom, respectively, due to which the homolysis of the O—O bond is facilitated. Nonionic surfactants affect the rate of ROOH decomposition *via* the formation of H bonds.

The rates of radical formation are necessary data to predict the surfactant effect on the rate and products of hydrocarbon oxidation.

The purpose of this work is to choose inhibitors for measuring the initiation rates in the microheterogeneous RH—Surf—ROOH systems. The oxidation of ethyl-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 419—425, March, 2002.

benzene initiated by the ROOH—cetyltrimethylammonium bromide (CTAB) system was used as the model reaction.

Experimental

Ethylbenzene was oxidized in a thermostatted reaction vessel equipped with a magnetic stirrer, a device for the introduction of additives during the reaction, and gas volumeter for monitoring the rate of O_2 absorption. The reaction was carried out at 60 °C and a constant oxygen pressure $P_{O_2} = 1$ atm.

Ethylbenzene (technical grade) was purified according to a standard procedure.[8] Cetyltrimethylammonium bromide (Serva) was used as received. α-Phenylethyl hydroperoxide (ROOH) was prepared by ethylbenzene autooxidation at 120 °C in a bubbling reactor with an O_2 flow. The reaction mixture containing CTAB, ROOH, and ethylbenzene was magnetically stirred at ~20 °C for 30 min, and then the reactor was connected to a gas volumeter. The concentrations of ROOH at the beginning and end of experimental run were determined iodometrically.

The rate of radical formation (W_i) was determined by the inhibitor method using different acceptors of free radicals. These were the dimer of 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione] (F_NF_N) synthesized according to a known procedure;[9] α-tocopherol (TP) (Sigma) was used without additional purification; 2-phenylindane-1,3-dione (FH), which is a blood anticoagulant named "phenyline" widely applied in medical practice, was prepared by a published procedure.[10] After the stationary rate of dioxygen absorption (W_{O_2}) was established, a concentrated solution of the inhibitor in chlorobenzene was introduced into the reaction mixture using a microsyringe, the induction period (τ) was measured, and the rate of chain initiation was calculated by the formula[1]

$$W_i = (f\,[\mathrm{InH}]_0)/\tau, \qquad \text{(I)}$$

where *f* is the stoichiometric coefficient of chain termination, and $[\mathrm{InH}]_0$ is the initial concentration of the inhibitor in the reaction mixture. Computer simulation of the kinetics of inhibited ethylbenzene oxidation was performed according to the published program.[11]

Results and Discussion

Hydroperoxide ROOH and CTAB taken separately have no effect on ethylbenzene oxidation at 60 °C (Fig. 1, curves *1* and *2*). When CTAB and ROOH are introduced together, O_2 absorption (see Fig. 1, curve *3*) is observed, and the amount of absorbed O_2 corresponds to the amount of ROOH that formed. The addition of inhibitors, acceptors of free radicals, ceases O_2 absorption and the appearance of induction periods (τ), at the end of which O_2 absorption recommences (see Figs. 1 and 2). This implies that the reaction of ROOH with CTAB produces free radicals ($I^\cdot$) initiating ethylbenzene chain oxidation

$$\mathrm{ROOH + CTAB} \longrightarrow \mathrm{I}^\cdot, \qquad (1)$$

$$\mathrm{I}^\cdot + \mathrm{RH} \longrightarrow \mathrm{IH} + \mathrm{R}^\cdot, \qquad (2)$$

$$\mathrm{R}^\cdot + \mathrm{O_2} \longrightarrow \mathrm{RO_2}^\cdot, \qquad (3)$$

$$\mathrm{RO_2}^\cdot + \mathrm{RO_2}^\cdot \longrightarrow \text{alcohol + ketone} + \mathrm{O_2}. \qquad (4)$$

In a solution the dimer 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione] (F_NF_N) reversibly dissociates to two 2-(*p*-dimethylaminophenyl)indane-1,3-dion-2-yl radicals $F_N^\cdot$. The $F_N^\cdot$ radicals, which are in equilibrium with F_NF_N, react with high rate constants ($\geq 10^8$ L (mol s)$^{-1}$) with alkyl and peroxyl radicals, providing efficient chain termination in the process of hydrocarbon oxidation.[12]

$$\mathrm{F_NF_N} \rightleftharpoons 2\,\mathrm{F_N}^\cdot \qquad (5)$$

$$\mathrm{F_N}^\cdot + \mathrm{R}^\cdot, \mathrm{RO_2}^\cdot \longrightarrow \text{products} \qquad (6)$$

The stoichiometric coefficient of chain termination *f* for the F_NF_N inhibitor is 2. It is known[12] that F_NF_N and $F_N^\cdot$ radicals do not virtually react with ROOH. According to the results of the UV spectral study of solutions of F_NF_N, the CTAB additives to the RH hydrocarbon containing no ROOH hydroperoxide do not affect the equilibrium concentration of the $F_N^\cdot$ radicals. As established, the F_NF_N additives result in the almost complete cessation of O_2 absorption during ethylbenzene oxidation (see Fig. 1). The repeated introduction of F_NF_N into the reaction mixture at the end of the induction period results in the same strong retardation. The induction time is proportional to the concentration of the introduced inhibitor. Therefore, the products of the reaction of the $F_N^\cdot$

