Kinetics of limonene autooxidation

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The kinetic parameters of the oxidizability of limonene, $k_p/(2k_t)^{0.5} = 6.0 \cdot 10^{-3}$ L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$, and of the bimolecular radical decomposition of hydroperoxides $2ek_d = 6.0 \cdot 10^{-6}$ L mol^{-1} s^{-1} were determined at 60 °C. The oxidation rate increases in the presence of micro additives of water. Average effective diameters of particles formed in the water—AOT—(*n*-decane + limonene) microemulsion were measured by the light scattering technique. The hydroperoxides were found to affect the size of the microemulsion particles.

Key words: limonene, kinetics of oxidation, micelles, microemulsions, particle size, sodium bis-(2-ethylhexyl)sulfosuccinate, methylene blue.

Limonene (LH) (4-isopropenyl-1-methylcyclohex-1-ene), a natural cycloolefin of the terpene series, is readily oxidized by molecular oxygen by a free-radical chain mechanism.[1,2] The oxidation product obtained at moderate temperatures is a mixture of isomeric hydroperoxides whose composition is dependent on the oxidation conditions.[3]

The rate of oxygen absorption (W_{O_2}) in the initiated oxidation of limonene is proportional to $w_i^{0.5}$, which is evidence for the square-law termination of chains. W_{O_2} increases nonlinearly with increasing $[LH]_0$, *i.e.*, deviates from the known equation (1) of the theory of the liquid-phase oxidation of hydrocarbons:[4]

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

where k_p is the effective constant of the rate of chain propagation, k_t is the effective constant of the rate of chain termination, w_i is the rate of initiation of the chains.

The value of the effective parameter $a = W_{O_2}/([LH]w_i^{0.5})$, analogous to $k_p/(2k_t)^{0.5}$, is increased by a factor of 1.5—2 when limonene is diluted with chlorobenzene.

In the present work much attention is given to the kinetic regularities of limonene autooxidation and to the radical decomposition of hydroperoxides providing degenerate chain branching, as well as to the effect of water and surfactants on the oxidation kinetics. The solubility and, hence, the water content in aromatic and polar organic solvents are rather high. Therefore, *n*-decane, but not chlorobenzene, was used as the solvent in order to study the effect of water and surfactants on the oxidation of limonene. Limonene and *n*-decane differ markedly in their reactivity in the reactions of free-radical oxidation (k_p and $k_p/(2k_t)^{0.5}$ for LH exceed by more than a factor of 10^2 the corresponding characteristics for *n*-decane) so that *n*-decane can be considered as a fairly inert solvent in the oxidation reaction of LH.

Experimental

Oxidation was carried out in an *n*-decane solution at 60 °C. D-Limonene (Koch-Light Laboratories Ltd., Colnbrook Buchs, England) was used without additional purification. *n*-Decane was purified by standard procedures.[5] The initiator, dicyclohexylperoxydicarbonate (PC), was reprecipitated from its solution in acetone into a methanol—water mixture (5:1). Sodium bis-(2-ethylhexyl)sulfosuccinate (AOT) (Fluka) was used without additional purification.

The rate of oxygen absorption was measured on a gasometric installation (the volume of the reaction mixture was 4 mL at P_{O_2} = 1 atm).[2] The concentration of peroxides was determined iodometrically. The size of the particles of the water—AOT—(*n*-decane + limonene) microemulsion was measured by the quasielastic laser light scattering technique. The water soluble dye, methylene blue (Sigma), was used as an optical probe in reverse microemulsion.

