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Kinetics of the Initiated and Inhibited Oxidation of Methyl Oleate in Homogeneous and Aqueous Emulsion Media

L. R. Yakupova* and R. L. Safiullin

Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences,
Ufa, 450054 Bashkortostan, Russia
**e-mail: jkupova@anrb.ru*

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Abstract—The kinetics of the 2,2'-azobisisobutyronitrile-initiated oxidation of methyl oleate (MO) in the medium of the oxidized substrate itself (homogeneous system) and in an aqueous solution of cetyltrimethylammonium bromide (aqueous emulsion system, AES) was studied. The oxidation was found to occur as a nonbranched chain reaction with quadratic-law chain termination in both neat methyl oleate ([MO] ≈ 2.6 mol/l) and AES. The temperature dependence of the oxidizability parameter for methyl oleate in the temperature range from 303 to 333 K was described by the following expressions:

$$\text{in an MO medium, } \log(k_2(2k_6)^{-0.5}) = (2.0 \pm 0.5) - (27.5 \pm 3.2)\theta^{-1}\ [\mathrm{l}^{0.5}\ \mathrm{mol}^{-0.5}\ \mathrm{s}^{-0.5}];$$
$$\text{and in the AES, } \log(k_2(2k_6)^{-0.5}) = (2.4 \pm 0.4) - (29.4 \pm 2.1)\theta^{-1}\ [\mathrm{l}^{0.5}\ \mathrm{mol}^{-0.5}\ \mathrm{s}^{-0.5}],$$

where $\theta = 2.303 \times 10^{-3} RT$ kJ/mol. The apparent rate constants for the inhibition of the reaction by 2,6-di-*tert*-butyl-4-methylphenol, quercetin, 5-hydroxy-6-methyluracil, and α-tocopherol in an MO medium and in the AES at 333 K were measured. The values of constants $fk_7 \times 10^{-4}$ were 1.4 ± 0.1 and 0.9 ± 0.1, 3.0 ± 0.1 and 2.4 ± 0.3, 2.5 ± 0.1 and 1.0 ± 0.1, and 90.7 ± 19.9 and 46.5 ± 16.5 l $\mathrm{mol}^{-1}\ \mathrm{s}^{-1}$, respectively.

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In recent years, esters of polyunsaturated fatty acids have been used as model oxidized substrates for testing inhibitors. The antioxidant activity of natural compounds is also studied in the aqueous phase, and the inhibitor can be both water- and fat-soluble [1–3]. For the quantitative estimation of the inhibition activity, one needs to know the kinetic parameters of the oxidation reactions of substrates. Unlike homogeneous systems, aqueous emulsion systems were quantitatively studied insufficiently well. The system based on the oxidation of ethyl and methyl oleates in aqueous solution in the presence of cetyltrimethylammonium bromide using copper(II) coordination compounds with α-amino acids as catalysts was developed [4]. However, the presence of variable-valence metals can impede the process, including because of the formation of complexes with inhibitors.

In the present work, the model system based on the oxidation of methyl oleate in an aqueous solution of cetyltrimethylammonium bromide initiated by 2,2'-azobisisobutyronitrile was used for the quantitative estimation of the antiradical activity of important synthetic and natural inhibitors. The rate constants for the inhibition of the reaction by 2,6-di-*tert*-butyl-4-methylphenol, quercetin, 5-hydroxy-6-methyluracil, and α-tocopherol in both an MO medium and the aqueous emulsion system were measured.

EXPERIMENTAL

Methyl oleate (MO, $C_{17}H_{33}COOCH_3$) (high-purity grade) was distilled three times under reduced pressure in argon and was stored in argon at a low temperature. 2,2'-Azobisisobutyronitrile (AIBN, $C_8H_{12}N_4$) was twice recrystallized from freshly distilled ethanol and was then dried in vacuo. Cetyltrimethylammonium bromide (CTAB, $CH_3(CH_2)_{15}N(CH_3)_3Br$) (Acros Organics, purity 99%) was not additionally purified. 2,6-Di-*tert*-butyl-4-methylphenol (ionol, $C_{15}H_{24}O$) was purified by recrystallization from ethanol, and the isolated crystals were dried and sublimed in vacuo. 3,3',4',5,7-Pentahydroxyflavone used (quercetin, $C_{15}H_{10}O_7 \cdot 2H_2O$) was high-purity grade [5]. 5-Hydroxy-6-methyluracil was recrystallized from hot water and dried in vacuo. α-Tocopherol ($C_{29}H_{50}O_2$) (Sigma, 96%) was used as received. Chlorobenzene was purified by concentrated sulfuric acid, washed with water, dried over calcined calcium chloride, and distilled in an inert atmosphere. Twice distilled water was used in experiments.

