

Asynchronous character of concerted mechanisms: decomposition into primitive processes

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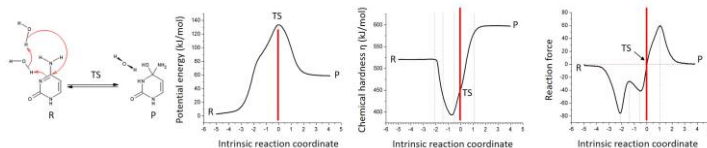


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Abstract

Some concerted mechanisms result from the combination of several simple processes in a very asynchronous manner. Some years ago, we proposed that such elementary reactions were characterized by peculiarities in their reaction profiles (e.g. shoulder in the potential energy profile, maximum in the hardness profile shifted with respect to the transition state, more than 2 extrema in the reaction force profile ; see Figure). [1]

On the other hand, several theoretical studies have shown that the use of an external electric field could affect the reaction rate but also the selectivity of a given reaction by modifying its mechanism. [2,3]



Here we propose to apply an external electric field to control the asynchronous character of simple concerted mechanisms and decompose them into primitive processes. The objective is to study to what extent these primitive processes follow reactivity principles such as the Maximum Hardness Principle [4] more than their parent concerted mechanisms.

Reference and notes

[1] V. Labet, et al *Physical Chemistry Chemical Physics* 2010, 12, 4142-4151.

[2] S. Shaik, et al *Nature Chemistry* 2016, 8, 1091-1098.

[3] A.C. Aragonès, et al *Nature*, 2016, 531, 88-91.

[4] A.K. Chandra and T. Uchimaru, *Journal of Physical Chemistry A*, 2001, 105, 3578-3582.