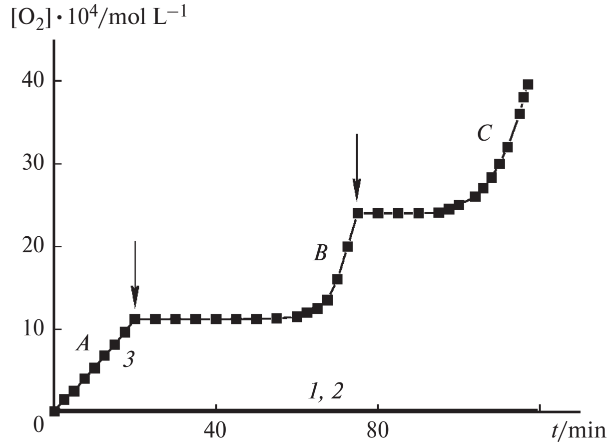

Fig. 1. Kinetic curves for O_2 absorption during ethylbenzene oxidation at 60 °C (arrows indicate the moments of introduction of the F_NF_N inhibitor). Concentrations of reactants/mol L^{-1}: *1*, [ROOH] = $1.7 \cdot 10^{-2}$ without CTAB; *2*, [CTAB] = $1.2 \cdot 10^{-3}$ without ROOH; *3*, [ROOH] = $1.7 \cdot 10^{-2}$ and [CTAB] = $1.2 \cdot 10^{-3}$. Rate of dioxygen absorption W_{O_2}/mol (L s)$^{-1}$: $1 \cdot 10^{-6}$ (region *A*), $1.9 \cdot 10^{-6}$ (region *B*), and $1.8 \cdot 10^{-6}$ (region *C*). Rate of radical initiation W_i/mol (L s)$^{-1}$ $1.8 \cdot 10^{-7}$ (regions *A*, *B*), $2.2 \cdot 10^{-7}$ (regions *B*, *C*). Concentration of the F_NF_N inhibitor/mol L^{-1}: $2.6 \cdot 10^{-4}$ (first introduction); $2.0 \cdot 10^{-4}$ (second introduction).

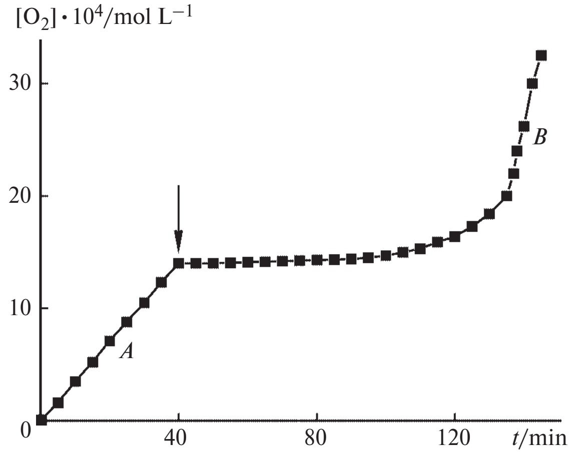

Fig. 2. Kinetic curves for O_2 absorption during the oxidation at 60 °C of ethylbenzene containing hydroperoxide and CTAB ($[ROOH] = 1.7\cdot10^{-2}$ and $[CTAB] = 1.2\cdot10^{-3}$ mol L^{-1}). Arrow indicates the introduction of the α-tocopherol inhibitor with a concentration of $2.4\cdot10^{-4}$ mol L^{-1}. Oxidation rate W_{O_2}/mol (L s)$^{-1}$: $0.6\cdot10^{-6}$ (region *A*); $1.4\cdot10^{-6}$ (region *B*). Rate of radical initiation $W_i = 0.94\cdot10^{-7}$ mol (L s)$^{-1}$ (regions *A*, *B*).

radical with free radicals (reaction (6)) have no effect on the oxidation rate (W_{O_2}) and do not interfere measuring the rate of radical initiation (W_i). In addition, it also follows from the obtained data that CTAB in this process acts as the catalyst for ROOH decomposition and is not consumed and deactivated in the process. Indeed, CTAB ($1.2\cdot10^{-3}$ mol L^{-1}) at $W_i = 2\cdot10^{-7}$ mol (L s)$^{-1}$ would be consumed within 100 min; however, the oxidation rate does not decrease even 2 h after the beginning of the reaction (see Figs. 1 and 2).

At the first introduction of F_NF_N, the initiation rate of the radicals W_i calculated from formula (I) is $1.8\cdot10^{-7}$ mol (L s)$^{-1}$, and at the repeated introduction it is $2.2\cdot10^{-7}$ mol (L s)$^{-1}$ (see Fig. 1). A slight increase in W_i is attributed to an increase in the ROOH concentration during ethylbenzene oxidation, which is indicated by O_2 absorption (ΔO_2). A comparison of the ROOH concentrations at the beginning and end of experimental run ($t = 118$ min) shows that ethylbenzene under these conditions is almost selectively oxidized to hydroperoxide according to the equality

$$[ROOH]_t = [ROOH]_0 + \Delta O_{2;t}. \qquad \text{(II)}$$

It is seen from the experimental data characterizing the influence of the initial concentrations of ROOH and CTAB on the rates of oxygen absorption (W_{O_2}) and radical initiation (W_i) that both W_{O_2} and W_i increase with an increase in the concentrations of ROOH and CTAB (Table 1) (W_{O_2} values were measured after the end of the induction period). In almost all experiments, the rate of O_2 absorption before the introduction of the inhibitor was somewhat lower than that after the end of the induction period (see Fig. 1), despite the ROOH concentration did not increase in the induction period. At the repeated introduction of the inhibitor, the W_{O_2} values before and after the induction period virtually coincided. It is most likely that the establishment of equilibrium of the Surf—ROOH microaggregates in the microheterogeneous