Kinetic experiments were carried out in a glass reactor loaded with an aqueous solution of CTAB (6 ml), methyl oleate (1.8 ml), and an initiator dissolved in chlorobenzene or methyl oleate (0.2 ml). Since the chain radical oxidation occurred in the organic phase under our experimental conditions, the concentrations of the substrate, initiator, and inhibitor were calculated from the total volume of loaded methyl oleate and solutions of the initiator and inhibitor ignoring the volume of water (it was shown by spectrophotometry that quercetin and 5-hydroxy-6-methyluracil were almost absent from the aqueous phase of the microheterogeneous system). An aqueous solution of CTAB was not added to the homogeneous system. When studying the inhibited oxidation in the AES, the order of loading the reactor was as follows: the inhibitor as a solution in methyl oleate, chlorobenzene, or 1,4-dioxane; methyl oleate; a solution of CTAB; and the initiator. The oxygen uptake was monitored using a multipurpose manometric differential setup in which a highly sensitive differential pressure gauge based on a silicon membrane cell served as the measuring element. The oxygen uptake rate in the liquid phase was calculated via a standard procedure [6]. The initial rate of inhibited oxidation was determined from the slope of the oxygen uptake versus time curve at the $t = 0$ point. The initial point in time was set to be 300 s after the introduction of the inhibitor into the reactor.

The initiation rate was determined by the equation $w_\mathrm{i} = 2ek_\mathrm{d}[\mathrm{AIBN}]$, where k_d is the rate constant for AIBN decomposition, and e is the probability of radical escape to the bulk. The rate constant for AIBN decomposition was calculated from reference data for the decomposition of this initiator in a hydrocarbon medium ($\log k_\mathrm{d} = 15 - 30.5/(4.575T \times 10^{-3})$) [7] at $2e = 0.65$ (in a medium of methyl linoleate [8]).

RESULTS AND DISCUSSION

Kinetics of Methyl Oleate Oxidation in the Substrate Medium

The liquid-phase oxidation of MO with atmospheric ixygen was carried out in the temperature range from 303 to 333 K, and the AIBN concentration was varied between 0.07×10^{-2} and 15.4×10^{-2} mol/l. The experimental results (Table 1) indicate a linear dependence between the parameters $w/[\mathrm{RH}]$ and $w_\mathrm{i}^{0.5}$. The oxidation rate is independent of the oxygen concentration ($[\mathrm{O_2}]$ from 2×10^{-3} to 1×10^{-2} mol/l). The dependence of the oxidation rate on the substrate concentration was studied at 333 K in the methyl oleate concentration range 0.6–2.6 mol/l. Chlorobenzene was used as the solvent (Table 1). A linear relationship is observed between w and $[\mathrm{RH}]$.

Thus, under our experimental conditions, MO oxidation proceeds via a radical chain mechanism with quadratic-law chain termination:

$$\mathrm{AIBN} \xrightarrow{k_\mathrm{i}} r^\bullet \xrightarrow{\mathrm{RH}} \mathrm{R}^\bullet, \qquad \text{(i)}$$

$$\mathrm{R}^\bullet + \mathrm{O_2} \xrightarrow{k_1} \mathrm{RO}_2^\bullet, \qquad \text{(I)}$$

$$\mathrm{RO}_2^\bullet + \mathrm{RH} \xrightarrow{k_2} \mathrm{ROOH} + \mathrm{R}^\bullet, \qquad \text{(II)}$$

$$\mathrm{RO}_2^\bullet + \mathrm{RO}_2^\bullet \xrightarrow{k_6} \text{ molecular products.} \qquad \text{(VI)}$$

The numbering of the reactions is the same as in the commonly accepted scheme of the liquid-phase oxidation of hydrocarbons.

