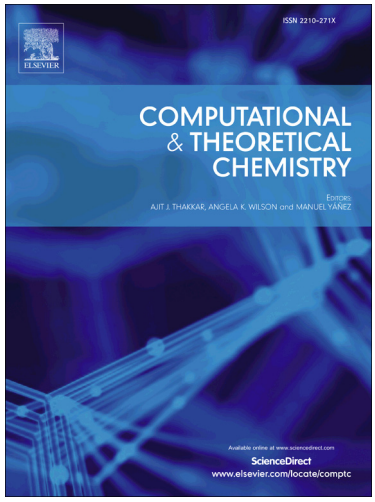


Theoretical calculations on the mechanism of the elimination kinetics of allyl cyclohexyl-, -amine, -sulfide, -ether, and allyl ethyl ether in the gas phase

Solanged Espinoza, Jesus Lezama, José R. Mora, Tania Cordova, Gabriel Chuchani

PII: S2210-271X(16)30182-7
DOI: http://dx.doi.org/10.1016/j.comptc.2016.05.010
Reference: COMPTC 2144

To appear in: *Computational & Theoretical Chemistry*

Received Date: 21 April 2016
Revised Date: 16 May 2016
Accepted Date: 16 May 2016

Please cite this article as: S. Espinoza, J. Lezama, J.R. Mora, T. Cordova, G. Chuchani, Theoretical calculations on the mechanism of the elimination kinetics of allyl cyclohexyl-, -amine, -sulfide, -ether, and allyl ethyl ether in the gas phase, *Computational & Theoretical Chemistry* (2016), doi: http://dx.doi.org/10.1016/j.comptc.2016.05.010

Theoretical calculations on the mechanism of the elimination kinetics of allyl cyclohexyl-, -amine, -sulfide, -ether, and allyl ethyl ether in the gas phase

Solanged Espinoza[a], Jesus Lezama[a], José R. Mora[b], Tania Cordova[c], Gabriel Chuchani[d*]

[a] *Departamento de Química, Escuela de Ciencias, Universidad de Oriente Núcleo Sucre, Cumana,Venezuela*

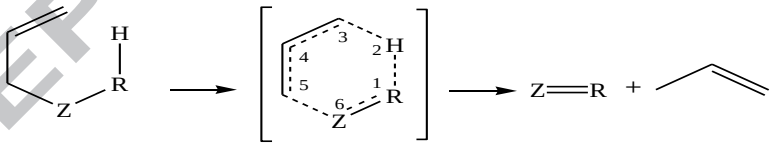
[b] *Departamento de Química, Universidad de San Francisco de Quito, Quito-Ecuador*

[c] *HyperCube, Inc., Gainesville. Florida. 32610, U.S.A.*

[d] *Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas1020A, Venezuela*

ABSTRACT

The mechanism of the gas-phase elimination allyl cyclohexyl amine, allyl cyclohexyl sulfide, allyl cyclohexyl ether, and allyl ethyl ether has been studied by using *ab initio* combined methods CBS-QB3, and Density Functional Theory CAM-B3LYP, MPW1PW91, PBE1PBE, M06, and M062X. Products formation is described below:



Z = NH, O, S
RH = C_6H_{11}, C_2H_5

Theoretical calculations of these reactions support the unimolecular process of these gas-phase eliminations. These thermal decompositions undergo a retro-ene type of mechanism and proceed through a non-planar concerted six-membered cyclic transition structure. The energy of activation follow the order allyl ethyl ether (187.0 kJ/mol) > N-allyl cyclohexyl amine (171.7 kJ/mol) > allyl cyclohexyl ether (170.5 kJ/mol) > allyl cyclohexyl sulfide (137.9kJ/mol). The polarization of C_5-Z_6 bond, and the electronegativity of the heteroatom (O, N) increases the reaction rate compared to allyl ethyl ether. Conversely, the S atom is positively charged and its electronic effect causes a high dissymmetry in the TS geometry,