Table 1. Rates of dioxygen absorption (W_{O_2}) and radical initiation (W_i) during ethylbenzene oxidation in the presence of ROOH and CTAB (60 °C)

No.	$[CTAB]\cdot10^3$	$[ROOH]_0\cdot10^2$	$([ROOH]_0 + \Delta O_2)^a\cdot10^2$	$W_{O_2}{}^{exp}\cdot10^6$ [b]	$W_i\cdot10^7$	$([ROOH]_0 + \Delta O_2)^c\cdot10^2$	$[ROOH]_t{}^d\cdot10^2$
	mol L^{-1}			mol (L s)$^{-1}$		mol L^{-1}	
1	1.2	0.47	0.52	0.50	0.40	0.60	0.60
2	1.2	0.50	0.59	0.70	0.50	0.70	0.66
3	1.2	0.90	1.00	0.80	0.80	1.10	1.10
4 [e]	1.2	1.10	1.24	1.40	0.90	1.38	1.30
5	2.0	1.60	1.70	1.30	2.60	1.84	1.80
6 [f]	1.2	1.70	1.80	1.80	1.80	1.94	—
	—	—	1.94	2.00	2.20	2.05	2.04
7	1.2	2.10	2.36	1.90	2.00	2.70	2.50
8 [f]	1.2	3.35	3.55	2.20	4.10	3.80	—
	—	—	3.80	2.50	4.30	4.15	4.10
9	4.0	1.60	1.70	2.20	19.00	1.97	2.00
10 [g]	1.2	6.20	—	3.30	—	7.60	8.00

[a] At the moment of inhibitor introduction.

[b] Experimental value.

[c] Determined at the end of experiment from the amount of absorbed dioxygen.

[d] Determined by iodometric titration.

[e] α-Tocopherol was used as the inhibitor.

[f] The F_NF_N inhibitor was repeatedly introduced without interruption of the oxidation process (similarly to Fig. 1).

[g] No inhibitor was introduced.

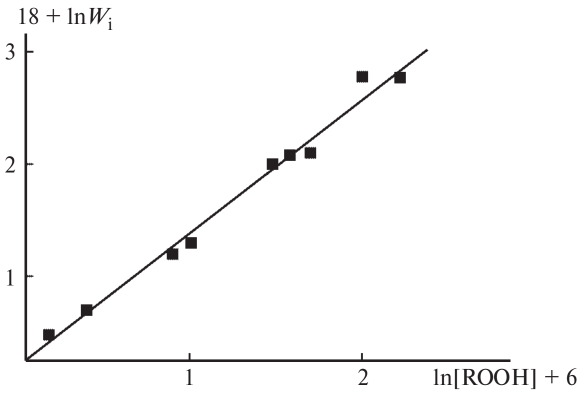

Fig. 3. Logarithmic plot of the rate of radical initiation (W_i) *vs.* hydroperoxide concentration [ROOH] ([CTAB] = $1.2 \cdot 10^{-3}$ mol L^{-1}).

system formed by the surfactant addition to the hydrocarbon medium containing ROOH requires a certain time. The time of equilibration depends on the surfactant and ROOH concentrations and temperature. Taking into account this fact, we introduced the inhibitor, as a rule, 30 min after the beginning of oxidation. Since almost all absorbed O_2 was consumed for ROOH formation, the increment of the ROOH concentration to the moment of inhibitor introduction equal to ΔO_2 was taken into account in analysis of the plot of the initiation rate W_i *vs.* [ROOH] (see Table 1).

At the constant CTAB concentration ($1.2 \cdot 10^{-3}$ mol L^{-1}), the initiation rate (W_i) is proportional to the ROOH concentration (see Table 1)

$$W_i = k_{ef}[\mathrm{ROOH}]. \qquad \text{(III)}$$

This plot in the logarithmic coordinates is a straight line (Fig. 3), whose slope n is 1.2. The fractional reaction order indicates a complicated mechanism of ROOH decomposition under the CTAB effect. The apparent rate constant of ROOH decomposition (k_{app}) is $1.1 \cdot 10^{-5}$ s^{-1}. This value much exceeds the rate constant of monomolecular decomposition of ROOH ($k_p = 1 \cdot 10^{12}\exp(-133700/RT)$ s^{-1}),[13] which is $1 \cdot 10^{-9}$ s^{-1} at 60 °C.

