Dynamical insights in the chemiluminescent decomposition of 1,2-dioxetane

Morgane Vacher[1], Anders M. Brakestad[1], Hans O. Karlsson[1], Ignacio Fdez. Galván[1], and Roland Lindh[1]

[1] *Department of Chemistry – Angström, Uppsala University, Uppsala, Sweden*

E-mail: morgane.vacher@kemi.uu.se

Chemiluminescence is the emission of light as a result of a chemical reaction. One the simplest molecules with chemiluminescent properties is 1,2-dioxetane. The basic understanding of today is that a thermally activated molecule decomposes and by doing so, it undergoes a non-adiabatic transition to an electronic excited state of the product, which then releases the excess energy in the form of light (Fig. 1).[1] While the yield of the chemiluminescent process is observed to be low in 1,2-dioxetane (approximately 0.3%), it increases to 35% by substituting the hydrogen atoms by methyl groups (Fig. 2). To understand and rationalise the experimental observations, time and efforts were until now devoted to theoretically investigate reaction mechanisms by computing cuts of potential energy surfaces and identifying critical points and pathways.[2,3]

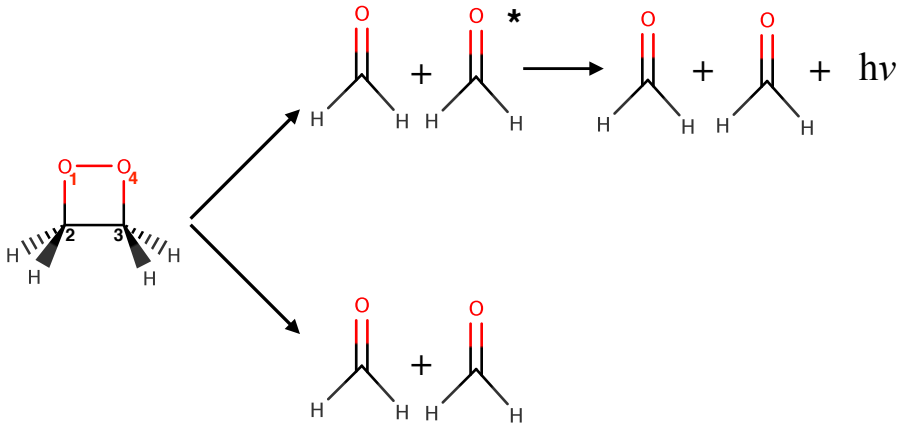

Figure 1: Dark and chemiluminescent decompositions of 1,2-dioxetane into two formaldehyde molecules.

In this work, we aim to provide a more realistic description of the chemiluminescence mechanism by simulating the actual dynamics of the system, i.e. how the nuclei and electrons move with time during the process.[4] To do so, we use "on-the-fly" methods to simulate Born-Oppenheimer and non-adiabatic dynamics of the decomposition reaction of 1,2-dioxetane and the methyl-substituted compounds. We propose a simple model to explain the increase in chemiluminescence yield upon methyl-substitution: by spending more time in the so-called "entropic trap" region where a manifold of states are degenerate, more population is transferred into the excited state of the product before dark decomposition occurs.

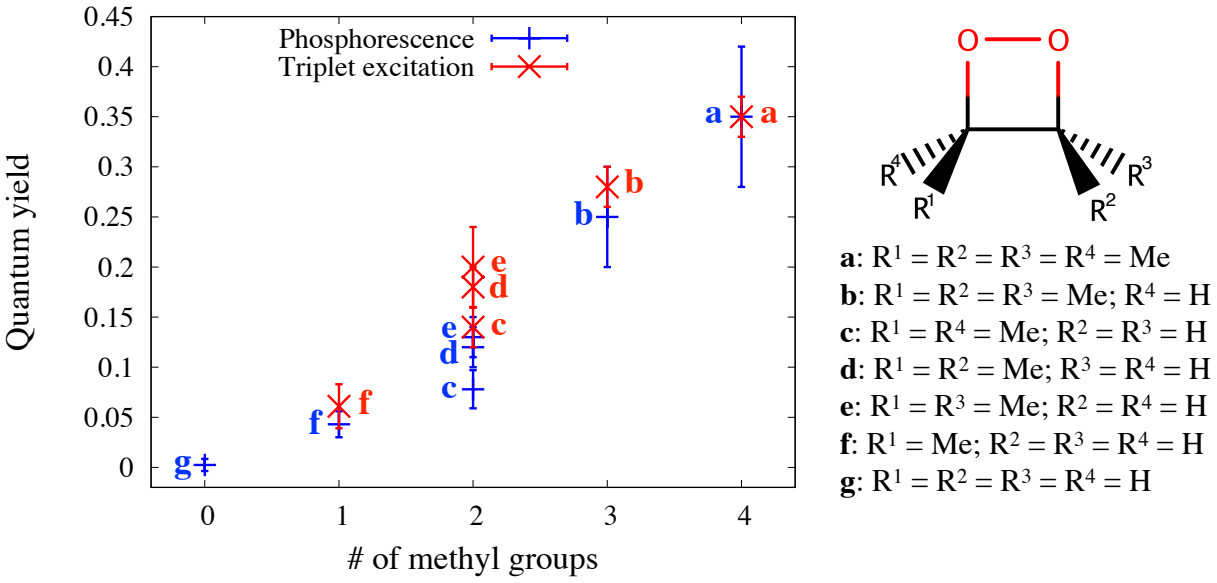

Figure 2: Measured phosphorescence (blue bar) and triplet excitation (red cross) yields upon decomposition of dioxetane molecules.

Funding: Swedish Research Council (Grant No. 2012-3910).

Acknowledgements: The simulations were performed on resources provided by the Swedish National Infrastructure for Computing (SNIC) at UPPMAX and NSC centers.

References:

[1] I. Navizet, Y.-J. Liu, N. Ferré, D. Roca-Sanjuán and R. Lindh, *Chem. Phys. Chem.*, **2011**, 12, 3064-3076.

[2] L. De Vico, Y.-J. Liu, J. W. Krogh and R. Lindh, *J. Phys. Chem. A*, **2007**, 111, 8013-8019.

[3] P. Farahani, D. Roca-Sanjuán, F. Zapata and R. Lindh, *J. Chem. Theory Comput.*, **2013**, 9, 5404-5411.

[4] M. Vacher, A. M. Brakestad, H. O. Karlsson, I. Fdez. Galván, and R. Lindh, *Submitted.*