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Temperature effect on the rate of formation of free radicals in CTAB-catalyzed decomposition of hydroperoxides

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The temperature effect on the rate of the decomposition of hydroperoxides and the rate of the formation of free radicals in the oxidation of ethylbenzene with molecular oxygen in the presence of α-phenylethyl hydroperoxide—cetyltrimethylammonium bromide (CTAB) as a catalytic system for free radical generation was studied by kinetic methods (from the oxygen consumption and hydroperoxide decomposition rates) and the inhibition method involving different acceptors of free radicals.

Key words: cetyltrimethylammonium bromide, 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione], 4-methyl-2-spirocyclohexyl-[3,4:3´,2´]-tetrahydrofurano-1,2,3,4-tetrahydroquinolin-1-oxyl, oxidation of ethylbenzene, α-phenylethyl hydroperoxide, catalysis of hydroperoxide decomposition, energy of activation.

The catalytic effect of cationic amphiphilic surfactants, particularly cetyltrimethylammonium bromide (CTAB), in free-radical oxidation is due to the accelerated decomposition of hydroperoxide ROOH into free radicals in mixed microaggregates of the inverted micelle type (ROOH—CTAB).[1—5] Earlier,[5] the kinetics of free radical generation in ethylbenzene oxidation with molecular oxygen at 60 °C in the presence of α-phenylethyl hydroperoxide (ROOH)—CTAB as a catalytic system was studied by the inhibition method using dimeric 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione] as a free radical acceptor. It was found[6,7] that under experimental conditions, CTAB affects only the radical initiation rate (W_i). The oxygen consumption rate during ethylbenzene oxidation in this system (W_{O_2}) is described by the known equation for the liquid-phase oxidation rate:

$$W_{O_2} = k_p/(2k_t)^{0.5}[RH](W_i)^{0.5}, \qquad (1)$$

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

In the present work, the temperature effects on the oxygen consumption and radical initiation rates were studied for oxidation of ethylbenzene in the presence of hydroperoxide and CTAB. In addition, we verified the validity of equation (1) at different temperatures and compared data for the temperature effects on the radical initiation and hydroperoxide decomposition rates in microaggregates formed by CTAB.

Experimental

Reagents and reaction mixtures were prepared and experiments and measurements were carried out as described earlier.[2,5] Ethylbenzene oxidation was carried out in a temperature-controlled reaction vessel with a magnetic stirrer and a gas volumeter for monitoring the oxygen consumption rate. In experiments of hydroperoxide decomposition, a flow reactor was used. Free radical acceptors were the earlier successfully used dimeric 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione] (**1**)[5] and a stable nitroxyl radical, namely, 4-(spirotetrahydrofuran-2´-yl)-2-spirocyclohexyl-1,2,3,4-tetrahydroquinolin-1-oxyl (**2**) synthesized according to a known procedure.[8] This nitroxyl radical is a specific trap for peroxyl radicals since their spin adducts, quinone nitrones, show a characteristic absorption band in the visible spectrum.[9] Electronic absorption spectra of the nitroxyl radical and quinone nitrone were recorded on an Ultrospec 1100 pro spectrophotometer.

Results and Discussion

Typical kinetic curves for oxygen consumption during ethylbenzene oxidation initiated by the catalytic ROOH—CTAB system are shown in Fig. 1 for different temperatures. It can be seen that at equal initial concentrations of the reagents, the oxygen consumption rate increases with temperature. Addition of inhibitor **1** interrupts the oxygen consumption, but then its rate returns to the original level. In all experiments (Table 1),[5] the

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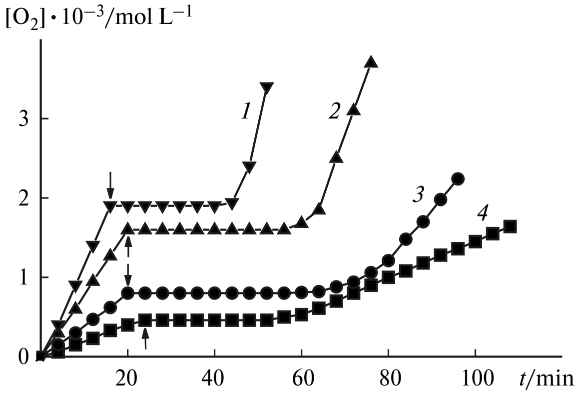