The plot of W_{O_2} *vs.* [ROOH] is nonlinear (Fig. 4, curve *1*). This is related to the free-radical mechanism of ethylbenzene oxidation, square chain termination in reaction (4), and a decrease in the length of the oxidation chain with an increase in the initiation rate (W_i). With these changes, the W_{O_2} increase is proportional to $(W_i)^{0.5}$ (see Fig. 4, curve *2*). The slope is $4.2 \cdot 10^{-3}$ (mol (L s)$^{-1}$)$^{0.5}$. According to the theory of chain processes,[1,13] the rate of ethylbenzene oxidation is described by the equation

$$W_{O_2} = k_2/(2k_4)^{0.5}[\mathrm{RH}](W_i)^{0.5}, \qquad \text{(IV)}$$

where k_2 and k_4 are the rate constants for chain propagation and termination in reactions (2) and (4), respectively. The $k_2/(2k_4)^{0.5}$ ratio for ethylbenzene oxidation[13,14] at 60 °C is $5.5 \cdot 10^{-4}$ (L (mol s)$^{-1}$)$^{0.5}$, which rather well agrees with the experimental results: $4.2 \cdot 10^{-3}/[\mathrm{RH}] = 5.1 \cdot 10^{-4}$ (L (mol s)$^{-1}$)$^{0.5}$. Coincidence of the parameters indicates that under experimental conditions CTAB influences only on the rate of radical initiation (W_i). An appropriate acceptor of free radicals for the determination of W_i in microheterogeneous systems by the inhibitor method is F_NF_N.

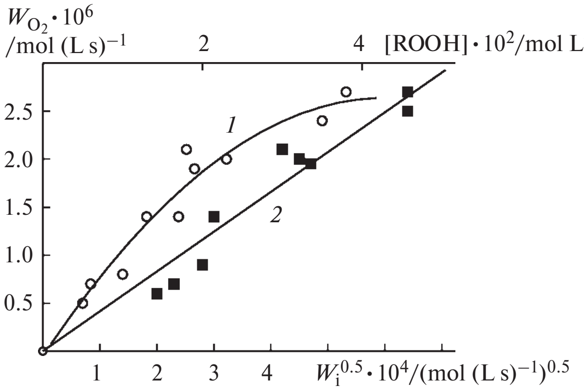

Fig. 4. Influence of the hydroperoxide concentration [ROOH] (*1*) and oxidation rate ($W_i^{0.5}$) (*2*) on the rate of ethylbenzene oxidation (W_{O_2}) with account for the correction coefficient ($\Delta = 0.5W_i$) to O_2 evolution during the recombination of the $RO_2^{\bullet}$ radicals in reaction (4) ($W_{O_2} = W_{O_2}^{exp} + \Delta$ mol (L s)$^{-1}$).

In the presence of aliphatic alcohols and some surfactants, the induction period caused by TP additives to lipid shortens.[15] This fact was attributed to both the formation of the Surf—TP complex, which decreases the reactivity of the inhibitor in the reaction with $RO_2^{\bullet}$, and the increase in the rate of side reactions of TP consumption (with O_2 and ROOH). α-Tocopherol efficiently retards O_2 absorption initiated by the ROOH—CTAB system (see Fig. 2), and the rate of radical initiation (W_i) calculated by formula (I) with account for the value $f = 2$ for TP[1] well agrees with the results obtained when F_NF_N was used as an inhibitor (see Table 1). Thus, in this system and at this temperature, α-tocopherol can also be used for the determination of W_i.

We performed computer simulation of the kinetic curves of O_2 absorption in initiated ethylbenzene oxidation in the presence of various inhibitors. The program[11] makes it possible to integrate numerically the differential equations for the consumption rate for each component of the complicated process without simplifications and using the quasi-steady-state approximation with respect to the radical concentrations. Simulation is of special interest because of the specific features of the inhibition effect of F_NF_N for which the equilibrium constant (K_{eq}) was experimentally determined

$$K_p = k_{dis}/k_{rec} = [F_N^{\bullet}]^2/([F_NF_N]_0 - [F_N^{\bullet}]/2). \qquad \text{(V)}$$

This constant K_{eq}, according to the data,[16] is $6.2 \cdot 10^2 \cdot \exp(-72300/RT)$ mol L^{-1}. The recombination rate constant for the $F_N^{\bullet}$ radicals was determined by the flash photolysis method ($k_{rec} = 3 \cdot 10^8$ L (mol s)$^{-1}$).[17] The kinetic analysis of the behavior of F_NF_N under the conditions of initiated ethylbenzene oxidation at 60 °C in the steady-state approximation[12] showed that the strong retardation observed in the presence of F_NF_N indicates the complete suppression of chain oxidation and linear chain termination.

$$W_i - k_6[RO_2^{\bullet}][F_N^{\bullet}] = 0 \qquad \text{(VI)}$$

The change in the $F_N^{\bullet}$ concentration in the retardation period is described by the equation

$$k_{dis}[F_NF_N] - k_{rec}[F_N^{\bullet}]^2 - W_i = 0. \qquad \text{(VII)}$$

The consumption of the $F_N^{\bullet}$ radicals in the chain termination process does not violate equilibrium (5) when the equality

$$k_{dis}[F_NF_N] \geq 10W_i. \qquad \text{(VIII)}$$

is fulfilled.

An important characteristics of the dimer—free radicals equilibrium is the time of equilibration. The concentration of the $F_N^{\bullet}$ radicals for dissociation of F_NF_N in a hydrocarbon medium is described by the quasi-steady-state equation[12]

$$d[F_N^{\bullet}]/dt = k_{dis}([F_NF_N]_0 - [F_N^{\bullet}]/2) - k_{rec}[F_N^{\bullet}]^2 = 0. \qquad \text{(IX)}$$

The integral form of equation (IX) at $[F_NF_N] \gg [F_N^{\bullet}]$ has the form

$$[F_N^{\bullet}] = [F_N^{\bullet}]_0[1 - \exp(-t/\theta)]/[1 + \exp(-t/\theta)], \qquad \text{(X)}$$

where $\theta = 0.5(k_{dis}k_{rec}[F_NF_N])^{0.5}$. The time of achievement of the quasi-steady-state concentration of the $F_N^{\bullet}$ radicals (95%) is $t_{st} = 4\theta_. = 1 \cdot 10^{-3}$ s (the k_{dis} and k_{rec} values are taken from the literature[12,17]), *i.e.*, much shorter than the duration of the experiment.

