
Revisiting classical light emitting systems: lophine, peroxyoxalate reaction and luciferin

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Abstract

Chemiluminescence (CL) and bioluminescence (BL) systems can all be described by a very general mechanism: (*i*) reaction between ground state species, (*ii*) generation of a high energy intermediate, (*iii*) formation of electronic excited states and (*iv*) light emission. Even for classical systems, over the years, much has been done in order to refine the rationalization of the processes that compose the overall light emitting transformation. Our research group has been working with classical CL and BL reactions, as to verify if new significant information can be obtained from these, prompting more discoveries and possible applications. Working with the CL of lophines (i.e., 2,4,5-triphenylimidazoles) we have observed that the generation of a 1,2-dioxetane intermediate is really evidenced by kinetic data, although the CL quantum yields of the base-catalysed decomposition of their hydroperoxides is very low (*ca.* 0.000001 E/mol). Such low emission yields would not be expected for the system used for the first description of a CL reaction (Radziszewski, 1877). Moreover, *o*-hydroxylated lophines can be applied at the detection of metallic species, observing the perturbation of the excited state intramolecular proton transfer once that a coordinated compound is generated. We also have successfully applied lophines as activators of the peroxyoxalate reaction, further supporting the nature of the electron transfer step on the chemiexcitation process. With regards to the peroxyoxalate reaction, we have observed that alcohols as solvents deeply affect the kinetics of the interaction between the oxalate ester and H₂O₂, even changing the identity of the rate-determining step. This is of importance, particularly considering studies in aqueous environments. Finally, we investigated the CL kinetics of thiazole-derived esters decomposition in basic media. These can be properly used as analogs to the firefly luciferin, the classical BL system, particularly providing additional information with respect to the involved peroxidic intermediate(s).

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