Fig. 1. Kinetic curves for oxygen consumption in the oxidation of ethylbenzene containing ROOH ($1.26\cdot10^{-2}$ mol L^{-1}) and CTAB ($1.2\cdot10^{-3}$ mol L^{-1}) at (*1*) 80 °C ($[\mathbf{1}] = 3.0\cdot10^{-4}$ mol L^{-1}, $\tau_{ind} = 23$ min), (*2*) 70 °C ($[\mathbf{1}] = 1.7\cdot10^{-4}$ mol L^{-1}, $\tau_{ind} = 41$ min), (*3*) 60 °C ($[\mathbf{1}] = 1.1\cdot10^{-4}$ mol L^{-1}, $\tau_{ind} = 52$ min), and (*4*) 50 °C ($[\mathbf{1}] = 0.34\cdot10^{-4}$ mol L^{-1}, $\tau_{ind} = 35$ min). Addition of inhibitor **1** is marked with arrows. (The curves of oxygen consumption are shifted in time for clarity.)

amount of consumed oxygen (ΔO_2) is virtually equal to the amount of the hydroperoxide formed.

$$[ROOH]_t = [ROOH]_0 + \Delta O_2, \tag{2}$$

where $[ROOH]_t$ and $[ROOH]_0$ are the current and initial concentrations of hydroperoxide, respectively.

Taking this into account, inhibitor **1** was added at such an instant t_1 that $[ROOH]_{t1}$ was (14±1) mmol L^{-1}; the induction period (τ) and therefore the initiation rate ($W_i = (2[\mathbf{1}]_0/\tau)$ were determined at equal concentrations of ROOH and CTAB. The experimental W_{O_2} and W_i values and the W_i values calculated by the formula

$$W_i = \{W_{O_2}/([RH]k_p/(2k_t)^{0.5})\}^2 \tag{3}$$

from experimental W_{O_2} values and the literature data for the parameter $k_p/(2k_t)^{0.5}$ are given in Table 1. According to known data,[6,7] $(k_p/(2k_t)^{0.5})\cdot10^4$ is 3.67, 5.5, 8.04, and 11.5 L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$ at 50, 60, 70, and 80 °C, respectively.

The apparent rate constant of radical initiation in the process ROOH—CTAB → $RO_2^{\bullet}$ is given by the formula

$$k_{app} = W_i/([CTAB]\,[ROOH]). \tag{4}$$

The k_{app} values are rather widely scattered (see Table 1), which indicates that the system is complex and that the reaction rate is affected by many factors.

The radical initiation rates in this system during ethylbenzene oxidation were measured in a flow reactor in a temperature range from 50 to 70 °C with the use of stable nitroxyl radical **2** as an acceptor of radicals. Twenty minutes after the beginning of oxidation, a solution of nitroxyl radical **2** in chlorobenzene was added to ethylbenzene containing CTAB (1.2 mmol L^{-1}) and a hydroperoxide (20 mmol L^{-1}) so that the concentration of radical **2** in the system was 0.13 mmol L^{-1}. The reaction solution was sampled every five minutes and the absorption spectra were recorded. The initiation rate is equal to the rate of formation of quinone nitrone ($\lambda_{max} = 371$ nm; $\varepsilon = 1.98\cdot10^4$ L mol cm^{-1}).[9]

The plot for k_{app} *vs.* temperature in Arrhenius coordinates is shown in Fig. 2 (curve *1*). The average

Table 1. Kinetic characteristics of ethylbenzene oxidation initiated by a ROOH—CTAB system (1.2 mmol L^{-1}) at different temperatures

T/°C	W_{O_2}* $\cdot10^6$	$W_i\cdot10^7$		$([ROOH]_0 + \Delta O_2)\cdot10^2$	$[ROOH]_t$** $\cdot10^2$	$k_{app}\cdot10^2$		
		Inhibition method (**1**)	From W_{O_2}	mol L^{-1}		From W_{O_2}	Inhibition method	
	mol L^{-1} s^{-1}						**1**	**2**
50	0.41	0.32	0.18	1.28	1.27	0.13	0.19	0.14
60	0.91	0.67	0.44	1.61	1.59	0.26	0.39	0.32
60	0.91	0.72	0.44	1.62	1.63	0.26	0.42	—
70	2.81	1.70	1.80	1.70	1.67	1.00	0.98	0.84
70	3.00	1.80	2.10	1.60	1.62	1.30	1.00	—
70	2.50	1.40	1.40	1.60	1.62	0.80	0.83	—
80	6.60	3.80	4.90	1.80	1.87	2.20	2.10	—
80	7.10	4.19	5.70	1.85	1.83	2.60	2.20	—
80	7.20	4.30	5.90	1.72	1.70	2.80	2.40	—
80	6.90	4.30	5.30	1.78	1.75	2.50	2.40	—

* Experimental values.

