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Features of α-phenylisopropyl hydroperoxide decomposition catalyzed by cetyltrimethylammonium bromide

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The features of cumene oxidation, α-phenylisopropyl hydroperoxide (ROOH) decomposition, and free radical formation in the presence of cetyltrimethylammonium bromide (CTAB) were studied by the kinetic methods and TLC product analysis. It was found that CTAB catalyzes ROOH decomposition to free radicals. The efficiency of an initiating system CTAB—ROOH is by a factor of 2.5 higher than that of a combination CTAB with α-phenylethyl hydroperoxide. In addition, CTAB catalyzes the reactions of ROOH with α-tocopherol and 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione]. The kinetic characteristics of these reactions were determined.

Key words: cetyltrimethylammonium bromide, 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione], α-tocopherol, cumene oxidation, α-phenylisopropyl hydroperoxide, catalysis, free radical initiation.

It has been shown previously[1,2] for ethylbenzene oxidation that the catalytic effect of cationic surfactant cetyltrimethylammonium bromide (CTAB) in liquid-phase oxidation is caused by the accelerated decomposition of hydroperoxide (ROOH) in reverse micelles (ROOH—CTAB) to form free radicals. Amphiphilic hydroperoxide favors the formation of combined microaggregates with CTAB in the hydrocarbon medium. The catalytic decomposition of the hydroperoxide occurs just in these microaggregates. The kinetic regularities of free radical formation during benzene oxidation initiated by a catalytic system α-phenylethyl hydroperoxide—CTAB were studied[3] by the inhibitor method using a 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione] dimer (F_NF_N) and α-tocopherol (TP) as free radical acceptors. It was found that CTAB affects only the rate of radical initiation (W_i) under the studied conditions. In this system, the rate of oxygen absorption (W_{O_2}) during ethylbenzene oxidation is described by the known equation for the rate of liquid-phase oxidation

$$W_{O_2} = k_p/(2k_t)^{0.5} \cdot [RH] \cdot (W_i)^{0.5}, \qquad (I)$$

where k_p and k_t are the rate constants of chain propagation and termination, respectively.

In this work, we studied the influence of CTAB on cumene oxidation and decomposition of α-phenylisopropyl hydroperoxide (ROOH) and the specifics of using the inhibitor method for measuring the rate of radical initiation by the CTAB—ROOH catalytic system.

Experimental

Cumene was oxidized in a chlorobenzene solution in a temperature-controlled reaction vessel equipped with a magnetic stirrer and a device for introducing different additives during the reaction. The vessel was connected to a gasometric system for monitoring the rate of O_2 absorption. Oxidation was carried out at 60 °C and a constant oxygen pressure P_{O_2} = 1 atm. A series of experiments was carried out in a glass temperature-controlled bubbling cells in an O_2 flow (1.6 L h^{-1}).

Cumene (RH) (Aldrich) and CTAB (Serva) were used as received. Chlorobenzene was purified by double distillation. α-Phenylisopropyl hydroperoxide (Aldrich) was mixed with an equal amount of diethyl ether, and the mixture was triply washed with a 1% solution of NaOH. The ethereal solution was thoroughly washed 4 times with distilled water. The washed-off solution was cooled to 0 °C to cause complete segregation of aqueous and ethereal layers, after which final separation was carried out. A 40% solution of NaOH was slowly added with stirring to a cooled ethereal solution of ROOH to precipitate ether-insoluble sodium salt of ROOH. The precipitate was triply washed with ether. Sodium salt of ROOH was dissolved in water with stirring, after which ether was added in an amount equal to the aqueous solution volume, and CO_2 was passed through the cooled mixture for 4 h with stirring. A solution of ROOH in ether was dried over calcined magnesium sulfate and filtered off. The ether was distilled off under reduced pressure to a constant weight.

An RH—CTAB—ROOH reaction mixture in chlorobenzene was magnetically stirred (stirring with an oxygen flow in a bubbling cell was used) at room temperature for 30 min. Then, the reactor was switched-on to a thermostat and a gasometric system.

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The concentration of ROOH was determined iodometrically at the beginning and end of each entry.

The rate of free radical formation (W_i) was determined by the inhibitor method. Free radical acceptors were F_NF_N and TP, which differ in structure and mechanism of their effect and have earlier[1,2] been tested successfully for ethylbenzene oxidation. After the steady-state rate of oxygen absorption (W_{O_2}) was established, a concentrated chlorobenzene solution of an inhibitor was injected with a microsyringe into the reaction mixture. The induction period (τ) was measured, and the rate of chain initiation was calculated by the formula[3]

$$W_i = f[\mathrm{InH}]_0/\tau, \qquad (2)$$

where f is the stoichiometric inhibition coefficient, and $[\mathrm{InH}]_0$ is the initial inhibitor concentration in the reaction mixture.

