

Theoretical study of the methylic reactivity of substituted alkenes

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Abstract

A PM3/UHF study of the methylic reactivity of a series of about fifty alkenes was carried out. Several MP2/6-31G** *ab initio* calculations were made for comparison. The semi-empirical method of calculation is proven to give good estimates of the reactivity under consideration. The computations brought to light the reactivity enhancement of alkenes when substituted on the same carbon of the double bond, whereas a lessening is observed when both carbons are substituted. An interpretation in terms of deformation (DEF) and interaction (INT) energies is made. Contrarily to phenyl, the vinyl group improves notably the reactivity of methylated and chlorinated mono or disubstituted alkenes. The prediction is made for the reactivity of more than fifteen compounds which were not studied experimentally. © 1998 Elsevier Science B.V.

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1. Introduction

The radical addition to ethylenic systems was the subject of numerous experimental [1–7] and theoretical investigations. Several *ab initio* calculations [8–19] more or less sophisticated were reported, in particular the works of Arnaud et al. [16,17], and Delbecq et al. [18], where the Morokuma energy decomposition analysis [20,21] was applied to elucidate the question of radical addition orientation. These authors suggest that the regioselectivity of this process is governed by the deformation energy of the reactants required to attain the transition state structure. In the same way, Canadell et al. [19] present a discussion on the origin of the anomalous regioselectivity of CH_3 on $\text{CF}_2=\text{CHF}$ and of the exceptions to the SOMO-HOMO rule. However, the major part of

these *ab initio* calculations are devoted to radical addition to acetylene or to ethylene, except for the recent works of Arnaud et al. [22] concerning CH_3 , CF_3 and OCH_3 addition reactions to substituted olefins, and Wong et al. [23–25] who studied the addition of methyl radical to monosubstituted alkenes. Until now, the number of studied compounds was very limited, because *ab initio* calculations are very time consuming. In a previous work [26], we applied the PM3 [27] and AM1 [28] semi-empirical methods, at the UHF and RHF levels to the study of the methylic reactivity of ethylene, butadiene, acrylonitrile, methyl acrylate, vinyl chloride and benzene. This study showed that PM3/UHF is the most appropriate semi-empirical technique for the study of methyl addition to alkenes, and that it leads good agreement with experiment.

In the present article, firstly we extend the PM3/UHF semi-empirical study of the radical methyl addition to a large series of unsaturated compounds of the

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