
General Chemiexcitation Mechanism in Cyclic Peroxide Decomposition

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Abstract

The generation of electronically excited states by a chemical transformation is intimately linked to the chemistry of peroxides, specifically of cyclic peroxides, which moreover are contained in four-membered rings. The concerted decomposition of these compounds, a reverse [2+2] cycloaddition reaction, leads to the formation of two carbonyl fragments, which possess two important properties, they are highly stable due to the strong carbon-oxygen double bond and they contain the carbonyl chromophore. Therefore, peroxide decomposition can be highly exothermic and the carbonyl product be formed in an excited state as this is "energetically accessible". In this contribution, we give a general introduction to the main chemiexcitation mechanisms in cyclic peroxide decomposition and comment on new insights and trends. The unimolecular decomposition of 1,2-dioxetanes occurs with the preferential formation of non-emissive triplet-excited species and different decomposition mechanisms are discussed for this transformation, which is more recently studied mainly by theoretical means. Contrarily, the catalyzed decomposition of 1,2-dioxetanones and similar peroxides occurs with preferential formation of singlet-excited products, although with relatively low efficiency. This transformation occurs by the chemically initiated electron exchange luminescence (CIEEL) mechanism and recent experimental studies indicate the importance of sterical hinderance on charge-transfer complex formation between an activator and the peroxide as reason for its low efficiency. Contrarily, the induced decomposition of 1,2-dioxetanes, which contain an electron rich moiety, proceeds with very high quantum efficiency. It has been shown that this process is initiated by an intramolecular electron transfer from the electro-rich moiety to the peroxide ring and should occur in an entirely intramolecular fashion. The peroxyoxalate reaction, on the other hand, is an extremely efficient chemiexcitation system and has been shown to proceed by an intermolecular CIEEL mechanism; 1,2-dioxetanedione appears to be the most probable high-energy intermediate formed in this transformation.

Keywords: Chemiluminescence, cyclic peroxides, chemiexcitation mechanisms, CIEEL, peroxyoxalate

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