Changes in the electronic absorption spectra of 2-(*p*-dimethylaminophenyl)indane-1,3-dion-2-yl radicals ($F_N^{\bullet}$) were detected directly during experiment in a temperature-controlled quartz cell (l = 3 cm) of a Specord UV—Vis spectrophotometer. The products of the reaction of F_NF_N with radicals formed in the ROOH—CTAB system in chlorobenzene were separated by TLC on films Silicagel/TLC-card and DC-Alufolien-Kieselgel, 0.2 mm, 60 Å (Fluka) in EtOH followed by the extraction of zones separated with ethanol and subsequent recording their electronic spectra on an Ultrospec 1100 pro spectrophotometer.

Results and Discussion

The kinetic curves of oxygen absorption during cumene oxidation in a chlorobenzene solution initiated by the CTAB—ROOH catalytic system are presented in Fig. 1. As for the oxidation of ethylbenzene,[1] hydroperoxide and CTAB taken separately exert no effect on cumene oxidation. When CTAB and ROOH are introduced in combination, O_2 is absorbed. The addition of inhibitors (free radical acceptors) ceases O_2 absorption during the induction period, after the end of which O_2 begins to absorb with a rate of the non-inhibited process. A comparison of the ROOH concentrations at the onset and end of experiment (~70 min) shows that cumene is oxidized almost selectively to hydroperoxide according to the equation

$$[\mathrm{ROOH}](t) = [\mathrm{ROOH}]_0 + \Delta O_2(t). \qquad (3)$$

The plot of the rate of O_2 absorption *vs.* ROOH concentration at a constant CTAB concentration is shown in Fig. 2. It is seen that a linear relation $W_{O_2} \sim [\mathrm{ROOH}]^{0.5}$ obeys in the studied concentration region $[\mathrm{ROOH}] \le 5 \cdot 10^{-2}$ mol L^{-1}. The relation shows that the rate of radical initiation can be presented by the equation

$$W_i = k_{\mathrm{eff}}[\mathrm{ROOH}]. \qquad (4)$$

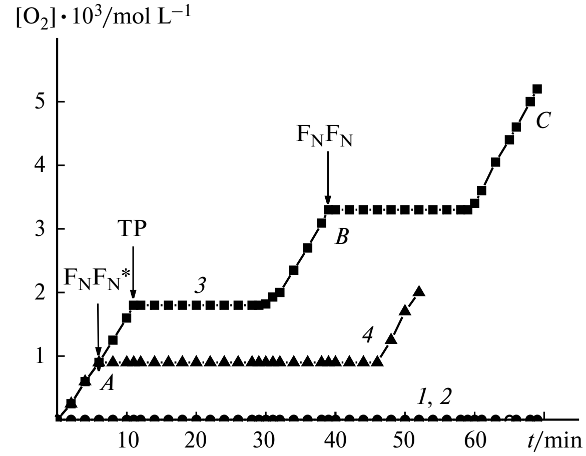

Fig. 1. Kinetic curves of O_2 absorption for cumene oxidation (1.8 mol L^{-1}) in a chlorobenzene solution at 60 °C (arrows indicate the moments of introduction of inhibitor additives). Concentrations of reactants/mol L^{-1}: *1*, [ROOH] = $3.0 \cdot 10^{-2}$ in the absence of CTAB; *2*, [CTAB] = $1.1 \cdot 10^{-3}$ in the absence of ROOH; *3*, [ROOH] = $2.9 \cdot 10^{-2}$ and [CTAB] = $1.1 \cdot 10^{-3}$; *4*, [AIBN] = $4 \cdot 10^{-2}$, [ROOH] = $3 \cdot 10^{-2}$, $[F_NF_N{*}] = 5.3 \cdot 10^{-4}$ (induction period 40 min). Rate of oxygen absorption W_{O_2}/mol L^{-1} s^{-1}: $2.6 \cdot 10^{-6}$ (region *A*), $3 \cdot 10^{-6}$ (region *B*), $3.3 \cdot 10^{-6}$ (region *C*). Concentrations of inhibitors InH/mol L^{-1} (induction period, τ/min): first introduction, [TP] = $4.5 \cdot 10^{-4}$ (20); second introduction, $[F_NF_N] = 5.3 \cdot 10^{-4}$ (22).

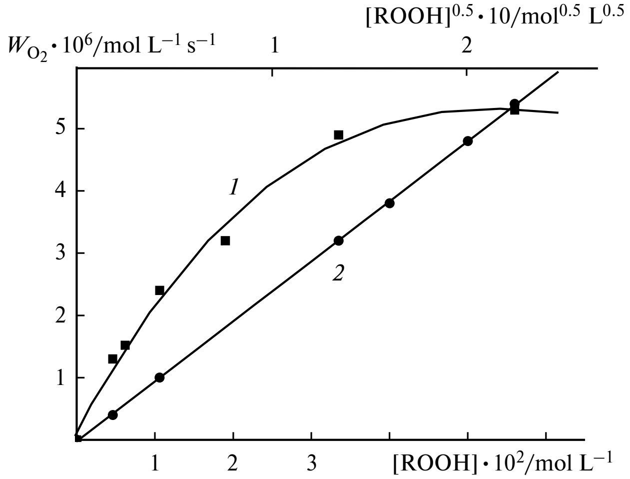

Fig. 2. Rate of oxygen absorption W_{O_2}/mol L^{-1} s^{-1} *vs.* hydroperoxide concentration [ROOH] (*1*) and $[\mathrm{ROOH}]^{0.5}$ (*2*) for cumene oxidation in a chlorobenzene solution at 60 °C, [RH] = 1.8 mol L^{-1} and [CTAB] = $1.1 \cdot 10^{-3}$ mol L^{-1}.