** At the end of the experiment.

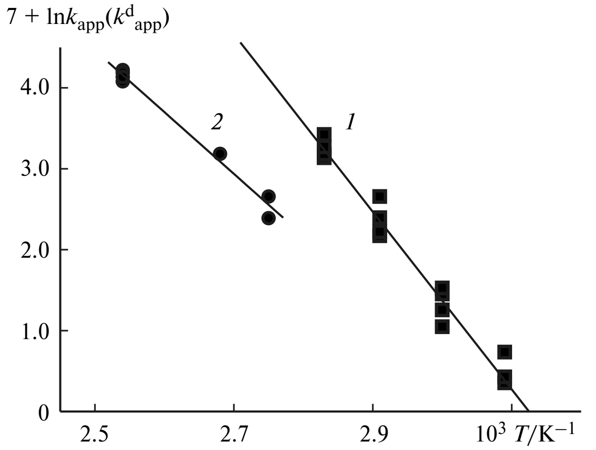

Fig. 2. Plots for (*1*) the apparent rate constant k_{app} and (*2*) k^{d}_{app} *vs.* temperature in Arrhenius coordinates.

energy of activation is 91.0±3.3 kJ mol^{-1}, k_{app} = $7.2 \cdot 10^{11}\exp(-91000/(RT))$ L mol^{-1} s^{-1}.

Earlier,[2] the energy of activation of this process was estimated at 50.2 kJ mol^{-1} by comparing the rates of the CTAB-catalyzed decomposition of α-phenylethyl hydroperoxide at 120 and 90 °C. Because of such discrepancies in temperature coefficients, the kinetics of accumulation and decomposition of ROOH in the presence of CTAB was studied in more detail.

The kinetic curves for ROOH decomposition in an inert atmosphere in the presence of CTAB can be described by the first-order equation (Fig. 3)

$$d[\mathrm{ROOH}]/dt = k'_{app}[\mathrm{ROOH}], \qquad (5)$$

or

$$\ln[\mathrm{ROOH}]_t/[\mathrm{ROOH}]_0 = k'_{app}t, \qquad (6)$$

where the rate constant k'_{app} depends on the concentration of CTAB. The initial segments of the kinetic curves deviate from a linear anamorphosis in semilogarithmic coordinates (see Fig. 3); the deviation the larger, the higher the CTAB concentration and the lower the temperature. Earlier,[5] it was noted that some time is required for the formation of quasistable surfactant—ROOH microaggregates in a microheterogeneous system obtained by mixing a surfactant with an ROOH-containing hydrocarbon medium. Taking this into account, the effect of CTAB on the rate of ROOH decomposition in an inert atmosphere at different temperatures was quantitatively characterized by k'_{app} and $k^{d}_{app} = k'_{app}/[\mathrm{CTAB}]$ (Table 2). The temperature dependence of k^{d}_{app} is satisfactorily described by the Arrhenius equation (Fig. 2, curve *2*)

$$k^{d}_{app} = (1.67 \cdot 10^{7})\exp(-63430/(RT)) \text{ L mol}^{-1} \text{ s}^{-1}.$$

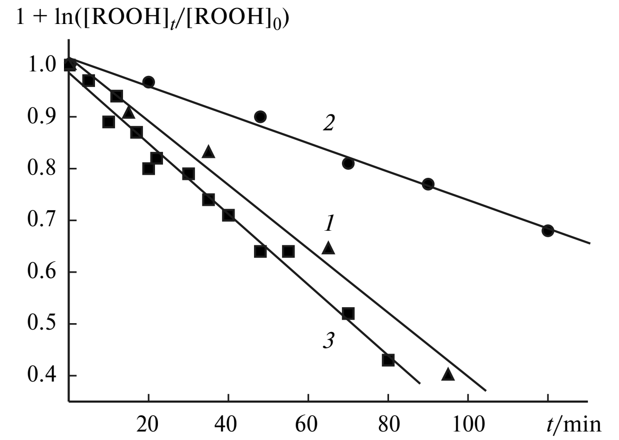

Fig. 3. Kinetic curves for the decomposition of α-phenylethyl hydroperoxide in ethylbenzene in the presence of CTAB in a nitrogen atmosphere at (*1*) 90 °C ($11 \cdot 10^{-2}$ mol L^{-1} ROOH + + $1 \cdot 10^{-2}$ mol L^{-1} CTAB), (*2*) 100 °C ($2.7 \cdot 10^{-2}$ mol L^{-1} ROOH + $2 \cdot 10^{-3}$ mol L^{-1} CTAB), and (*3*) 120 °C ($(2.7—4.5) \cdot 10^{-2}$ mol L^{-1} ROOH + $2 \cdot 10^{-3}$ mol L^{-1} CTAB).