The known kinetic scheme of ethylbenzene oxidation[14] includes the radical initiation *via* ROOH decomposition with the apparent rate constant found experimentally (Scheme 1). The published values of rate constants at 60 °C were used for chain propagation and termination. Calculation was performed for different inhibitors (a,b,c,d) differed by both the inhibition mechanism and rate constants of the reactions with radicals.

The 2-phenylindane-1,3-dion-2-yl ($F^{\bullet}$) radicals that formed do not react with the $RO_2^{\bullet}$ radicals, unlike the above considered 2-(*p*-dimethylaminophenyl)indane-1,3-dion-2-yl ($F_N^{\bullet}$) radicals.[20]

Scheme 1

Chain initiation

Hydrocarbons

Variant A: $ROOH \longrightarrow RO_2^{\bullet}$, $k = 1 \cdot 10^{-5}$ s^{-1}.

Variant B: $ROOH \longrightarrow RO^{\bullet}$, $k = 1 \cdot 10^{-5}$ s^{-1};

$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet}$, $k = 5 \cdot 10^5$ L (mol s)$^{-1}$;[13]

$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$, $k^* = 2 \cdot 10^9$ L (mol s)$^{-1}$;[1,13]

(since oxidation was conducted under a constant O_2 pressure, $[O_2]$ = const was included into the apparent rate constant $k = 2 \cdot 10^7$ s^{-1}).

Propagation

$RH + RO_2^{\bullet} \longrightarrow ROOH + R^{\bullet}$, $k = 2.4$ L (mol s)$^{-1}$;[14]

$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$, $k^* = 2 \cdot 10^7$ L (mol s)$^{-1}$.[1,13]

Chain termination

$RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow$ alcohol + ketone + O_2, $k = 9{,}5 \cdot 10^6$ L (mol s)$^{-1}$;[18]

$RO_2^{\bullet} + R^{\bullet} \longrightarrow ROOR$, $k = 6 \cdot 10^7$ L (mol s)$^{-1}$.[13]

Chain termination on inhibitors (F_NF_N, TP, ionol, FH)

$F_NF_N \longrightarrow F_N^{\bullet} + F_N^{\bullet}$, $k_{F_NF_N} = 0.9$ s^{-1};[12,17]

$F_N^{\bullet} + F_N^{\bullet} \longrightarrow F_NF_N$, $k_{F_NF_N} = 3 \cdot 10^8$ L (mol s)$^{-1}$;[17]

$F_N^{\bullet} + RO_2^{\bullet} \longrightarrow FOOR$, $k_{F_NF_N} = 3 \cdot 10^8$ L (mol s)$^{-1}$;[12]

$F_N^{\bullet} + RO^{\bullet} \longrightarrow FOR$, $k_{F_NF_N} = 3 \cdot 10^8$ L (mol s)$^{-1}$;[12]

$F_N^{\bullet} + R^{\bullet} \longrightarrow FR$, $k_{F_NF_N} = 3 \cdot 10^8$ L (mol s)$^{-1}$.[12]

Phenols

$RO_2^{\bullet} + PhOH \longrightarrow ROOH + PhO^{\bullet}$, $k_{TP} = 2 \cdot 10^6$;[18] $k_{ion} = 2 \cdot 10^4$ L (mol s)$^{-1}$;[19]

$RO_2^{\bullet} + PhO^{\bullet} \longrightarrow$ products, $k_{TP} = 3 \cdot 10^8$;[20] $k_{ion} = 6.6 \cdot 10^8$ L (mol s)$^{-1}$;[21]

$PhO^{\bullet} + PhO^{\bullet} \longrightarrow$ products, $k_{TP} = 3 \cdot 10^3$;[22] $k_{ion} = 1{,}5 \cdot 10^4$ L (mol s)$^{-1}$;[21]

$RO_2^{\bullet} + FH \longrightarrow ROOH + F^{\bullet}$, $k_{FH} = 2 \cdot 10^4$ L (mol s)$^{-1}$;[23]

$F^{\bullet} + F^{\bullet} \longrightarrow FF$, $k_{FH} = 3 \cdot 10^8$ L (mol s)$^{-1}$.[17]

α-Phenylethyl hydroperoxide is decomposed by CTAB in the initiation stage. Several mechanisms of ROOH decomposition effected by tetraalkylammonium bromides are described in the literature. For example, it was established[24] that when *tert*-butyl hydroperoxide decomposes in the presence of tetraethylammonium bromide (TEAB) in a solution of *n*-propanol, the bimolecular reaction between ROOH and the Br^- ion occurs with the rate constant $k = 4.0 \cdot 10^8 \cdot \exp(-81500/RT)$ L (mol s)$^{-1}$, which is $5.7 \cdot 10^{-5}$ L (mol s)$^{-1}$ at 60 °C

$$\mathrm{ROOH + Br^- \longrightarrow ROOH^{-} + Br^{\bullet} \longrightarrow}$$
$$\mathrm{\longrightarrow RO^{\bullet} + OH^- + Br^{\bullet}.}$$