Table 1 contains the experimental $W_{O_2}^{\mathrm{exp}}$ values and the W_i values determined by the inhibitor method and calculated using the equation for the rate of liquid-phase hydrocarbon oxidation with quadratic chain termination (1) from the experimental $W_{O_2}^{\mathrm{exp}}$ and known values of the $k_p/(2k_t)^{0.5}$ parameter by the formula

$$W_i = \{W_{O_2}^{\mathrm{exp}}/[\mathrm{RH}] \cdot k_p/(2k_t)^{0.5}\}^2. \qquad (5)$$

According to published data,[3,4] for cumene at 60 °C, $k_p/(2k_t)^{0.5} = 2.6 \cdot 10^{-3}$ L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$. We obtained the

Table 1. Kinetic characteristics of oxidation of cumene (1.8 mol L^{-1}) initiated by a CTAB—ROOH system with additives of inhibitors (60 °C)

Entry	[CTAB]·10^3	[ROOH]$_0$·10^2	([ROOH]$_0$ + ΔO$_2$)^a·10^2	$W_{O_2}{}^{exp}$·10^6 /mol L^{-1} s^{-1}	[InH]·10^4 /mol L^{-1}	τ /min	W_i·10^7/mol L^{-1} s^{-1}	
	mol L^{-1}						Inhibition method	With respect to W_{O_2}
1^b	1.00	2.00	2.10	1.90	3.00^c	20	5.00	1.64
	—	—	2.20	2.05	6.00^c	25	8.00	1.90
	—	—	2.30	2.10	9.00^c	29	10.00	2.00
2	1.08	1.70	2.40	2.40	2.20^d	20	3.70	2.70
3^b	1.10	2.90	3.19	2.60	4.50^c	20	7.50	3.00
	—	—	3.30	3.00	5.30^d	22	8.00	4.00
4^e	1.00	1.60	3.35	3.10	21.5^d	40	17.90	4.30
5	1.20	2.90	3.16	3.05	5.00^c	20	8.30	4.20
6	1.25	2.35	2.56	3.00	4.50^c	19	7.90	3.20
7	1.33	1.65	1.93	2.50	1.10^d	11	3.00	2.40
8	0.50	2.20	2.35	1.30	1.10^d	18	2.00	0.80

^{a} At the moment of inhibitor introduction.

^{b} The inhibitor was introduced several times without interruption of oxidation (similarly to Fig. 1).

^{c} The inhibitor is α-tocopherol.

^{d} The inibitor is F_NF_N.

^{e} Measured from hydroperoxide accumulation in a bubbling cell, $W_{O_2}{}^{exp} = W_{ROOH}$.

same $k_p/(2k_t)^{0.5}$ value from the data on the rate of O$_2$ absorption for the AIBN-initiated oxidation of cumene.

As can be seen from the data in Table 1, the W_i values calculated from the induction periods are higher than those obtained using formula (5). The higher are the concentrations of inhibitors TP and F_NF_N, the greater are the differences. The accelerated inhibitor consumption means that other routes of inhibitor consumption occur along with the reactions with radicals that initiate cumene oxidation. All experimental data on the consumption of TP and F_NF_N at an unchanged CTAB concentration (Fig. 3) can be linearized in the coordinates W_{InH}/[ROOH]—[InH], where W_{InH} = [InH]$_0$/τ is the average rate of inhibitor consumption in the induction period. This implies that the rate of TP and F_NF_N consumption is described by the known[3,5—7] equation

$$-\mathrm{d}[\mathrm{InH}]/\mathrm{d}t = W_i/f + k_{\mathrm{eff}}{}^{\mathrm{InH}}[\mathrm{InH}][\mathrm{ROOH}]. \qquad (6)$$