Results and Discussion

A series of experiments on the initiated oxidation of LH (Table 1) was carried out in order to obtain the quantitative characteristics of the oxidizability of limonene in an *n*-decane solution. PC was used as the initiator of free radicals, since for this compound the rate constant of decomposition and the coefficient of radical escape from the solvent cage in *n*-decane (2*e*) have been reliably measured:[6]

$$k_0 = 10^{15.44}\exp\{-124300/RT\}\ \text{s}^{-1}, \text{ and } 2e = 1.5.$$

It follows from the data of Table 1 that W_{O_2} is proportional to $w_i^{0.5}$ in *n*-decane as in chlorobenzene, while the

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Table 1. Kinetics of initiated limonene oxidation in *n*-decane (60 °C, $w_i = 2ek_0[\mathrm{PC}]$, ν is the chain length)

$[\mathrm{LH}]_0$ /mol L^{-1}	$w_i \cdot 10^7$	$W_{O_2} \cdot 10^6$	ν	$\frac{W_{O_2} \cdot 10^3}{w_i^{0.5}[\mathrm{LH}]_0}$
	mol L^{-1} s^{-1}			
3.09	2.13	7.44	35	5.2
1.54	2.13	4.08	19	5.7
0.77	2.13	2.95	14	8.3
0.39	2.13	1.89	8.8	10.0
1.54	0.64	2.34	37	6.0

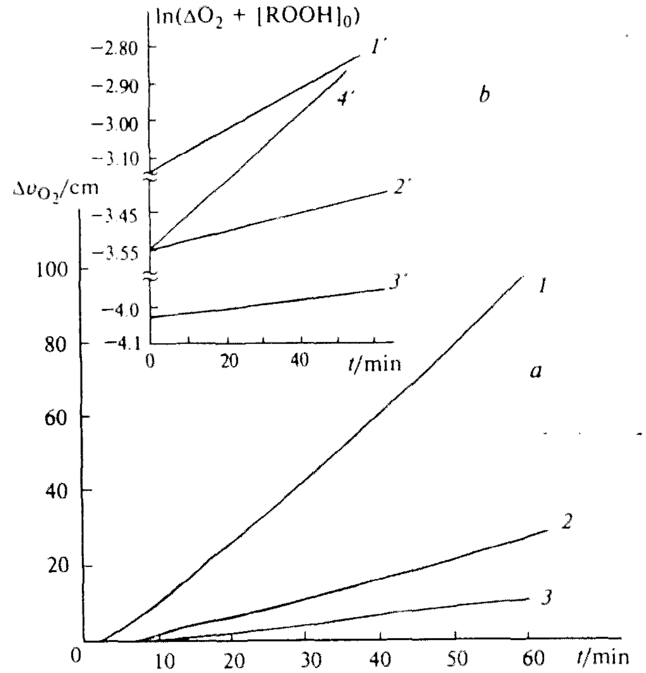

Fig. 1. Kinetic curves of oxygen absorption at varied initial limonene concentrations (*a*, *1—3*) and anamorphoses of the kinetic curves in the coordinates of Eq. (4) (*b*, *1'—3'*). $[\mathrm{LH}]_0$, mol L^{-1}: 6.18 (*1*); 3.09 (*2*); 1.54 (*3*). $[\mathrm{ROOH}]_0 \cdot 10^2$, mol L^{-1}: 4.5 (*1*); 2.9 (*2*); 1.8 (*3*). *n*-Decane, 60 °C. *4'* — anamorphosis of the kinetic curve (*4*) of Fig. 3.

effective parameter $a = W_{O_2}/(w_i^{0.5}[\mathrm{LH}]_0)$ increases with the dilution of limonene. The value of *a* in *n*-decane is somewhat lower than in chlorobenzene. As is known from the literature,[7] when the oxidation of olefins is carried out in different solvents, the parameter $k_p/(2k_t)^{0.5}$ increases as the polarity of the solvent increases; thus, its value for cyclohexene at 60 °C is $0.8 \cdot 10^{-3}$ L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$ in cyclohexane and $1.1 \cdot 10^{-3}$ L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$ in chlorobenzene.[8]

