The Chemiluminescence of Molecular Crystals from Organic Peroxides

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Abstract

The core reaction of all known bioluminescence and most organic chemiluminescence reactions is the thermal decomposition of peroxides.[1] These compounds can readily decompose in an exothermic reaction forming excited-state molecules. Upon relaxation to the ground state, the products emit light. Due to the intrinsic instability of the peroxo-group, the chemiluminescence of organic peroxides has been mainly studied in solution. Only few examples in solid state have been reported e.g. by incorporating cyclic peroxides into polymers and visualizing their mechanical properties by luminescence imaging.[2] The details of the solid-state chemiluminescence have remained unexplored thus far.

This has inspired us to investigate the behavior of crystalline cyclic and open organic peroxides upon heating. Since organic peroxides are known to be highly explosive, our target molecules had to be selected while considering safety risks with handling such compounds in large quantities. Moreover, good crystallinity was requested for single crystal x-ray diffraction . Adamantylidene-adamantane-dioxetane (**1**) and Lophine-hydroperoxide (**2**) were ultimately selected as representatives of cyclic- and hydro-peroxides that comply with these requirements. When crystals of (**1**) or (**2**) were heated above 373 K, they started to emit light. This process can be followed spectroscopically, by using luminescence spectroscopy, and in a spatially resolved mode by applying low-light microscopy techniques [3]. Single crystal diffraction analyses as well as luminescence kinetic studies provided insights into the reaction mechanisms and allowed comparison with the analogous reactions in solution.

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