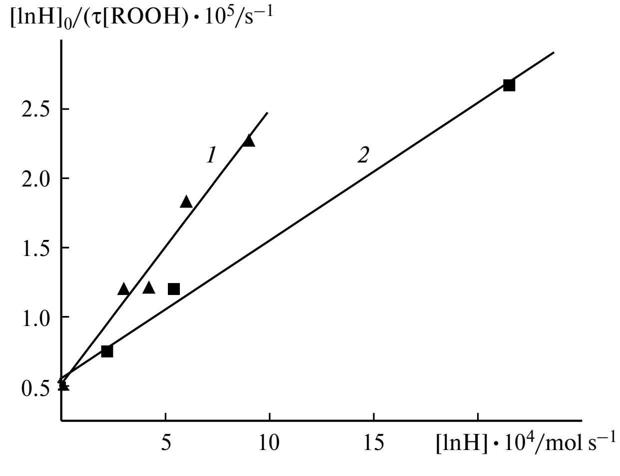

Fig. 3. Plot of [InH]$_0$/(τ·[ROOH]) *vs.* [InH] at [CTAB] = (1.05±0.05)·10^{-3} mol L^{-1} and TP (*1*) and F_NF_N (*2*) used as inhibitors (see Table 1).

Equation (6) characterizes the consumption of an inhibitor that interacts directly with hydroperoxide. The first term of this equation proportional to [ROOH] (see Eq. (4)) takes into account the inhibitor consumption in the reaction with radicals formed upon ROOH decomposition catalyzed by CTAB; f is the stoichiometric inhibition coefficient, for both inhibitors f = 2. The second term of Eq. (6) takes into account an additional consumption of the inhibitor in the reaction of InH with ROOH. When CTAB is absent, the rate of inhibitor consumption is described by Eq. (2) despite the presence of hydroperoxides in cumene (*cf.* Fig. 1, curve *4*). Hence, the inhibitors are assumed to react with the CTAB-activated ROOH. The apparent rate constants of the reaction of InH with ROOH were found from the slope of the linear plots in Fig. 3: $k_{app}{}^{TP}$ and $k_{app}{}^{F_NF_N}$ are 2.1·10^{-2} and 1.1·10^{-2} L mol^{-1} s^{-1}, respectively. In other words, TP is oxidized by activated ROOH almost twofold more actively than the F_NF_N.

The section cut in the ordinate at [InH] → 0 is equal to the halved apparent rate constant of ROOH decomposition to free radicals k_{app} = (1.01±0.09)·10^{-5} s^{-1}. With allowance for this k_{app} value, the initiation rate can be calculated by Eq. (4). For instance, W_i = 1.0·10^{-5}×2·10^{-2} = 2.0·10^{-7} mol L^{-1} s^{-1}, which is close to W_i calculated from the experimentally determined oxygen absorption rate for the same concentrations of the reactants (CTAB and ROOH) by Eq. (5) (see Table 1).

The apparent rate constant of ROOH decomposition to free radicals in the presence of CTAB 10^4-fold exceeds the rate constant of ROOH decomposition in cumene in the absence of CTAB: according to published data,[8] $k_{\rm ROOH} = 5 \cdot 10^7 \exp[-26000/(RT)]$ L mol^{-1} s^{-1}, *i.e.*, at 60 °C $k_{\rm ROOH}[\rm RH] = 2.7 \cdot 10^{-9}$ s^{-1} even in neat cumene. A comparison of the determined kinetic parameters of the CTAB-catalyzed decomposition of ROOH with the earlier obtained results for ethylbenzene hydroperoxide (EHP) under similar conditions[2] shows that (1) the apparent rate constant of EHP decomposition catalyzed by 1 m*M* CTAB ($k_{\rm app}' = 0.4 \cdot 10^{-2}$ L mol^{-1} s^{-1}) is 2.5-fold lower than $k_{\rm app}$ for ROOH under similar conditions; (2) the EHP—CTAB system exhibits no consumption of the inhibitors TP and $\rm F_NF_N$ in other reactions except for the reaction with free radicals, *i.e.*, $k_{\rm app}{}^{\rm TP}$ and $k_{\rm app}{}^{\rm F_NF_N}$ are zero.

Phenol-derived inhibitors are known[6,9] to be oxidized with peroxides.

$$\rm PhOH + ROOH \longrightarrow PhO^{\bullet} + H_2O + RO^{\bullet}$$

In particular, *p*-methoxyphenol (MP) reacts with ROOH in a chlorobenzene solution with the rate constant $k_{\rm MP/ROOH} = 8.9 \cdot 10^9 \exp[-23300/(RT)]$ L mol^{-1} s^{-1}, *i.e.*, at 60 °C $k_{\rm MP/ROOH} = 4 \cdot 10^{-6}$ L mol^{-1} s^{-1}.[9] At the same time, in the case of *tert*-butyl hydroperoxide (THP), $k_{\rm MP/THP} = 8.1 \cdot 10^{-8}$ L mol^{-1} s^{-1} at 60 °C. For the TP—THP pair, $k_{\rm TP/THP} = 1.6 \cdot 10^8 \exp[-21220/(RT)]$ L mol^{-1} s^{-1}, *i.e.*, $k_{\rm TP/THP} = 1.7 \cdot 10^{-6}$ L mol^{-1} s^{-1} (see Ref. 6) at 60 °C. Assuming that the rate constant of the reaction of ROOH with TP is by two orders of magnitude higher than $k_{\rm TP/THP}$, we have that $k_{\rm TP/ROOH} \approx 2 \cdot 10^{-4}$ L mol^{-1} s^{-1} at 60 °C. This value is substantially lower than $k_{\rm app}{}^{\rm TP} = 2.1 \cdot 10^{-2}$ L mol^{-1} s^{-1}, which was found for the reaction of TP with ROOH in the presence of 1 mmol CTAB. In other words, 1 mmole of CTAB almost 100-fold accelerates the reaction of ROOH with TP. The activity of CTAB is retained when new portions of TP are added to the reaction mixture (see Table 1, entry *1*), which makes it possible to consider CTAB as a catalyst of the reaction of TP with ROOH.