The proposed[25] mechanism of tetralin hydroperoxide decomposition (110 °C) in the presence of tetraalkylammonium halides includes the intermediate formation of the adduct

$$\mathrm{ROOH + Q^+X^- \longrightarrow ROOH...X^-Q^+.}$$

The intermolecular hydrogen bond weakens the O—O bond in the adduct, which results in its homolytic cleavage followed by the transfer of one electron from the halide ion (Cl, Br, I) to the hydroxyl radical

$$\mathrm{ROOH...X^-Q^+ \longrightarrow RO^{\bullet} + Q^+OH^- + X^{\bullet}.}$$

According to the published data,[26] O_2 plays a substantial role in the mechanism of catalytic effect of CTAB in ethylbenzene oxidation. It is assumed that cationic CTAB facilitates the decomposition of ROOH in microaggregates at the ROO^-—H^+ bond, and the radicals are formed in the presence of O_2

$$\mathrm{ROOH + O_2 \longrightarrow RO_2^{\bullet} + O_2^{\bullet -} + H^+,}$$
$$\mathrm{O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet},}$$
$$\mathrm{HO_2^{\bullet}, RO_2^{\bullet} + RH, O_2 \longrightarrow RO_2^{\bullet},}$$
$$\mathrm{RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow alcohol + ketone + O_2.}$$

The authors[27—29] believe that the direct activation of O_2 occurs during the interaction with the surfactant cation. Other researchers[30,31] believe that the function of the ammonium cation is only the transporting of the Br^- ion, which is the real catalyst for ROOH decomposition.[24]

In computer simulation we considered two variants of radical formation at the initiation stage. In the case of $RO^{\bullet}$ formation (variant B), O_2 is absorbed during the induction period (for strong inhibitors F_NF_N and phenols) with the rate $W_i = k_{ef}[ROOH] = 1.8 \cdot 10^{-7}$ L (mol s)$^{-1}$ (Fig. 5, curve *4*). In fact, the primary $RO^{\bullet}$ radicals with high reactivity exchange at the initiation stage for the $R^{\bullet}$ radicals, which rapidly add O_2. In the case of $RO_2^{\bullet}$ formation (variant A), in the induction period (for F_NF_N and phenols) dioxygen is not absorbed (see Fig. 5, curves *5* and *6*).

It is seen from the experimental kinetic curves (see Figs. 1 and 2) that the F_NF_N and TP additives result in the complete retardation of oxidation and cessation of O_2 absorption in the induction period. This suggests that, regardless of the type of radicals ($RO^{\bullet}$, $OH^{\bullet}$, $RO_2^{\bullet}$) formed by ROOH decomposition, the $RO_2^{\bullet}$ radicals come into the oxidized ethylbenzene bulk. This agrees with the concept on the catalytic decomposition of ROOH in the ROOH—CTAB microaggregate-microreactors in which ROOH decomposition is facilitated and the radicals that formed exchange for $RO_2^{\bullet}$ in the microreactor cage

$$\left\{\begin{array}{l}\mathrm{ROOH + CTAB \longrightarrow RO^{\bullet}, OH^{\bullet} \xrightarrow{ROOH}} \\ \qquad \mathrm{\longrightarrow RO_2^{\bullet} + ROH\ (H_2O)}\end{array}\right\} \longrightarrow \mathrm{RO_2^{\bullet}.}$$

Calculations show that the kinetic curves of O_2 absorption for F_NF_N and TP (see Fig. 5, curves *5*, *6*) and ROOH consumption (see Fig. 5, curves *5′* and *6′*) almost coincide, despite different mechanisms of inhibition. Both inhibitors completely suppress the O_2 absorption and ROOH accumulation. ROOH is consumed in the induction period (see Fig. curves *5′* and *6′*). It is remarkable that the kinetic curves in the presence of F_NF_N and TP