The experimental data obtained are satisfactorily described by the equation

$$w = k_2 (2k_6)^{-0.5} [\mathrm{RH}] w_\mathrm{i}^{0.5}. \qquad (1)$$

Hereinafter, k_2 and $2k_6$ are the rate constants for chain propagation and termination on peroxide radicals of methyl oleate, respectively. The values of $k_2(2k_6)^{-0.5}$, which characterize the oxidizability of methyl oleate, were determined by Eq. (1) using the data presented in Table 1. The temperature dependence of $k_2(2k_6)^{-0.5}$ in the coordinates of the Arrhenius equation is linear and is described by the equation

$$\begin{aligned} \log\left(k_2 (2k_6)^{-0.5}\right) &= (2.0 \pm 0.5) \\ -\,(27.5 \pm 3.2)\,\theta^{-1} &\left[\mathrm{l}^{0.5}\ \mathrm{mol}^{-0.5}\ \mathrm{s}^{-0.5}\right] (r = 0.986), \end{aligned} \qquad (2)$$

where $\theta = 2.303 \times 10^{-3} RT$ kJ/mol.

It should be mentioned that the temperature dependence of the oxidizability parameter $k_2(2k_6)^{-0.5}$ agrees satisfactorily with the published data [9], according to which $\log(k_2(2k_6)^{-0.5}) = 2.9 - 34.1\theta^{-1}$ $[\mathrm{l}^{0.5}\ \mathrm{mol}^{-0.5}\ \mathrm{s}^{-0.5}]$.

Kinetics of Methyl Oleate Oxidation in Aqueous Emulsion

Methyl oleate was oxidized in an aqueous solution of CTAB (1.8×10^{-3} mol/l) at a volume ratio of the organic and aqueous phases of 1 : 3. According to [4], at this ratio of the reactants, the concentration of the emulsifier corresponds to the critical micelle concentration. The reaction was studied in the temperature range from 303 to 333 K, and the AIBN concentration was varied from 0.05×10^{-2} to 31.5×10^{-2} mol/l. The change in the CTAB concentration from 0 to 1.8×10^{-3} mol/l exerted no effect on the oxidation rate of methyl oleate. The experimental data indicate that the oxidation rate is independent of the oxygen concentration ($[\mathrm{O_2}]$ from 2×10^{-3} to 1×10^{-2} mol/l) and a linear dependence between $w/[\mathrm{RH}]$ and $w_\mathrm{i}^{0.5}$ is observed in the temperature range studied.

Table 1. Dependences of the methyl oleate oxidation rate on the concentrations of the initiator and substrate and on the temperature

T, K	[AIBN] × 10^2, mol/l	[RH], mol/l	$w_i \times 10^9$, mol l^{-1} s^{-1}	$w \times 10^7$, mol l^{-1} s^{-1}	$k_2(2k_6)^{-0.5} \times 10^3$, $l^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$	k_2, l mol^{-1} s^{-1}
303	0.65	2.7	0.5	0.4	2.1 ± 0.3	1.6
	3.1	2.7	2.2	2.3		
	7.7	2.2	5.4	3.3		
	15.4	1.5	10.8	3.1		
313	0.4	2.8	1.3	3.7	2.6 ± 0.2	2.5
	0.7	2.7	2.6	3.4		
	3.1	2.7	10.9	7.6		
	5.8	1.7	20.4	7.7		
323	1.4	2.7	22.5	14.7	3.7	3.7
333	0.068	2.7	4.5	10.4	5.6 ± 0.3	5.3
	0.17	2.2	11.3	15.0		
	0.26	1.8	17.7	15.1		
	0.65	0.6	43.8	10.4		
	0.65	1.2	43.8	17.2		
	0.65	1.8	43.8	16.8		
	0.65	2.1	43.8	20.2		
	0.65	2.4	43.8	23.2		
	0.65	2.6	43.4	23.2		
	1.4	2.7	93.7	33.5*		
	1.4	2.7	93.7	46.3		
	1.4	2.6	93.7	40.2*		
343	0.068	2.7	17.3	28.6	9.5 ± 0.6	7.4
	0.17	2.2	43.2	46.8		

Note: The constant k_2 was calculated via Eq. (2) assuming that $2k_6$ is almost temperature-independent, being 1×10^6 l mol^{-1} s^{-1} [14].
* Oxidation in an oxygen atmosphere.

The dependence of the oxidation rate on the substrate concentration was studied at 333 K, and chlorobenzene was used as the solvent (Table 2). A linear dependence between w and [RH] is observed with a change in the substrate concentration from 0.44 to 2.95 mol/l.