Data on the kinetics and mechanism of the reactions of $\rm F_NF_N$ with hydroperoxides are virtually lacking. Therefore, the reaction of $\rm F_NF_N$ with ROOH in the absence and presence of CTAB was studied in more detail. As turned out, when $\rm F_NF_N$ (3 mmol) was stored with ROOH (20 mmol) at 60 °C in a chlorobenzene solution for several hours, the concentrations of the reactants remained almost unchanged. In the presence of CTAB, an accelerated consumption of both reagents was observed (Fig. 4), *i.e.*, CTAB can be considered also as the catalyst of the reaction of ROOH with $\rm F_NF_N$.

The $\rm F_NF_N$ dimer in solution dissosiates reversibly to two radicals $\rm F_N{}^{\bullet}$

$$\rm F_NF_N \rightleftharpoons 2\,F_N{}^{\bullet}. \qquad (7)$$

The equilibrium constant of this reaction in a benzene solution at 60 °C is $K_{\rm FNFN} = 2.3 \cdot 10^{-8}$ mol s^{-1}.[10] The steady-state concentration of $\rm F_N{}^{\bullet}$ is established within fractions of second.[1,11] The $\rm F_N{}^{\bullet}$ radicals, which are equilibrated with $\rm F_NF_N$, react rapidly ($k_{{\rm FNR}i} = 3 \cdot 10^8$ L mol^{-1} s^{-1})[11,12] with alkyl, peroxy, and other radicals, providing efficient chain termination in hydrocarbon oxidation[11]

$$\rm F_N{}^{\bullet} + R^{\bullet}\ (RO_2{}^{\bullet}) \longrightarrow Products.$$

The electronic absorption spectra of the $\rm F_N{}^{\bullet}$ radicals in the visible region are characterized by high molar absorption coefficients (benzene): $\varepsilon = 1.66 \cdot 10^4$ (430 nm), $1.1 \cdot 10^4$ (650 nm), and $1.41 \cdot 10^4$ L mol^{-1} cm^{-1} (704 nm).[10] In solvents of different polarity (from benzene to acetonitrile), these bands exhibit[13] only a bathochromic shift, while the molar absorption coefficients remain unchanged. The presence of an intense absorption band in the long-wave region makes it possible to monitor the kinetics of $\rm F_N{}^{\bullet}$ consumption in complex systems, because the region at $\lambda = 650$—800 nm is transparent for almost all hydrocarbons.

The absorption spectra of the ROOH—CTAB—$\rm F_NF_N$ reaction mixture at different moments after mixing of the reactants are presented in Fig. 4, *a*. The reaction was carried out in a chlorobenzene solution in which the absorption spectrum of the $\rm F_N{}^{\bullet}$ radicals have maxima at $\lambda_{\rm max} = 666$ ($\varepsilon = 1.1 \cdot 10^4$ L mol^{-1} cm^{-1}) and 724 nm ($\varepsilon = 1.41 \cdot 10^4$ L mol^{-1} cm^{-1}). Immediately after the reactants were mixed, the concentration of the $\rm F_N{}^{\bullet}$ radicals became $2.4 \cdot 10^{-5}$ mol L^{-1}. This enables us to determine the equilibrium concentration in chlorobenzene: $K_{\rm e} = [\rm F_N{}^{\bullet}]^2/[F_NF_N] = 5.3 \cdot 10^{-8}$ mol L^{-1}. This value exceeds $K_{\rm e}$ in benzene by a factor of 2.5. Most likely, an increase in the solvent polarity increases $K_{\rm e}$, because in more polar acetonitrile $K_{\rm e}$ is higher ($16.6 \cdot 10^{-8}$ mol L^{-1} at 60 °C).[13]

Separately taken ROOH and CTAB have no effect on the equilibrium concentration of the $\rm F_N{}^{\bullet}$ radicals. When ROOH and CTAB are present in combination, the absorbance of the $\rm F_N{}^{\bullet}$ radicals decreases down to their complete consumption for 100 min. As can be seen from the data in Fig. 4, *c* (curve *1*), an accelerated consumption of ROOH occurs in the presence of $\rm F_NF_N$, and after the complete consumption of $\rm F_N{}^{\bullet}$ and, hence, $\rm F_NF_N$ the rate of ROOH consumption decreases and becomes equal to the rate of its consumption in the absence of $\rm F_NF_N$.

