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Experiment and computer analysis of kinetics in the chemiluminescence oxygen-aftereffect method

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Abstract

The possibilities of the chemiluminescence method of the oxygen aftereffect used for the experimental determination of the rate constant (k_t) of the free-radical oxidation-chain termination during the disproportionation of hydrocarbon peroxide radicals were investigated. The model process referred to the oxidation of cyclohexene in the presence of an initiator. The verification of the method's abilities was carried out by means of computer mathematical modeling using the kinetic scheme of the process consisting of 16 elementary stages. It has been shown that the proposed kinetic scheme of the initiated chain free-radical oxidation adequately describes the process and the experimentally recorded kinetics of the cyclohexene chemiluminescence.

With the help of mathematical modeling, it has been established that the application of the calculation formula for the oxygen aftereffect method for estimating the value of the rate constant of the oxidation-chain termination through the disproportionation reaction of the peroxide radicals of the hydrocarbon under investigation is permissible at the rate constant of the chain-propagation reaction by the initiator peroxide radical exceeding 1 $l{\cdot}mol^{-1}s^{-1}$.

The value of $k_t = 2.8{\cdot}10^6$ $l{\cdot}mol^{-1}s^{-1}$ experimentally acquired at 60 °C for the rate constant of the oxidation chain termination by the disproportionation reaction of cyclohexene peroxide radicals may be considered sufficiently substantiated and recommended for carrying out the kinetic calculations.

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