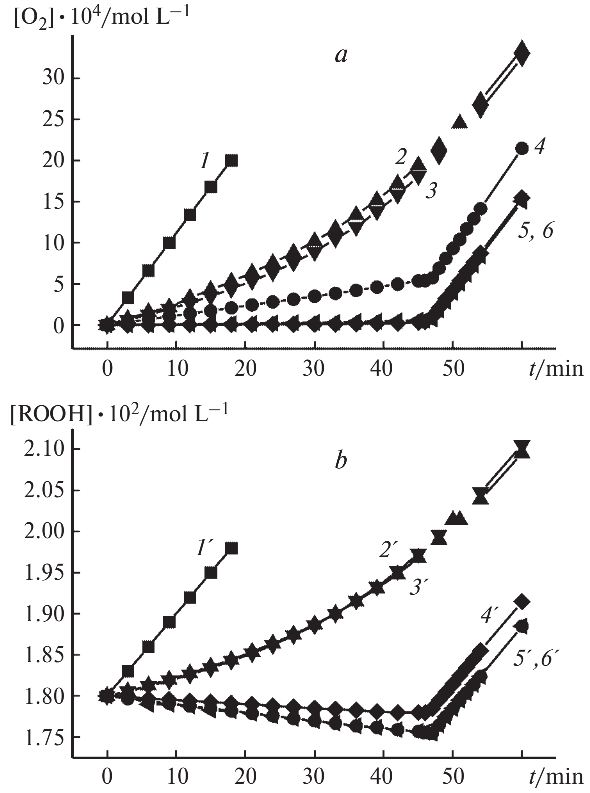

Fig. 5. Calculated kinetic curves for O_2 absorption (*a*) and accumulation—consumption of ROOH (*b*) obtained by the simulation of the kinetic scheme of ethylbenzene oxidation at 60 °C. The $RO_2^{\bullet}$ (curves *1*, *1′*, *2*, *2′*, *3*, *3′*, *5*, *5′*, *6*, and *6′*) and $RO^{\bullet}$ (curves *4* and *4′*) radicals are formed at the initiation stage. Concentration of the inhibitor/mol L^{-1}: *1*, *1′*, 0; *2*, *2′*, [FH] = $5 \cdot 10^{-4}$; *3*, *3′*, [ionol] = $2.5 \cdot 10^{-4}$; *4*, *4′*, $[F_NF_N] = 2.5 \cdot 10^{-4}$; *5*, *5′*, $[F_NF_N] = 2.5 \cdot 10^{-4}$; and *6*, *6′*, [TP] = $2.5 \cdot 10^{-4}$.

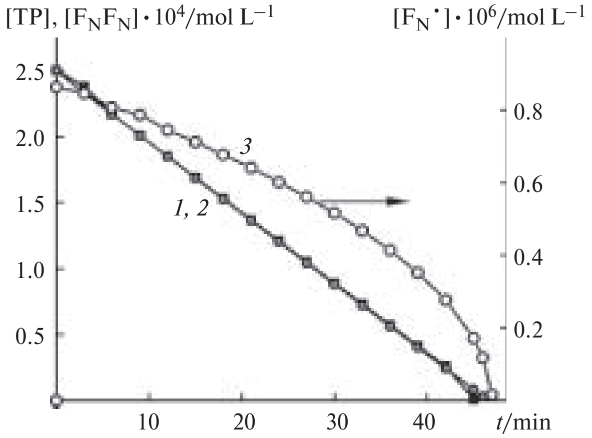

Fig. 6. Calculated kinetic curves for the consumption of the F_NF_N, $F_N{}^\bullet$ (*1*, *2*) and TP (*3*) inhibitors in the induction period from the data of simulation of the kinetic scheme of ethylbenzene oxidation at 60 °C.

virtually coincide in the induction period. The ROOH concentration decreases with the constant rate $W_i/2 = 0.9 \cdot 10^{-7}$ mol (L s)$^{-1}$ (Fig. 6). The $F_N{}^\bullet$ radicals are consumed with the constant rate $W_{cons} = 1.6 \cdot 10^{-10}$ mol (L s)$^{-1}$ only in the first half of the induction period (23 min), and then the rate of their consumption increases (see Fig. 6). The equilibrium constant ($K_{eq} = [F_N{}^\bullet]^2/[F_NF_N] = 2.9 \cdot 10^{-9}$ mol L^{-1}) retains its value to the almost complete disappearance of F_NF_N in the reaction system. The time of the dimer $\rightleftharpoons$ free radicals equilibration is $t_{st} = 5 \cdot 10^{-3}$ s. Owing to the fact that in the presence of F_NF_N in a hydrocarbon medium the equilibrium concentration of the $F_N{}^\bullet$ radicals, which react with the $RO_2{}^\bullet$, $RO^\bullet$, and $R^\bullet$ radicals with a high rate constant, is permanently maintained, the F_NF_N dimer is a strong inhibitor analogous to TP and convenient for measuring the rates of radical initiation by the inhibitor method with the constant stoichiometric coefficient of chain termination $f = 2$.

Weak inhibitors like ionol or 2-phenylindane-1,3-dione, which react with the $RO_2{}^\bullet$ radicals with low rate constants ($k = 2 \cdot 10^4$ L (mol s)$^{-1}$), are not suitable for measuring W_i. For example, in the presence of ionol ($2.5 \cdot 10^{-4}$ mol L^{-1}) and FH ($5 \cdot 10^{-4}$ mol L^{-1}), O_2 absorbs slowly (see Fig. 5, curves *2* and *3*) and ROOH is accumulated (see Fig. 5, curves *2´* and *3´*).

Thus, we established by calculations that the kinetic characteristics of the F_NF_N dimer (rate constants of dissociation (k_{dis}) and recombination (k_{rec}) of $F_N{}^\bullet$ radicals) and high reactivity of $F_N{}^\bullet$ radicals in chain termination (see Scheme 1), providing the efficient retardation of ethylbenzene oxidation, describe satisfactorily the experimental results.

The catalytic effect of CTAB on ethylbenzene oxidation is caused by the accelerated decomposition of ROOH in the surfactant microreactors with the escape of the $RO_2{}^\bullet$ radicals to the solvent bulk followed by the chain radical oxidation of ethylbenzene.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-32222).