A comparison of the rates of $\rm F_NF_N$ and ROOH consumption suggests the following.

(1) Rate of ROOH consumption in the absence of $\rm F_NF_N$ is equal to $W_{\rm ROOH} = 4.7 \cdot 10^{-7}$ mol L^{-1} s^{-1}, and the

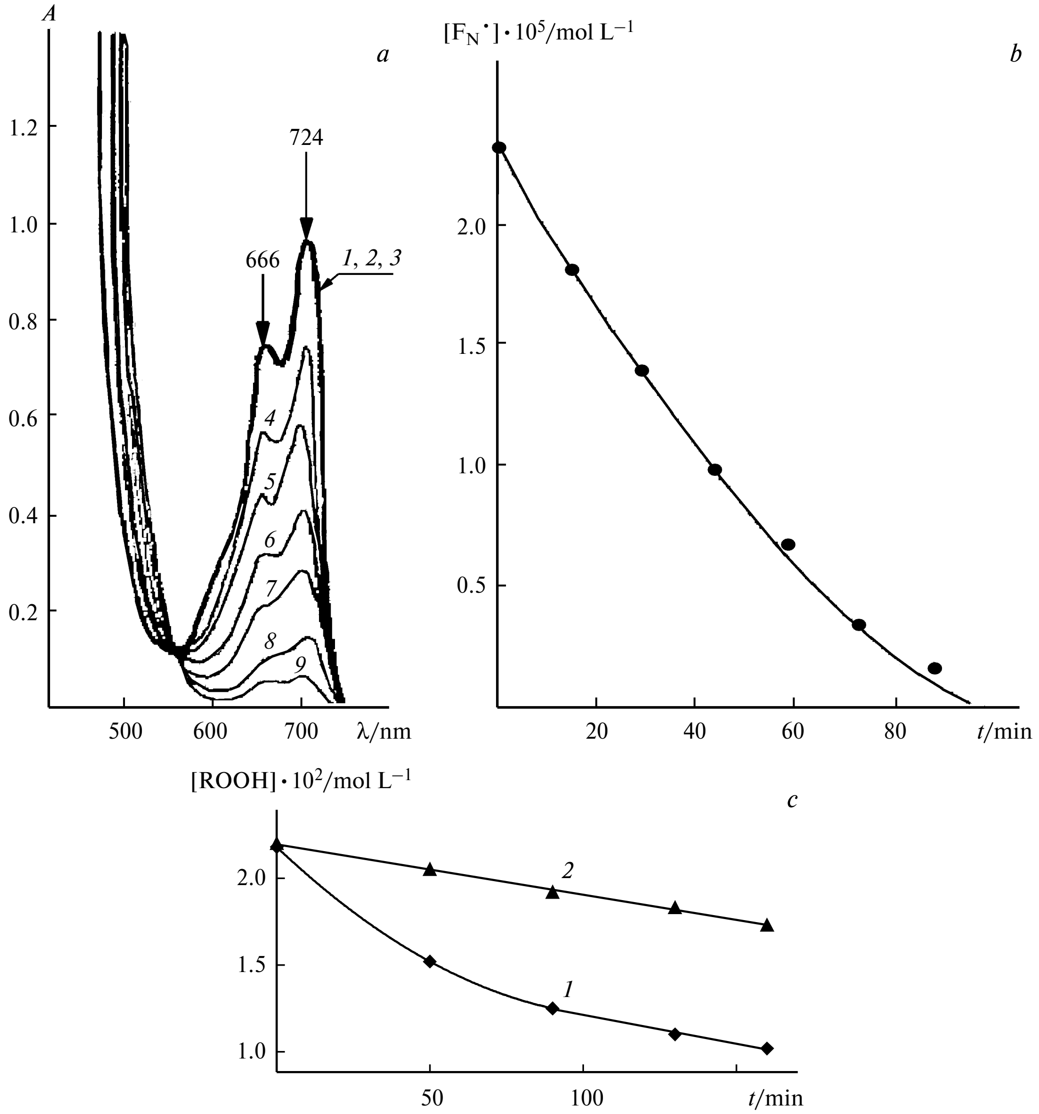

Fig. 4. Electronic absorption spectra of radicals $F_N{}^•$ (*a*) and the kinetics of $F_N{}^•$ consumption (*b*) in a reaction mixture F_NF_N ($1 \cdot 10^{-2}$ mol L^{-1})—ROOH ($2.2 \cdot 10^{-2}$ mol L^{-1})—CTAB ($1.6 \cdot 10^{-3}$ mol L^{-1}) in chlorobenzene at 60 °C. *a*. Absorption spectra of solutions of F_NF_N (*1*), F_NF_N—CTAB (*2*), and F_NF_N—CTAB—ROOH (*3—9*) in 0 (*3*), 15 (*4*), 30 (*5*), 45 (*6*), 60 (*7*), 75 (*8*), and 90 min (*9*) after mixing. *c*. Kinetic curves of ROOH decomposition in a mixture F_NF_N ($1 \cdot 10^{-2}$ mol L^{-1})—ROOH ($2.2 \cdot 10^{-2}$ mol L^{-1})—CTAB ($1.6 \cdot 10^{-3}$ mol L^{-1}) (*1*) and in a mixture ROOH ($2.2 \cdot 10^{-2}$ mol L^{-1})—CTAB ($1.6 \cdot 10^{-3}$ mol L^{-1}) (*2*).

