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# Molecular chemiluminescence of terpinolene

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## Abstract

The chemiluminescence kinetics in a model system of a thermal free-radical oxidation terpinolene was studied at temperatures of 60 and 70 °C and upon the influence of an antioxidant (α-tocopherol). The use of light filters has shown that the chemiluminescence occurs in the blue region of the spectrum, which is characteristic for molecules containing ketone groups in the electronically excited state. The chemiluminescence kinetic curves acquired while introducing in such a model system of a highly active antioxidant tocopherol, differ significantly from the curves in systems with other substrates (e.g., ethylbenzene) so that the moment of introduction of the antioxidant is not followed by an abrupt decrease in luminescence intensity, as it could be due to a fast decrease in the concentration of free radicals. Such kind of kinetics can be explained by a nominal contribution of the free-radical chemiluminescence mechanism into the overall emission intensity in the system. After the introduction of tocopherol into the system, the smooth gradual decrease of the chemiluminescence intensity is observed, which is attributed to the gradual thermal conversion of the intermediate oxidation product (presumably, dioxetane) through a non-radical mechanism to form the electronically excited product subsequently emitting a photon (the molecular chemiluminescence). The gentle decrease in the chemiluminescence intensity continues throughout the induction period, during which the antioxidant (tocopherol) is been consumed, which prevents the development of the chain process through scavenging free radicals. Then, the emission intensity growth resumed at the same rate, which was prior to the introduction of tocopherol into the model system. Kinetic scheme used for computer simulation of the process under present study consists of 18 elementary reactions, and involves the following steps: 1) the emergence of free radicals, 2) propagation of the oxidation chain to form peroxides, 3) branching the oxidation chain through hydroperoxide decomposition 4) isomerization of peroxide radicals into the dioxetane radical, 5) progagation of the oxidation chain to form dioxetanes, 6) termination of the oxidation chain (including a disproportionation of peroxy radicals, accompanied by the chemiluminescence), 7) thermal non-radical decay of dioxetane species followed by molecular chemiluminescence. The used kinetic scheme was sufficient to explain the results, confirming the assumption that the light emission is generated mainly by the molecular (non-radical) mechanism.

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