Thus, in an aqueous emulsion medium methyl oleate is oxidized via the chain radical mechanism with quadratic-law chain termination. The temperature dependence of the apparent rate constant $k_2(2k_6)^{-0.5}$ in the coordinates of the Arrhenius equation is linear and is described by the equation

$$\log\left(k_2(2k_6)^{-0.5}\right) = (2.4 \pm 0.4) - (29.4 \pm 2.1)\theta^{-1}\left[1^{0.5}\ \mathrm{mol}^{-0.5}\,\mathrm{s}^{-0.5}\right] (r = 0.995), \quad (3)$$

where $\theta = 2.303 \times 10^{-3} RT$ kJ/mol.

A comparison between Eq. (2) and Eq. (3) shows that the presence of an aqueous solution of CTAB exerts no noticeable effect on the kinetics of the initiated oxidation of methyl oleate.

Measurement of the Apparent Rate Constant of Inhibition

The introduction of a tested compound into oxidized methyl oleate decreases the rate of oxygen uptake, because an additional channel appears for the consumption of peroxide radicals in reaction (VII)

$$\mathrm{RO}_2^{\bullet} + \mathrm{InH} \xrightarrow{k_7} \mathrm{ROOH} + \mathrm{In}^{\bullet}, \quad \text{(VII)}$$

$$\mathrm{In}^{\bullet} + \mathrm{RO}_2^{\bullet} \rightarrow \text{inactive products.} \quad \text{(VIII)}$$

As follows from the experimental data (Tables 3 and 4), in the presence of the inhibitor in a medium of oxidized methyl oleate, the chain length is at least 3 units and, hence, the chain regime is retained. In this case, the following equation [10] is applicable to the quantitative estimation of the efficiency of inhibition:

$$F = w_0/(w - w_i) - (w - w_i)/w_0 = fk_7[\mathrm{InH}](2k_6 w_i)^{-0.5}, \quad (4)$$

where w_0 and w are the initial oxygen uptake rates in the absence and in the presence of the inhibitor,

Table 2. Dependences of the methyl oleate oxidation rate in an aqueous emulsion medium on the concentrations of the initiator and substrate and on the temperature

T, K	[AIBN] × 10^2, mol/l	[RH], mol/l	$w_i \times 10^9$, mol l^{-1} s^{-1}	$w \times 10^7$, mol l^{-1} s^{-1}	$k_2(2k_6)^{-0.5} \times 10^3$, $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$	k_2, l mol^{-1} s^{-1}
303	0.6	2.95	0.4	1.4	2.1 ± 0.2	2.5
	1.6	2.81	1.1	1.8		
	3.0	2.68	2.1	2.0		
	6.7	2.36	4.7	3.1		
	16.8	1.48	11.8	3.3		
	21.0	1.48	14.7	4.2		
313	0.2	2.94	0.7	3.2	3.4 ± 0.3	3.5
	0.6	2.95	2.1	4.0		
	1.0	2.95	3.4	7.1		
	2.0	2.95	7.0	8.2		
	2.1	2.80	7.4	7.0		
	3.9	2.95	13.6	13.4		
	10.5	2.21	37.0	14.1		
323	0.2	2.95	3.8	7.4	4.7 ± 0.4	4.8
	0.3	1.48	5.0	7.9		
	1.0	2.88	16.0	17.8		
	1.6	2.95	25.7	14.8		
	3.9	2.95	62.1	36.0		
	4.2	2.66	67.4	28.7		
	10.5	2.21	168.6	45.7		
	31.5	1.48	505.7	49.8		
333	0.05	2.21	3.5	8.7	5.9 ± 0.2	6.3
	0.21	0.44	14.1	3.3		
	0.21	0.88	14.1	5.9		
	0.21	1.77	14.1	9.1		
	0.21	2.21	14.1	11.7		
	0.21	2.66	14.1	17.6		
	0.21	2.95	14.1	19.3		
	0.21	2.25	14.1	12.0		
	0.21	2.7	14.1	16.0		
	0.21	2.95	14.1	19.0		
	0.28	2.95	18.7	20.3 ± 2.2		
	0.30	2.95	20.1	31.6*		
	0.48	2.95	32.1	27.0 ± 1.0		
	0.62	2.95	41.5	35.9 ± 1.8		
	1.57	2.66	105.2	51.4		
	3.93	2.21	263.1	64.8		
	6.29	1.77	421.0	68.1		
343	0.15	2.95	38.3	37.4	6.9 ± 0.5	8.3
	0.30	2.95	76.6	53.7		
	0.62	2.95	158.4	86.2		
	0.98	2.95	250.3	107.4		

Note: MO : H_2O = 1 : 3 (vol/vol), [CTAB] = 1.8×10^{-3} mol/l. The constant k_2 was calculated via Eq. (3) assuming that $2k_6$ is almost temperature-independent, being 1×10^6 l mol^{-1} s^{-1} [14].