rate of radical initiation at specified concentrations of ROOH and CTAB calculated from relation (4) is equal to $W_i = 3.8 \cdot 10^{-7}$ mol L^{-1} s^{-1}. It follows from the ratio $W_i/W_{ROOH} = 0.8$ that the yield of radicals upon the CTAB-catalyzed decomposition of ROOH is 0.8.

(2) Average rates of consumption of F_NF_N and ROOH in the F_NF_N—ROOH—CTAB system are almost $1.7 \cdot 10^{-6}$ mol L^{-1} s^{-1}. This implies that F_NF_N and ROOH react in a stoichiometric ratio of 1 : 1, and F_NF_N is mainly consumed in the direct interaction with ROOH activated by CTAB.

Analysis of an ROOH—CTAB—F_NF_N reaction mixture by TLC after F_NF_N was consumed showed at least four colored products, whose optical spectra are shown in Fig. 5. The spectra are characterized by absorption maxima in the UV region at λ_{max} = 259—263 nm (absorption region of the F_NF_N dimer) and in the visible region at $\lambda_{max} \approx$ 300—353 nm. These data indicate the formation of at least four products F_NX, where F_N is a half of the F_NF_N dimer, and X is the radical formed upon ROOH decomposition. The presence of several F_N—X adducts is likely related to specific features of ROOH decomposition, namely, to the induced decomposition characteristic of tertiary hydroperoxides[3] and participation of several types of radicals in the chain process.[14,15].

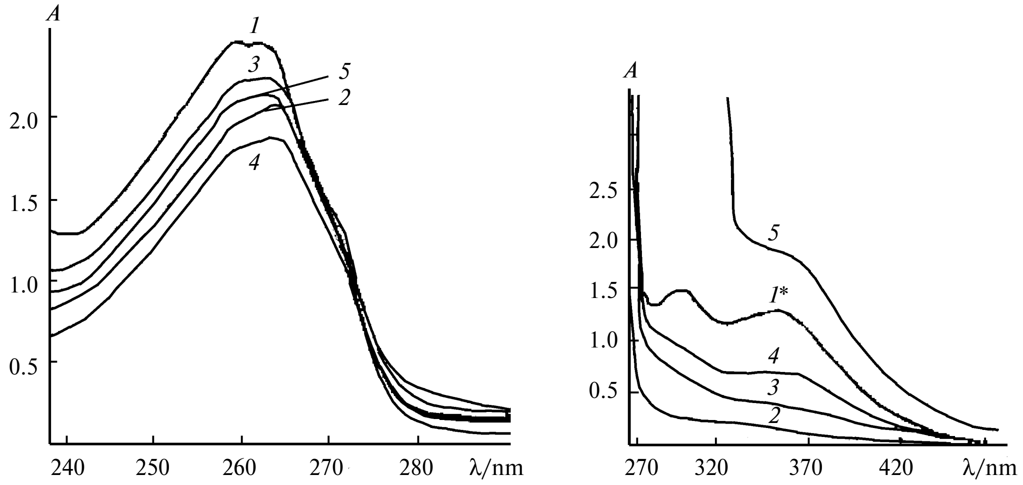

Fig. 5. Electronic absorption spectra of dimer F_NF_N (*1*, *1**) and colored reaction products (*2*—*5*) formed in a mixture F_NF_N—ROOH—CTAB in chlorobenzene at 60 °C after they were separated by TLC at $[F_NF_N] = 1.3 \cdot 10^{-5}$ (*1*) and $1.3 \cdot 10^{-4}$ mol L^{-1} (*1**) (EtOH, l = 1 cm); *2*, $R_f = 0.30$ (crimson-colored narrow band); *3*, $R_f = 0.56$ (green broad band); *4*, $R_f = 0.64$ (yellow broad band); *5*, $R_f = 0.70$ (red—orange band).

The induced decomposition of ROOH is known[3] to proceed *via* Scheme 1.