References

1. N. M. Emanuel´, E. T. Denisov, and Z. K. Maizus, *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* [*Chain Reactions of Hydrocarbon Oxidation in Liquid Phase*], Nauka, Moscow, 1965, 375 pp. (in Russian).
2. T. V. Sirota and O. T. Kasaikina, *Neftekhimiya*, 1994, **34**, 467 [*Petroleum Chemistry*, 1994, **34** (Engl. Transl.)].
3. T. V. Sirota, N. M. Evteeva, and O. T. Kasaikina, *Neftekhimiya*, 1996, **36**, 169 [*Petroleum Chemistry*, 1996, **36** (Engl. Transl.)].
4. Z. S. Kartashova, T. V. Maksimova, E. V. Koverzanova, and O. T. Kasaikina, *Neftekhimiya*, 1997, **37**, 153 [*Petroleum Chemistry*, 1997, **37** (Engl. Transl.)].
5. Z. S. Kartasheva, T. V. Maksimova, T. V. Sirota, E. V. Koverzanova, and O. T. Kasaikina, *Neftekhimiya*, 1997, **37**, 249 [*Petroleum Chemistry*, 1997, **37** (Engl. Transl.)].
6. L. J. Csanyi and K. Jaky, *J. Mol. Cat. A*, *Chem.*, 1997, **120**, 125.
7. L. P. Panicheva, V. A. Turnaev, S. A. Yakovleva, and A. Ya. Yuffa, *Neftekhimiya*, 1994, **34**, 453 [*Petroleum Chemistry*, 1994, **34** (Engl. Transl.)].
8. *Organic Solvents. Physical Properties and Methods of Purification*, Ed. A. Weissberger, Interscience Publ., New York—London, 1955.
9. O. Ya. Neiland and G. Ya. Vanag, *Izv. Akad. Nauk LatvSSR*, *Ser. Khim.* [*Bulletin of Latvian Academy of Sciences*], 1963, 69 (in Russian).
10. G. Ya. Vanag, *Izv. Akad. Nauk LatvSSR* [*Bulletin of Latvian Academy of Sciences*], 1964, 210 (in Russian).
11. E. F. Brin and S. O. Travin, *Khim. Fizika*, 1991, **10**, 630 [*Chem. Phys.*, 1991, **10** (Engl. Transl.)].
12. A. B. Gagarina, L. M. Pisarenko, and N. M. Emanuel´, *Dokl. Akad. Nauk SSSR*, 1975, **221**, 640 [*Dokl. Chem.*, 1975 (Engl. Transl.)].
13. D. Gal, E. A. Blumberg, A. Ya. Valendo, and N. M. Emanuel, *Acta Chim. Acad. Sci. Hung.*, 1970, **66**, 55.
14. N. M. Emanuel´ and D. Gal, *Okislenie etilbenzola* [*Oxidation of Ethylbenzene*], Nauka, Moscow, 1984, 372 (in Russian).
15. O. T. Kasaikina, V. D. Kortenska, and Z. S. Kartasheva, *Colloids Surf. A*, *Physicochem. Eng. Aspects*, 1999, **149**, 29.
16. L. M. Pisarenko, V. I. Nikulin, and A. B. Gagarina, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1987, 1237 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **37**, 1086 (Engl. Transl.)].
17. L. M. Pisarenko, V. I. Nikulin, and I. V. Khudyakov, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1988, 1734 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **38**, 1544 (Engl. Transl.)].
18. N. G. Khrapova, E. B. Burlakova, E. N. Karpukhina, and E. B. Sinkina, *Neftekhimiya*, 1978, **18**, 724 [*Petroleum Chemistry*, 1978, **18** (Engl. Transl.)].

19. V. A. Belyakov, E. A. Shanina, V. A. Roginskii, and V. B. Miller, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1975, 2685 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **25**, No. 12 (Engl. Transl.)].
20. V. A. Roginskii, *Fenol´nye antioksidanty. Reaktsionnaya sposobnost´ i effektivnost´* [*Phenol Antioxidants. Reactivity and Efficiency*], Nauka, Moscow, 1988, 247 (in Russian).
21. A. A. Roginskii, *Khim. Fizika*, 1985, **4**, 1244 [*Chem. Phys.*, 1985, **4** (Engl. Transl.)].
22. G. W. Burton and E. J. Doba, *J. Am. Chem. Soc.*, 1985, **107**, 7053.
23. A. B. Gagarina, L. M. Pisarenko, V. V. Moiseev, and N. M. Emanuel´, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1975, 1041 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **25**, No. 5 (Engl. Transl.)].
24. E. T. Denisov, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1967, No. 6, 1608 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1967, **16**, No. 6 (Engl. Transl.)].
25. E. Napadensky and Y. Sasson, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 65.
26. T. A. Maksimova, *Ethylbenzene Oxidation in Microheterogeneous Systems Formed by Surfactant Additives*, Ph. D. (Chem.) Thesis, Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 2000, 125 pp. (in Russian).
27. K. Ohkubo and T. Yamabe, *Bull. Jpn. Petrol. Inst.*, 1970, **12**, 130.
28. K. Ohkubo and H. Kanaeda, *Bull. Jpn. Petrol. Inst.*, 1971, **13**, 177.
29. K. Ohkubo and K. Yoshinaga, *Bull. Jpn. Petrol. Inst.*, 1977, **19**, 73.
30. M. Harustik, M. Hronec, and J. Ilavki, *React. Kinet. Catal. Lett.*, 1988, **37**, 215.
31. M. Harustik, M. Hronec, and J. Ilavki, *J. Mol. Catal*, 1988, **48**, 335.

Received May 16, 2001;
in revised form October 16, 2001