The absorption of oxygen during the oxidation of limonene in the absence of an initiator occurs with autoacceleration (Fig. 1). The amount of absorbed oxygen is nearly equal to the amount of hydroperoxides formed:

$$\Delta O_2 = \Delta[\mathrm{ROOH}]. \qquad (2)$$

The kinetic curves presented in Fig. 1 belong to samples differing in their starting concentrations of LH and ROOH. The kinetic processing of these curves (Fig. 2) shows a linear dependence of the autooxidation rate on the ROOH concentration, *i.e.*, $W_{O_2} \sim [\mathrm{LH}] \cdot [\mathrm{ROOH}]$. This type of dependence of the rate of a process on the concentration of reagents is characteristic of liquid-phase degenerate-branched oxidation processes, where the rate of radical formation w_i is proportional to $[\mathrm{ROOH}]^2$ (bimolecular decomposition of hydroperoxides), and the O_2 absorption rate is described by Eq. (3):[4,9]

$$W_{O_2} = a\,[\mathrm{LH}]\,(2ek_d\,[\mathrm{ROOH}]^2 + w_0)^{0.5}, \qquad (3)$$

where w_0 is the rate of chain initiation, $2ek_d$ is the effective constant of the rate of the bimolecular decomposition of hydroperoxides. The integral dependence (at $w_0 \ll 2ek_d\,[\mathrm{ROOH}]^2$) corresponds to this equation:

$$\ln(\Delta O_2 + [\mathrm{ROOH}]_0) = \ln[\mathrm{ROOH}]_0 + (k_p/(2k_t)^{0.5})[\mathrm{LH}](2ek_d)^{0.5}t. \qquad (4)$$

The kinetic curves of O_2 absorption (Fig. 1) become linear in the coordinates of Eq. (4) (Fig. 1, *b*), and the tangent of the slope of the anamorphoses is proportional to [LH] (Fig. 2, curve *2*). From the data obtained it follows that the effect of dilution of limonene under autooxidation conditions on the value of parameter *a* is less pronounced than that in initiated oxidation, which might be associated with a less reliable value of the initiation rate. Nevertheless, if one assumes $a = 0.6 \cdot 10^{-2}$ (L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$) (see Table 1; for methylcyclohexene in Ref. 4 $k_p/(2k_t)^{0.5} = 3.5 \cdot 10^{-3}$ (L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$) at 60 °C) and takes into account the linear dependences represented in Fig. 2, it is possible to estimate the effective rate constant of the radical decomposition of ROOH, $2ek_d = (6.0 \pm 0.2) \cdot 10^{-6}$ L mol^{-1} s^{-1}, which is close to the corresponding values for hydroperoxides of other olefins.[4,9,10]

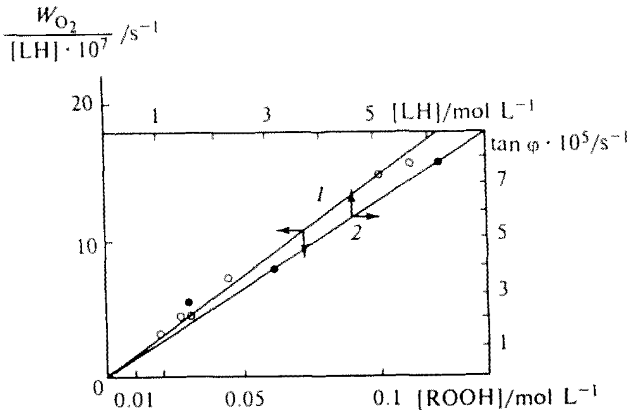

Fig. 2. Dependence of the specific rate of oxygen absorption during limonene oxidation on hydroperoxide concentration (*1*) and the dependence of the slope of the anamorphoses (see Fig. 1, *b*) on the initial limonene concentration (*2*). *n*-Decane, 60 °C.

In the complicated degenerate-branched process of hydrocarbon oxidation, the AOT and water additives can differently affect the rates of propagation, branching, and termination of the chain. Under conditions of initiated oxidation, the reactions of propagation and termination of the chain are mostly affected. In autooxidation, along with above reactions, a significant contribution to the kinetics of the process is made by the free-radical decomposition of hydroperoxides. Therefore, we studied the effect of water and AOT under both operating conditions of limonene oxidation.