* Oxidation in an oxygen atmosphere.

Table 3. Dependence of the methyl oleate oxidation rate on the inhibitor concentration

[InH] × 10^4, mol/l	τ, s	$w \times 10^7$, mol l^{-1} s^{-1}	$k_7 \times 10^{-4}$, l mol^{-1} s^{-1}	$fk_7 \times 10^{-4}$, l mol^{-1} s^{-1}
Ionol, homogeneous medium				
0.18	1000	20.0	0.9	1.4 ± 0.1
0.26	1300	16.2	0.9	
0.89	3000	5.7	–	
1.28	4500	3.7	0.8	
2.14	8000	4.0	0.6	
Ionol, aqueous emulsion medium				
0.25	1500	17.1	–	0.9 ± 0.1
0.43	2000	12.6	–	
0.60	2900	10.9	0.7	
0.85	–	11.1	0.3	
1.27	5500	6.0	0.5	
1.69	7300	4.2	0.6	
Quercetin, homogeneous medium				
0.106	500	9.2	–	3.0 ± 0.1
0.163	600	7.3	1.6	
0.271	1000	8.0	1.6	
0.542	2200	3.6	1.6	
0.813	2200	2.8	2.2	
1.08	3800	2.0	1.3	
1.36	4300	1.7	1.4	
Quercetin, aqueous emulsion medium				
0.02	90	25.6	–	2.4 ± 0.3
0.035	150	20.0	–	
0.09	650	18.4	–	
0.16	800	12.5	–	
0.20	1200	15.2	1.6	
0.40	2000	14.1	1.6	
0.57	3100	1.4	1.0	
5-Hydroxy-6-methyluracil, homogeneous medium				
0.18	800	11.9	2.1	2.5 ± 0.1
0.27	900	7.7	2.4	
0.36	1000	6.1	2.4	
0.72	2400	4.6	2.0	
0.89	3000	3.3	–	
3.66	6000	1.1	1.8	
5-Hydroxy-6-methyluracil, aqueous emulsion medium				
0.09	400	24.4	–	1.0 ± 0.1
0.18	500	16.0	–	
0.89	1500	6.9	1.2	
0.98	1500	6.0	1.3	
3.66	2800	9.3	1.3	

Note: MO : H_2O = 1 : 3 (vol/vol), [CTAB] = 1.8×10^{-3} mol/l, [RH] = 2.6 mol/l, $w_i = 4 \times 10^{-8}$ mol l^{-1} s^{-1}, 333 K. The constant k_7 was calculated via Eq. (5), and the parameter fk_7 was calculated using Eq. (4).

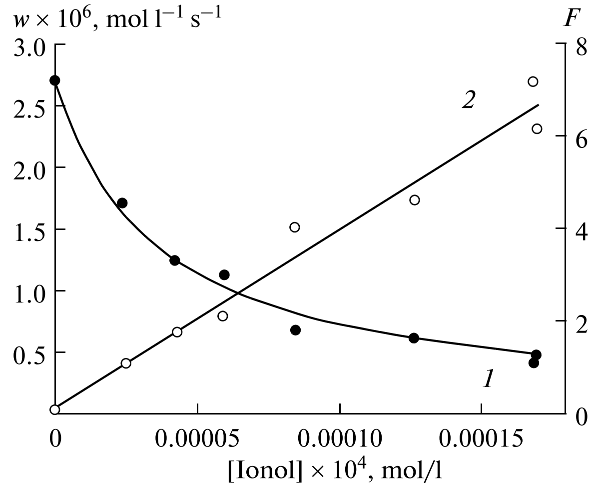

Fig. 1. (*1*) Initial methyl oleate oxidation rate and (*2*) the parameter F ($r = 0.99$) versus the ionol concentration. Reaction conditions: AES, 333 K, $w_i = 4 \times 10^{-8}$ mol l^{-1} s^{-1}.

respectively; [InH] is the initial concentration of the inhibitor; $2k_6$ and fk_7 are the rate constants for chain termination on radicals $RO_2^{\bullet}$ (reaction (VI)) and on inhibitor molecules (reaction (VII)), respectively; and f is the stoichiometric inhibition coefficient.

