

The 18-Crown-6-Benzoyl Peroxide–KBr Supramolecular System in the Initiation of Homolytic Chain-Radical Cumene Oxidation

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Abstract—The ability of the benzoyl peroxide–potassium bromide–18-crown-6 system to initiate the liquid-phase oxidation of cumene at 298 K was found. Individual components of the initiating system, as well as the oxidation product (hydroperoxide), do not participate in the initiated oxidation reaction. The rate of initiation was determined using the inhibitor method and by measuring the initial rate of oxidation.

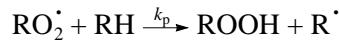
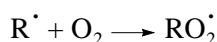
The reactions of hydrocarbon oxidation at low temperatures (near-room temperatures) can take place only in the presence of initiating systems. Presently, the number of known systems of this kind is low; among them are the amine–peroxide systems [1]. The hydroperoxide–transition metal salt systems [2], as well as the hydroperoxide–tetraethylammonium bromide systems [3], are effective at somewhat higher temperatures (70–80°C).

The aim of this work was to study a system that consists of benzoyl peroxide (BP) and potassium bromide as a complex with 18-crown-6 (18C6). This system initiates chain-radical oxidation processes at much lower temperatures than that in the case of a hydroperoxide-containing system.

The liquid-phase reaction of cumene oxidation was performed in a homogeneous medium (acetonitrile–cumene, 1 : 1 by volume) at 298 K. The initial concentrations of the components of this initiating system were 0.05 and 0.005 mol/l for benzoyl peroxide and KBr · 18C6, respectively. A solution of the KBr · 18C6 complex was prepared by dissolving equivalent amounts of the salt and the crown ether in acetonitrile at 298 K for 48 h. The concentrations of bromide anions and peroxides in the reaction medium were monitored by argentometric titration and IR spectroscopy, respectively. Molecular oxygen was an oxidizing agent.

The rate of oxidation was determined from the rate of oxygen consumption at a constant pressure (1 atm). The reaction was performed in a kinetic region, that is, in the region where the rate of oxidation was maximum and independent of the shaking rate of the reaction vessel.

The reaction scheme of the chain-radical oxidation of cumene is the following:



In this case, the rate of oxidation (w_{ox}) is described by the equation [4]

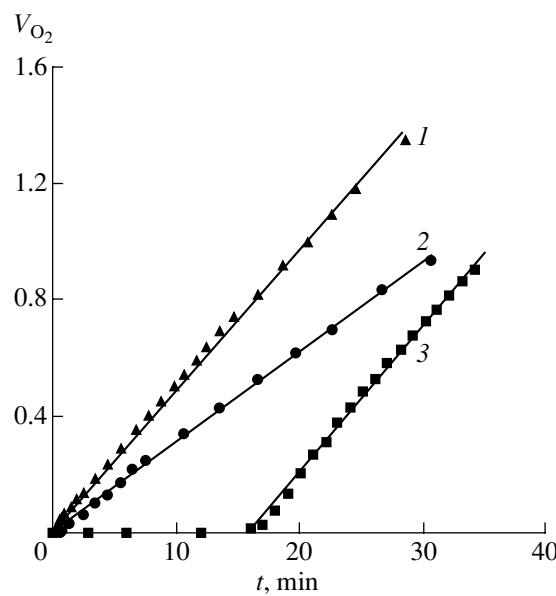
$$w_{\text{ox}} = (k_p / \sqrt{k_t}) [\text{RH}] \sqrt{w_i},$$

where [RH] is the cumene concentration (mol/l); w_i is the rate of initiation; and k_p and k_t are the reaction rate constants of chain propagation and termination, respectively.

We found that cumene was not oxidized in the presence of only the KBr · 18C6 complex at 298 K. This complex did not initiate cumyl hydroperoxide degradation under the experimental conditions, and cumene oxidation was not detected for 90 min.

The addition of benzoyl peroxide and the KBr · 18C6 complex to cumene resulted in the rapid oxidation of cumene at a rate of 1.72×10^{-6} mol l⁻¹ s⁻¹ at 298 K. In the presence of only benzoyl peroxide, the rate of cumene oxidation under these conditions was 0.055×10^{-6} mol l⁻¹ s⁻¹, that is, lower by a factor of 30. Consequently, the combined action of the components of the initiating system is responsible for the effective oxidation even at low temperatures.

The figure demonstrates the kinetic curves of oxygen consumption at 298 K at the following concentrations in acetonitrile: [BP] = 0.05 mol/l and [KBr · 18C6] = 0.05 mol/l or [BP] = 0.05 mol/l and [KBr · 18C6] = 0.005 mol/l. It can be seen that the rate of oxidation remained almost unchanged in the first 30 min, and it depended on the amount of the KBr · 18C6 complex in the supramolecular system.



Volume of consumed oxygen as a function of time for the reaction of cumene oxidation in the presence of the benzoyl peroxide-18-crown-6-KBr system in acetonitrile at 298 K: (1) $[BP] = 0.05 \text{ mol/l}$, $[KBr \cdot 18C6] = 0.05 \text{ mol/l}$, and $[InH] = 0 \text{ mol/l}$; (2) $[BP] = 0.05 \text{ mol/l}$, $[KBr \cdot 18C6] = 0.005 \text{ mol/l}$, and $[InH] = 0 \text{ mol/l}$; and (3) $[BP] = 0.05 \text{ mol/l}$, $[KBr \cdot 18C6] = 0.056 \text{ mol/l}$, and $[InH] = 0.001 \text{ mol/l}$.

The study of the oxidation rate as a function of initial reactant concentrations will be continued.

As in [3], an induction period that appeared on the addition of an inhibitor (α -naphthol) to the reaction mixture demonstrated the occurrence of chain-radical steps in the reaction of cumene oxidation. The induc-

tion period depended on inhibitor concentration, and the rate of initiation by the supramolecular system can be calculated (taking into account that the inhibition efficiency is equal to 2 [5]) as follows:

$$w_i = \frac{[InH]}{t_{ind}} 2,$$

where $[InH]$ is the inhibitor concentration (mol/l) and t_{ind} is the induction period (s).

The rate of initiation was equal to $1.074 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$ at $[BP] = 0.05 \text{ mol/l}$, $[KBr \cdot 18C6] = 0.056 \text{ mol/l}$, and $[InH] = 0.001 \text{ mol/l}$. The contribution of the radical path was 3.8%.

Thus, the crown ether-benzoyl peroxide-KBr supramolecular system is an effective initiator for the chain-radical reactions of low-temperature hydrocarbon oxidation.

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