In the absence of surfactants water is almost insoluble in *n*-decane and unoxidized limonene; it forms a separate phase even when 30 μL of water are mixed with 4 mL of the reaction mixture (limonene—*n*-decane, 1 : 2, 1 : 4). However, a stable, optically transparent microemulsion is obtained with a large amount of water if AOT is added. The diameter of the microemulsion particles at the concentration ratio $[H_2O]/[AOT] = 20$ was measured by the quasielastic laser light scattering technique; it is equal to 85 Å, which is in good agreement with the literature data[11—13] on the structure of microemulsions stabilized by this surfactant. If limonene oxidation is initiated by PC, AOT and micro amounts of water, added together or separately, they have little effect on the rate of oxidation (Fig. 3, curves *1'—4'*). Previously, we have demonstrated that water and surfactants have no effect on PC decomposition. Even for normal SDS micelles the PC decomposition is described by the same parameters as in an *n*-decane solution.[14] It is evident that in the reverse microemulsion, PC decomposition and the initiation, propagation, and termination of the oxidation chains of limonene are localized in the oil phase; therefore, the presence of the microemulsion particles does not affect these reactions.

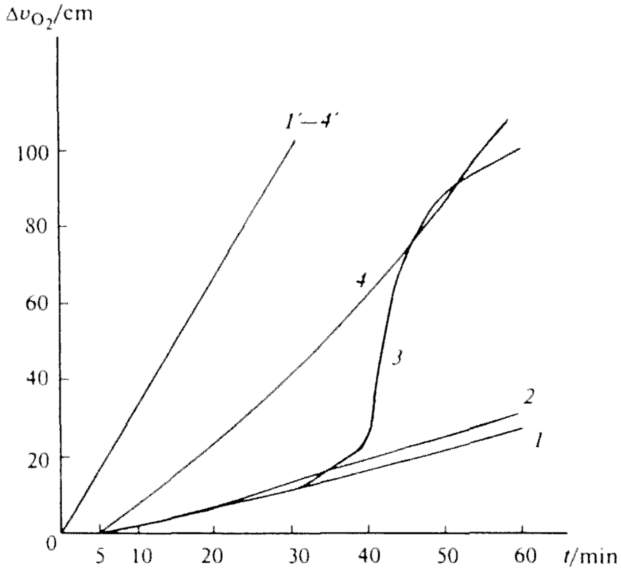

Fig. 3. Kinetic curves of oxygen absorption during limonene autooxidation (3.09 mol L^{-1} in *n*-decane) (*1—4*) and the oxidation of limonene (1.54 mol L^{-1} in *n*-decane) initiated by $2.0 \cdot 10^{-3}$ mol L^{-1} of PC (*1'—4'*); without additives (*1, 1'*), in the presence of $4.6 \cdot 10^{-2}$ mol L^{-1} of AOT (*2, 2'*), 0.92 mol L^{-1} of water (*3, 3'*), and a mixture of $4.6 \cdot 10^{-2}$ mol L^{-1} of AOT + 0.92 mol L^{-1} of water (*4, 4'*).

In the absence of an initiator, the AOT additives alone have no effect on the oxidation rate (Fig. 3); however, they result in acceleration of the process if microquantities of water are present. Kinetic curve *4* (Fig. 3) is linearized in the coordinates of Eq. (4). In the presence of AOT and water the effective value of $2ek_d$ is increased by an order of magnitude and amounts to $8.5 \cdot 10^{-5}$ L mol^{-1} s^{-1}. Water itself has an accelerating effect, but the O_2 absorption is uneven in the absence of AOT. The kinetic curves are not reproducible, as a rule; delayed induction periods followed by rises and jumps of the pressure in the gasometer are observed. Obviously, the water in the hydrocarbon medium is unevenly dispersed in the absence of a surfactant (water was added just before the experiment), and the sharp changes in the rate are due to the slow and nonuniform process of the establishment of a gasodynamic equilibrium in the system.

