Four-membered cyclic peroxides as carriers of chemical energy

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Abstract

Four-membered ring peroxides, namely 1,2-dioxetanes and 1,2-dioxetanones, have been extensively studied as model systems for chemiluminescence and bioluminescence transformations, as these compounds can be synthesized, purified and characterized. Much of our mechanistic knowledge about chemiluminescence transformations comes from the studies on the decomposition of 1,2-dioxetanes and 1,2-dioxetanones. Additionally, these high-energy peroxides could also have implications in biological systems where the decomposition of cyclic peroxides could lead to the endogenous formation of electronically excited species with possible physiological or pathological functions. This concept was first proposed independently by Giuseppe Cilento and Emil White which called it dark photochemistry, or photochemistry in the absence of light. In this talk, a general historical introduction on this research area will be given and some recent developments of dark chemiexcitation discussed. White and coworkers were able to show that several biologically relevant "photochemical" transformations could be simulated in vitro using 1,2-dioxetane decomposition as the source of triplet-excited species. Whereas, Cilento and coworkers studied the occurrence of excited state formation in several enzymatic transformation and showed that these enzymatically formed triplet excited species could occur in vivo and lead to "dark" photochemical transformations. Some of the most relevant transformations obtained by dark chemiexcitation are: (i) transformation of colchicine into lumicolchicines, initiated by 1,2-doxeten decomposition and peroxidase catalyzed aldehyde oxidation; (ii) formation of pyrimidine dimeres by [2+2] cycloaddition reaction, triplet sensitized through 1,2-dioxetane cleavage; (iii) different photochemical reactions of DNA due to excited state and photochemical reaction initiated by 1,2-dioxetane cleavage, as evidence by the W. Adam research group; (iv) more recently the involvement of cyclic peroxide in melanine photo-toxicity has been evidenced by D. E. Brash and coworkers.

Keywords: Chemiluminescence, cyclic peroxides, 1, 2, dioxetanes, dark chemiexcitation, photobiology without light

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