

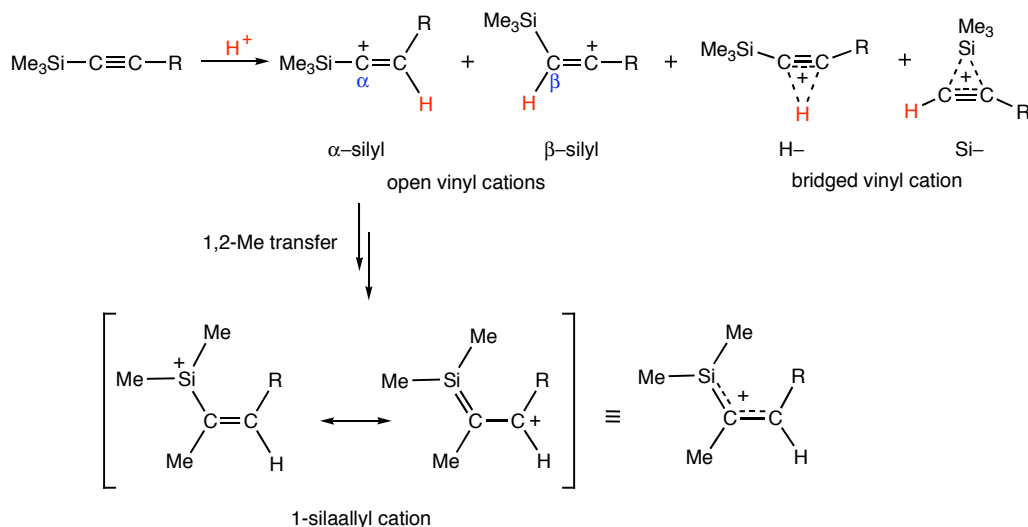
Computational study of the isomerization of silyl-substituted vinyl cations

Helena Čičak and Zlatko Mihalić

Laboratory of Organic Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia

Recently, silyl-substituted unsaturated carbocations have been invoked as intermediates in the formation of neutral silylated products arising from the reaction of radiolytically formed Me_3Si^+ with alkynes in a gaseous medium at atmospheric pressure.¹ FT-ICR results has testified that equivalent cationic adducts, which are generated by protonation of trimethylsilylacetylenes, may store enough internal energy to dissociate to reagents and/or to undergo isomerization.²

The aim of this work is to explore the part of the potential energy surfaces of silyl-substituted vinyl cations $\text{Me}_3\text{SiC}_2\text{RH}^+$ ($\text{R} = \text{H}, \text{Me}, \text{SiMe}_3$), which includes vinyl and silaallyl isomers and related transition structures, by quantum-chemical calculations.



Our investigation has shown some new characteristics of these potential energy surfaces, not previously observed for $\text{H}_3\text{SiC}_2\text{H}_2^+$,³ which include new structural isomers (minima) and strong dependence of calculation method and/or basis set used.

- [1] B. Chiavarino, M. E. Crestoni and S. Fornarini, *J. Am. Chem. Soc.*, **120** (1998) 1523.
 [2] B. Chiavarino, M. E. Crestoni and S. Fornarini, *Chem. Commun.*, (2002) 1418.
 [3] A. E. Ketvirts, D. K. Bohme and A. C. Hopkinson, *J. Phys. Chem.*, **98** (1994) 13225.