Chemical Reactions with two different elementary Transition States – Crypto Three-State System. Photo-/ Thermo-chemical aspects and VB rationalization.

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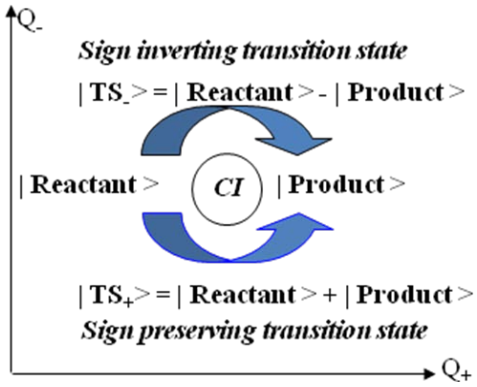
It is commonly assumed that the chemical reaction is determined by the unique transition state (TS), and the two-state approach is a basic model for the analysis of the chemical reaction. However, during the last 10 years, various examples of chemical reactions with two different TSs were reported.[1] Lucid VB arguments allow to identify reactions with two different TSs as a crypto three state system, where the Reactant and the Product are defined by the combinations of the three dominant VB structures.



2D domain based on the two minima - the Reactant (**R**) and the Product (**P**), which are connected by two different TSs can include the S_0/S_1 conical intersection according to the Longuet-Higgins theorem.[2] This is a situation which constitutes a necessary and sufficient condition for a photochemical reaction bearing a single product.[3]
Two different transition states detected (on the CAS level of calculation) for the cis-trans isomerization around polar double bonds, azo-compounds, charge shift in aliphatic radical-cations, conjugated radicals, H atom *vs.* proton-coupled electron transfer *etc*..
Symmetry allowed reactions have the $\mathbf{TS}_+$=(**R+P**). Symmetry forbidden reactions served by $\mathbf{TS}_-$=(**R-P**) which is a preferable route (lower barrier) in some of studied cases.
The principles of the design of *crypto three-state system* are represented for both types of systems – with two different and two equivalent TSs. The electronic mechanisms leading to the chemical reaction with two TSs are described.
The reduction in rate due to non-adiabatic recrossing near the conical intersection[4] is discussed in connection with a different types of the reactions with two TSs.

[1]] Zilberg S., Haas Y., *JACS*, 125:1810, 2003; Zilberg S., Haas Y., *Photochem.Photobiol Sci*., 2:1256, 2003; De VikoL., Garavelli M., Bernardi F. & Olivucci M., *JACS*, 127:2433, 2005; Tishchenko O., Truhlar D., Ceulemans A. & M-T. Nguen, *JACS*, 130:7000, 2008; Gozem S, ShapiroI, Ferre N. & Olivucci, *Science*, 237: 1225, 2012.
[2] Longuet-Higgins, H. C., *Proc Roy Soc London, A*, 344:147, 1975.
[3] Haas Y., Cogan S. & Zilberg S., *Int. J. Quantum Chem.*, 102: 961,2005.
[4] Butler L.J., *Annu. Rev. Phys. Chem*., 49:125, 1998.