The results of measuring the size of particles of the water—AOT—(*n*-decane—limonene, 4 : 1) microemulsion in an oxidized specimen containing 0.1 mol L^{-1} of hydroperoxides was unexpected. Two types of particles with average diameters (*d*) 37 Å and 560 Å are observed in this emulsion, while the average diameter of particles in the micellar AOT solution containing no hydroperoxides is 85 Å.

As is known, the diameter of the particles of water—oil microemulsions stabilized by AOT is mostly determined by the ratio $R = [H_2O]/[AOT]$,[11—13] and is described by the relationship

$$d \approx 2\,(11\ \text{Å} + 1.5[H_2O]/[AOT]), \qquad (5)$$

where the thickness of the AOT shell is 11 Å. According to this equation the ratio $[H_2O]/[AOT] = 5$ corresponds to particles with $d = 37$ Å. The $[H_2O]/[AOT]$ value to a larger extent defines the state of water in reversed micelles and AOT—bound water microemulsions of the hydrate layer and/or free water in the microemulsion core.[11—13]

We studied the state of water in the water—AOT—*n*-decane system by analysing the optical spectra of dyes.[15] The changes in the ratios of the optical density of a water soluble dye, methylene blue (MB), at its absorption maximum (D_{max}, 644 nm) and that at the nearest minimum or shoulder (D_{min}, 614 nm) depending on the $[H_2O]/[AOT]$ ratio at various starting AOT concentrations are represented in Fig. 4. The inflection observed on the curves at $R = 4—6$ becomes more pronounced as [AOT] increases. It has been accepted[11,13] that the inflection is due to a transition from reversed micelles to microemulsions and to the appearance of so-called free water in the central part of the microemulsion particles. Comparing these data and the R values for the

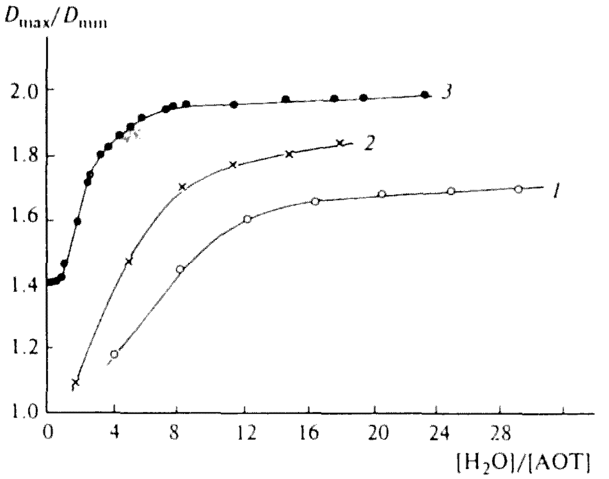

Fig. 4. Dependence of the D_{max}/D_{min} ratio on the relative content of water $[H_2O]/[AOT]$ in a water—*n*-decane microemulsion stabilized by AOT. $[AOT] \cdot 10^2$, mol L^{-1}: 0.8 (*1*); 2.0 (*2*); 20 (*3*). $[MB] = 3.75 \cdot 10^{-5}$ mmol in 2.5 mL of microemulsion.

particles with $d = 37$ Å, one can assume that they are reverse AOT micelles containing merely hydrate water.

The simplest explanation of the results obtained is as follows. AOT forms no common aggregates with hydroperoxides localized in the bulk phase because of the peculiar geometry of its structure, namely the presence of two hydrocarbon fragments. The microemulsion particles serve as micropools of water, which with the ROOH accumulating in the oxidate, goes into the bulk due to secondary bondings with the hydroperoxide groups. Large particles ($d = 560$ Å) with a broad size distribution apparently are the hydroperoxide aggregates "glued together" by water; these aggregates can include other oxidation products (alcohols, ketones) formed, for instance, as a result of recombination of radicals. Water facilitates the formation of aggregates and the radical decomposition of hydroperoxides which eventually manifests itself as an increased oxidation rate.

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