Scheme 1

$$ROOH \longrightarrow RO^\bullet + {}^\bullet OH$$

$$RO^\bullet + ROOH \longrightarrow RO_2^\bullet + DPC$$

$$ROOH + {}^\bullet OH \longrightarrow RO_2^\bullet + H_2O$$

$$RO^\bullet \longrightarrow {}^\bullet CH_3 + AP$$

$$\begin{tikzcd}
RO_2^\bullet + RO_2^\bullet \arrow[r] & {[ROOOOR]} \arrow[r] \arrow[d] & ROOR + O_2 \\
 & 2\,RO^\bullet + O_2 &
\end{tikzcd}$$

$${}^\bullet CH_3 + O_2 \longrightarrow CH_3OO^\bullet$$

$$CH_3OO^\bullet + ROOH \longrightarrow CH_3OOH + RO_2^\bullet$$

$$CH_3OO^\bullet + CH_3OO^\bullet \longrightarrow CH_3OH + CH_2O + O_2$$

$$CH_3OO^\bullet + RO_2^\bullet \longrightarrow CH_2O + DPC + O_2$$

DPC is dimethylphenylcarbinol, AP is acetophenone

The highly reactive $F_N^\bullet$ radicals provide accepting of radicals of different types: F_NO_2R, F_NOR, F_NCH_3, and $F_NO_2CH_3$.

The earlier[3] analysis of the kinetics of O_2 absorption during ethylbenzene oxidation initiated by a CTAB—EHP system suggested that the observed complete inhibition of O_2 absorption in the induction period (see Fig. 1) indicates that these are the $RO_2^\bullet$ radicals rather than $RO^\bullet$, which are formed by EHP decomposition, that escape from microaggregates {CTAB...ROOH} into the hydrocarbon volume. Otherwise, the experimentally detected O_2 absorption with the rate of radical initiation would be observed in the induction period. Several F_N—X adducts found during the CTAB-catalyzed decomposition of ROOH in a chlorobenzene solution indicates that F_NF_N is additionally consumed in the interaction with ROOH directly in a microaggregate, where ROOH are activated in a strong electrostatic field of an ionogenic surfactant micelle.

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References

1. L. M. Pisarenko and O. T. Kasaikina, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 419 [*Russ. Chem. Bull.*, *Int. Ed.*, 2002, **51**, 449].
2. L. M. Pisarenko, T. V. Maksimova, Z. S. Kartasheva, and O. T. Kasaikina, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 1419 [*Russ. Chem. Bull.*, *Int. Ed.*, 2003, **52**, 1500].
3. N. M. Emanuel′, E. T. Denisov, and Z. K. Maizus, *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* [*Chain Reactions of Hydrocarbon Oxidation in the Liquid Phase*], Nauka, Moscow, 1965, 375 pp. (in Russian).
4. H. W. Melville and S. Richards, *J. Chem. Soc.*, 1954, 944.

5. V. A. Roginskii, *Fenol´nye antioksidanty. Reaktsionnaya sposobnost´ i effektivnost´* [*Phenol Antioxidants. Reactivity and Efficiency*], Nauka, Moscow, 1988, 247 pp. (in Russian).
6. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants. Bond Dissociation Energies, Rate Constants, Activation Energies and Enthalpies of Reactions*, CRC Press, Boca Raton, Florida, 2000, 289 pp.
7. E. T. Denisov, T. G. Denisova, and T. S. Pokidova, *Handbook of Free Radical Initiators*, J. Wiley and Sons, Chichester—New York—Weinheim—Brisbane—Singapure—Toronto, 2003, 793 pp.
8. V. L. Antonovskii, E. T. Denisov, and L. V. Solntseva, *Kinet. Katal.*, 1965, **6**, 815 [*Kinet. Catal.*, 1965, **6** (Engl. Transl.)].
9. V. S. Martem´yanov, E. T. Denisov, and L. A. Samoilov, *Izv. Akad. Nauk*, *Ser. Khim.*, 1972, 1039 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, **21**, 994 (Engl. Transl.)].
10. L. M. Pisarenko, V. I. Nikulin, and A. B. Gagarina, *Izv. Akad. Nauk*, *Ser. Khim.*, 1988, 1734 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37** (Engl. Transl.)].
11. A. B. Gagarina, L. M. Pisarenko, and N. M. Emanuel´, *Dokl. Akad. Nauk SSSR*, 1975, **221**, 640 [*Dokl. Chem.*, 1975 (Engl. Transl.)].
12. L. M. Pisarenko, V. I. Nikulin, and I. V. Khudyakov, *Izv. Akad. Nauk*, *Ser. Khim.*, 1988, 1734 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **38**, 1544 (Engl. Transl.)].
13. L. M. Pisarenko, V. I. Nikulin, M. P. Blagorazumov, O. Ya. Neiland, and L. L. Paulinsh, *Izv. Akad. Nauk*, *Ser. Khim.*, 1990, 1525 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39** (Engl. Transl.)].
14. D. G. Hendry, *J. Am. Chem. Soc.*, 1967, **89**, 5433.
15. V. L. Antonovskii and S. L. Khursan, *Fizicheskaya khimiya organicheskikh peroksidov* [*Physical Chemistry of Organic Peroxides*], IKTs Akademkniga, Moscow, 2003, 391 pp. (in Russian).

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