The typical dependence of the initial rate of methyl oleate oxidation on the inhibitor concentration and the results of experimental data processing in the coordinates of Eq. (4) are given in Fig. 1. The observed linear dependence of F on [InH] makes it possible to calculate the inhibition rate constant fk_7. The dependences of the methyl oleate oxidation rate on the concentrations of the compounds studied are presented in Table 3 along with the values of fk_7.

The oxygen uptake curves were also fitted to the following equation [10]:

Table 4. Dependence of the methyl oleate oxidation rate on the α-tocopherol concentration in the homogeneous system and in the AES at 333 K

$w_i \times 10^8$, mol l^{-1} s^{-1}	[InH] × 10^6, mol/l	[RH], mol/l	τ, s	$w \times 10^7$, mol l^{-1} s^{-1}	$k_7 \times 10^{-5}$, l mol^{-1} s^{-1}
Homogeneous system					
2.2	25.4	1.4	2800	0.6	3.0
4.3	1.9	2.7	90	6.3	5.0
4.3	3.2	2.8	210	3.2	4.6
4.1	5.2	2.8	295	2.9	3.8
4.1	5.4	2.8	330	1.2	5.6
4.4	6.1	0.9	260	2.3	3.9
4.1	6.1	2.8	3100	1.2	4.2
4.3	10.3	2.6	600	2.8	3.3
9.3	10.3	2.6	245	4.9	7.4
Average value $k_7 = (4.5 \pm 1.0) \times 10^5$ l mol^{-1} s^{-1} $fk_7 = (9.1 \pm 2.0) \times 10^5$ l mol^{-1} s^{-1} at $f = 2$					
Aqueous emulsion medium (MO : H_2O = 1 : 3 vol/vol, [CTAB] = 1.8×10^{-3} mol/l)					
4.1	5.2	2.8	100	15.6	1.5
4.0	14.9	2.4	700	2.8	3.8
4.0	29.9	2.8	2000	1.5	2.5
4.0	59.6	2.8	3200	1.0	1.5
Average value $k_7 = (2.3 \pm 0.8) \times 10^5$ l mol^{-1} s^{-1} $fk_7 = (4.6 \pm 1.7) \times 10^5$ l mol^{-1} s^{-1} at $f = 2$					

Note: The constant k_7 was determined using Eq. (5).

