

# Assessment in the competition between steric and electronic effects in the elimination kinetic of hydrogen in 1,4-cyclohexadienes in the gas phase. Quantum chemical theory calculations.

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1,4-Cyclohexadienes may undergo to a unique pericyclic reaction where a molecule of hydrogen is eliminated and an aromatic system is formed. Previous experimental investigations led to several authors to propose that the rate coefficients of this reaction depend in the stability of the reactants. However, there is not a clear idea about the influence of electronic and steric effects in the mechanism of these reactions. Theoretical calculations on the kinetic of hydrogen elimination of seven cyclohexadienes substituted with alkyl groups in the positions of 1, 2, 3 and 6 in the ring by using the levels of theory MP2 y DFT (B3LYP, MPW1PW91, PBEPBE,  $\omega$ B97XD, CAM-B3LYP, M06 y M062X) methods with different basis sets were carried out. Kinetics, thermodynamic parameters, transition state geometry, NBO charges and Wiberg bond indexes and Synchronicity parameter of these reactions were determined in the evaluation of these transformations. The results of the MPW1PW91/6-31++G(d,p) and MP2/6-31G(d,p) level of theories agree reasonably with the experimental values, especially in the case of MPW1PW91 functional. The analyses of the evolution of distances and bond angles during the process of the reaction, and the charges obtained from the natural orbitals NBO indicated that the reaction is controlled by a subtle equilibrium between electronic and steric factors. The steric factors are related in favoring the approach of the reactive hydrogens of the molecule. This appears to derive from the stabilization of the boat structure where the reactant must acquire before eliminating H<sub>2</sub>, or through a distortion of the H-C-H angles. On the other hand, the electronic effects show variation in the charges with respect to the symmetric elimination of hydrogen, thus favoring the simultaneous breaking of  $\sigma$ C-H. Depending on substituent, steric acceleration (Me and Et substituted at carbons 1 and 2), or steric and electronic accelerations (Me substitution at carbons 3 and 6), or steric hindrance (3 bridged carbon bonded at 1 and 2) may occur.