Asynchronous concerted mechanisms: coupling the reaction force constant and ELF / QTAIM analyses to locate primitive processes

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Many chemical reactions can involve either a stepwise or a concerted mechanism (synchronous or asynchronous). For some of them, it is possible to progressively switch from one type of mechanism to the other by modifying certain parameters of the reaction: nature of the solvent, nature of the substituents, intensity of a correctly oriented external electric field. This is the case, for example, with Diels-Alder and double proton transfer (DPT) reactions, which are the focus of this study.

For Diels-Alder reactions, we played on the nature of the diene and dienophile substituents to modify the reaction mechanism. For DPT reactions, we played on the strength of an external electric field oriented along the proton transfer direction, [1] in accordance with the reaction axis rule.[2]

To better understand the gradual transition from one type of mechanism to the other, we followed the evolution of the reaction force[3] (F) and reaction force constant[4] (κ) along the intrinsic reaction coordinate. We compared these evolutions with those of ELF or QTAIM descriptors adapted to describe the processes involved in these 2 types of reaction.

It appears that the minima of the reaction force constant (global quantity) correspond to particular points in the reaction profiles of the ELF / QTAIM descriptors (local quantities) (see Figure 1). This suggests that by coupling the 2 types of analysis, we can quantify the degree of asynchronicity of concerted mechanisms.

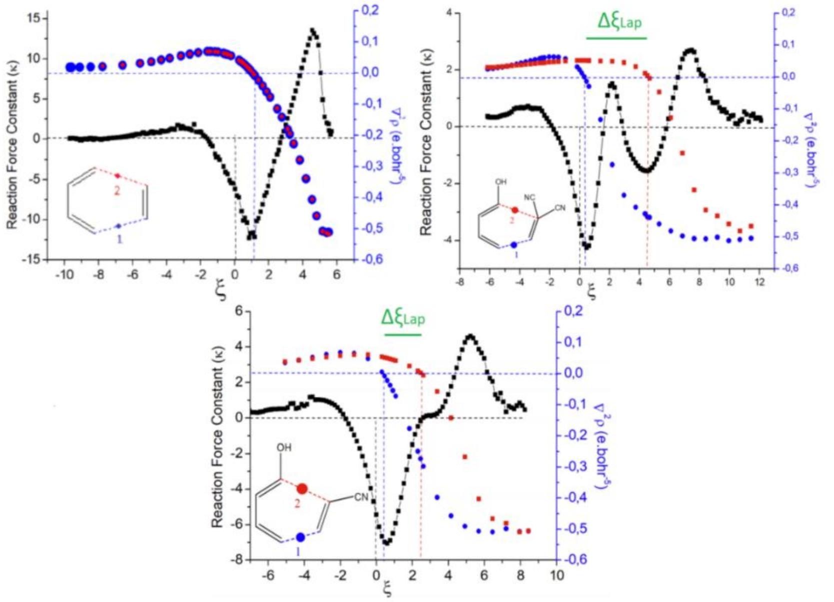

Figure 1. Superposition, for 3 Diels-Alder reactions, of the reaction force constant profile (black) and that of the Laplacian of electron density computed at the bond critical points of the two C-C bonds formed during the reaction (red and blue)

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