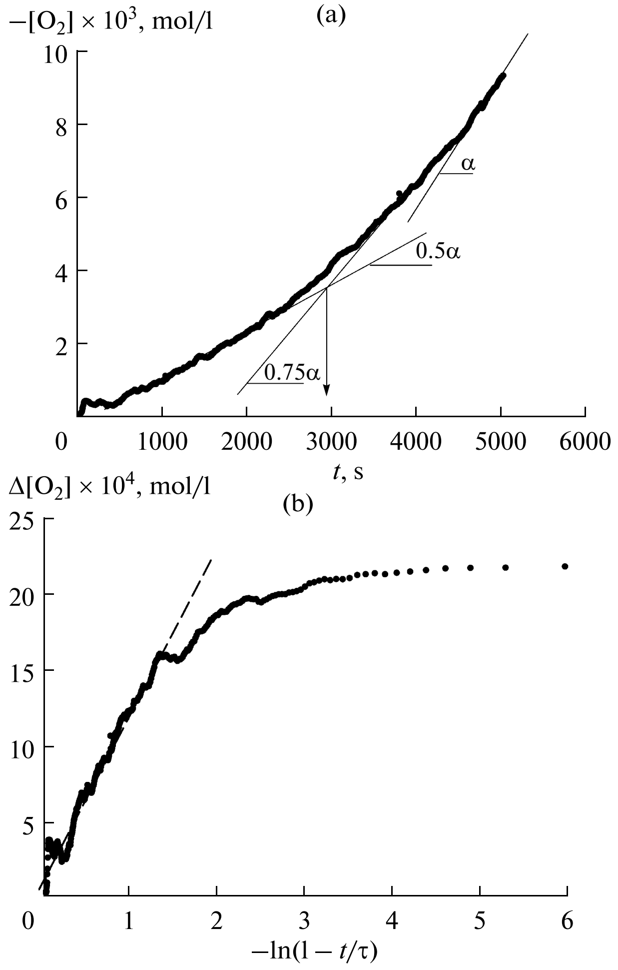

Fig. 2. (a) Oxygen uptake curve for methyl oleate oxidation in the presence of ionol (6×10^{-5} mol/l) and (b) its semilogarithmic anamorphosis in the coordinates of Eq. (5). Reaction conditions: 333 K, $w_i = 4 \times 10^{-8}$ mol l^{-1} s^{-1}, [MO] = 2.7 mol/l, MO : H_2O = 1 : 3 (vol/vol), [CTAB] = 1.8×10^{-3} mol/l; α is the slope angle of the straight line corresponding to the uninhibited reaction; and 0.5α and 0.75α are the slope angles of the tangents to the oxygen uptake curves, whose intersection point makes it possible to determine the induction period.

$$-[O_2] = (k_2/k_7)[RH]\ln(1 - t/\tau). \quad (5)$$

The induction period τ was determined graphically as the position of the intersection point of two tangents to the kinetic curve, whose slope ratios are 0.5 and 0.75 of the slope ratio of the straight line corresponding to the uninhibited reaction [11] (see Fig. 2).

At rather high initial concentration of the inhibitor, the region of the kinetic curve of the oxygen uptake corresponding to the induction period can satisfactorily be linearized in the coordinates of Eq. (5), which makes it possible to determine the ratio k_2/k_7. The typical oxygen uptake curve of the for methyl oleate oxidation in the AES under the conditions of inhibition by ionol and its semilogarithmic anamorphosis are presented in Fig. 2. In the calculation of constant k_7 it was accepted that the constant k_2 is 5.3 l mol^{-1} s^{-1} in a homogeneous medium and 6.3 l mol^{-1} s^{-1} in an aqueous emulsion medium (Tables 1 and 2). These numerical values of the constants were determined from Eqs. (2) and (3) under the condition that $2k_6 = 10^6$ l mol^{-1} s^{-1} [14]. The values of constants k_7 for the reaction in the presence of ionol are listed in Table 3. As can be seen, the inhibition rate constants calculated by Eqs. (4) and (5) are satisfactorily consistent if $f = 1.8$.

The rate constants for inhibition by quercetin and 5-hydroxy-6-methyluracil are given in Table 3, and that for α-tocopherol is presented in Table 4. The results obtained show that in aqueous emulsion the efficiency of inhibition by the compounds studied somewhat decreases. The most significant decrease in the rate constant is observed for inhibition by 5-hydroxy-6-methyluracil. This is not due to the redistribution of the inhibitor between the organic and aqueous phases. In particular cases, as it was shown,

Table 5. Influence of the medium on the inhibition rate constant of methyl oleate oxidation by ionol and α-tocopherol

Inhibitor	T, K	System	$fk_7 \times 10^{-4}$, l mol^{-1} s^{-1}
Ionol	303	styrene in chlorobenzene	2.8 [15]
	333	ethylbenzene in chlorobenzene	5.0 [13]
	333	methyl oleate in chlorobenzene (1.5 mol/l)	2.6 [16]
	343	methyl oleate (2.37 mol/l)	1.4 [12]
	333	methyl oleate (2.6 mol/l)	1.4 ± 0.1*
α-Tocopherol	303	styrene in chlorobenzene	640 [15]
	333	ethylbenzene in chlorobenzene	660 [13]
	333	methyl oleate in chlorobenzene (1.5 mol/l)	720 [16]
	333	methyl oleate in chlorobenzene	620 [17]
	333	methyl oleate (2.6 mol/l)	90.7 ± 19.9*

* Our data.

the inhibitor is almost absent from the aqueous phase of the system. In the case of 5-hydroxy-6-methyluracil, there is another distinction, namely, coefficient f decreases to 1.

The values of fk_7 measured in the systems where methyl oleate was the oxidized substrate using ionol and α-tocopherol are given in Table 5. The literature data [12, 13] show that the efficiency of inhibition depends on the nature of the substrate used and its concentration. The rate constant measured for ionol, whose hydroxyl group is hindered by the *tert*-butyl substituents, depends weakly on the nature and concentration of the substrate. The authors [12, 13] believe that the phenol group of α-tocopherol forms a hydrogen bond with the ester group of methyl oleate, resulting in a noticeable decrease in fk_7.

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