Kinetics of limonene autooxidation

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The kinetic parameters of the oxidizability of limonene, \( k_p/(2k_t)^{0.5} = 6.0 \cdot 10^{-3} \text{ L}^{0.5} \text{ mol}^{-0.5} \text{ s}^{-0.5} \), and of the bimolecular radical decomposition of hydroperoxides \( 2ek_d = 6.0 \cdot 10^{-6} \text{ L} \text{ mol}^{-1} \text{ s}^{-1} \) 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. The oxidation product obtained at moderate temperatures is a mixture of isomeric hydroperoxides whose composition is dependent on the oxidation conditions.

The rate of oxygen absorption \( W_{O_2} \) in the initiated oxidation of limonene is proportional to \( w_1^{0.5} \), which is evidence for the square-law termination of chains. \( W_{O_2} \) increases nonlinearly with increasing \( [\text{LH}]_0 \), i.e., deviates from the known equation (1) of the theory of the liquid-phase oxidation of hydrocarbons:

\[
W_{O_2} = W_{ROOH} = k_p/(2k_t)^{0.5}[\text{LH}]w_1^{0.5},
\]

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, \( w_1 \) is the rate of initiation of the chains.

The value of the effective parameter \( a = W_{O_2}/w_1^{0.5} \), 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 in 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 kinetics. Limonene and n-decane differ markedly in their reactivity in the reactions of free-radical oxidation \( (k_p \text{ and } k_p/(2k_t)^{0.5} \text{ for LH exceed by more than a factor of } 10^2 \text{ the corresponding characteristics for n-decane}) \) 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., Coinbrook Buchs, England) was used without additional purification. n-Decane was purified by standard procedures. The initiator, dicyclohexylperoxydicarbonate (PC), was precipitated 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 \( P_{O_2} = 1 \text{ atm} \)). 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 (2e) have been reliably measured:

\[
k_0 = 10^{13.44} \exp[-124300/(RT)] \text{ s}^{-1}, \quad \text{and} \quad 2e = 1.5.
\]

It follows from the data of Table 1 that \( W_{O_2} \) is proportional to \( w_1^{0.5} \) in n-decane as in chlorobenzene, while the
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., 

\[ W_{O_2} = a \cdot \left[ \frac{W_{ROOH}}{[LH]} \right] \]  

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 \([ROOH]^2\) (bimolecular decomposition of hydroperoxides), and the \( O_2 \) absorption rate is described by Eq. (3).^4^9

\[ \ln(\Delta O_2 + [ROOH]_0) = \ln[ROOH]_0 + \left( \frac{k_p}{(2k_0^{0.5})[LH]} \right) \left( \frac{2k_d}{[ROOH]} \right)^{0.5}, \]  

where \( w_0 \) is the rate of chain initiation, \( 2k_d \) is the effective constant of the rate of the bimolecular decomposition of hydroperoxides. The integral dependence (at \( w_0 < K_{2k_d}^{0.5}[ROOH] \)) corresponds to this equation:

\[ \ln(\Delta O_2 + [ROOH]_0) = \ln[ROOH]_0 + \left( \frac{k_p}{(2k_0^{0.5})[LH]} \right) \left( \frac{2k_d}{[ROOH]} \right)^{0.5}, \]  

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 \( a = 0.6 \cdot 10^{-2} \) \((L^{0.5} \text{ mol}^{-0.5} \text{ s}^{-0.5})\) (see Table 1; for methylcyclohexene in Ref. 4 \( k_p/(2k_i)^{0.5} = 3.5 \cdot 10^{-3} \) \((L^{0.5} \text{ mol}^{-0.5} \text{ s}^{-0.5})\) 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, \( 2k_d = (6.0 \pm 0.2) \cdot 10^{-6} \) \( \text{L mol}^{-1} \text{s}^{-1} \), which is close to the corresponding values for hydroperoxides of other olefins. \(^4\)^9

\[ \frac{W_{O_2}}{[LH]^{0.5}} = \frac{a \cdot [ROOH]}{[LH]} \]  

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

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

\[ \Delta O_2 = \Delta [ROOH]. \]  

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