The obtained apparent energy of activation of ROOH decomposition in an inert atmosphere (E_D = 63.43±3.16 kJ mol^{-1}) is higher than the E value found previously,[2] but is nearly 1.5 times lower than the energy of activation of radical formation (E_R) in this system in the presence of oxygen. As can be seen in Table 1, at 50—80 °C in the presence of oxygen, α-phenylethyl hydroperoxide is virtually the sole product of the initial oxidation of ethylbenzene in the concentration range studied. This was confirmed by oxidation of ethylbenzene in a flow reactor with periodical sampling for analysis of the ROOH content. The kinetic curve for ROOH accumulation at equal initial concentrations of the reagents ($[\mathrm{ROOH}]_0 = 9 \cdot 10^{-3}$ mol L^{-1}, [CTAB] = $1.2 \cdot 10^{-3}$ mol L^{-1}, 70 °C) virtually coincides with the kinetic curve for oxygen consumption (see Table 1).

At high current concentrations of hydroperoxide and elevated temperatures with oxygen as an oxidant, the ROOH concentration rapidly reaches a maximum value. The higher the CTAB concentration in ethylbenzene oxi-

Table 2. Kinetic characteristics of the CTAB-catalyzed decomposition of α-phenylethyl hydroperoxide

T/°C	[CTAB]	[ROOH]	$k'_{app} \cdot 10^4$ /s^{-1}	$k^{d}_{app} \cdot 10^2$ /L mol^{-1} s^{-1}
	mmol L^{-1}			
90	1	100	0.13	1.3
90	10	110	1.03	1.0
100	2	27	0.44	2.2
120	10	100	5.40	5.4
120	10	115	6.20	6.2
120	3	60	1.80	6.0
120	2	27	1.10	5.5
120	2	45	1.14	5.7

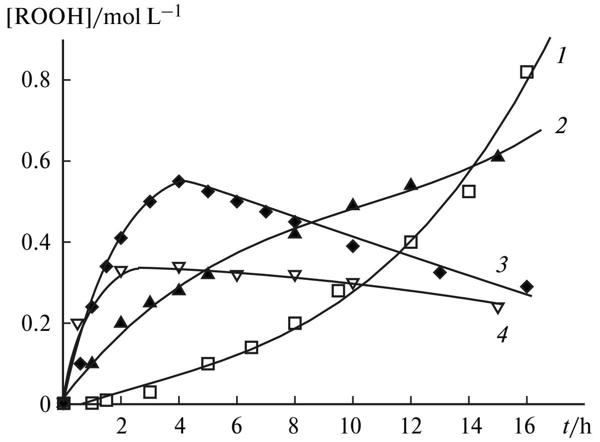

Fig. 4. Kinetic curves for accumulation of hydroperoxides in the oxidation of ethylbenzene in the presence of CTAB at 120 °C. The concentration of CTAB is (*1*) 0, (*2*) 1, (*3*) 10, and (*4*) 20 mmol L^{-1}.

dation, the higher the initial rate of ROOH accumulation, the lower the maximum concentration of ROOH, and the shorter the time required for this concentration to be reached (Fig. 4). Earlier,[2] it was noted that the oxidation of ethylbenzene in the presence of CTAB and its autooxidation yield the same products.

Comparison of the k_{app} and $k^{\mathrm{d}}_{\mathrm{app}}$ values (see Fig. 2) showed that the rate of the catalytic decomposition of ROOH into radicals in the presence of oxygen is higher than the overall rate of ROOH consumption in an inert atmosphere (at least, at temperatures >60 °C). At elevated temperatures, inhibitors and the radicals formed from them react with hydroperoxides, a hydrocarbon, and oxygen, which hinders direct determination of the radical initiation rate by the inhibition method. However, a large discrepancy between E_{D} and E_{R} values and the higher rates of ROOH decomposition under oxidation conditions suggest that oxygen is involved in the catalytic decomposition of ROOH in CTAB microaggregates.

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