Mechanistic Investigations of the Chemiexcitation Step of Marine Imidazopyrazinones

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Abstract

The imidazopyrazinone core is a common link among the substrates of marine organisms of eight *phyla*, being present in known chemi-/bioluminescent substrates, such as Coelenterazine, *Cypridina* luciferin, Coelenterazine disulfonate and dehydrocoelenterazine. The elucidation of the mechanism behind chemiexcitation of marine imidazopyrazinones is essential for future applications in bioimaging, biomedicine and bioanalysis.
Here, we analyze the details of the chemiexcitation mechanism for these molecules by using a combined experimental and computational approach. The energy and kinetic profiles of these reactions were obtained with luminometric and spectroscopic methods, which demonstrated that the reaction rate and light intensity have an opposite pH-dependent behavior: whereas the reaction rate increases with increasing pH, the intensity of emitted light decreases with increasing pH.

Electronic structure calculations allowed us to correlate lower reaction rates with the thermolysis of neutral dioxetanone, due to higher activation energies. The higher light production at lower pH was also attributed to the thermolysis of neutral dioxetanone, as this species has access to a long region of the potential energy surface (PES) where the ground and excited states are degenerated, contrary to the anionic species. Contrary to expected, there was not found any clear relationship between electron (ET)/charge (CT) transfer (occurring between the electron-rich moiety and dioxetanone) and chemiexcitation, which cast some doubts in the use of either CIEEL or CTIL theories to explain imidazopyrazinone-based chemiexcitation.
Finally, it was found evidence to support that attractive electrostatic interactions between the CO2 and oxyluciferin moieties allow neutral dioxetanone to spend time in the PES region of degeneracy, while repulsive interactions for anionic dioxetanone lead to a quicker CO2 detachment.

Keywords: Chemiluminescence, Dioxetanone, Coelenterazine, Cypridina Luciferin, Imidazopyrazinones, Density Functional Theory, Luminometry

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