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Theoretical study of chemical reactivity of the main species in the α-pinene isomerization reaction

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Abstract

α-Pinene is an important chemical raw material for products widely used in perfumery, pharmaceutical and other applications. The main industrial processing of pinene is the acidic isomerization reaction to produce camphene. Density functional theory calculations were used to obtain the quantum-chemical descriptors for the theoretical analysis of the reactivity of pinene and its main compounds that are formed under the reaction conditions in order to compare with experimental results and establish new ideas on how to improve the camphene yield. These calculations were done in Gaussian 03W using TPSS/TPSS and 6-31+G (d,p) basis set and PBE/DND with the DMol3 module incorporated in Materials Studio 4.1.

Keywords: α-pinene; Camphene; Reactivity; DFT

1. Introduction

The isomerization of pinene to produce camphene has been the subject of intense research, mainly with the objective to improve catalytic systems [1–5] industrially, the isomerization is performed with acid catalysts. Currently the used catalyst is TiO_2 acidified with H_2SO_4, which must be prepared "*in situ*" since this catalyst is not available commercially [1]. Typical yield of camphene is around 35–45%, so the challenge for this reaction is to improve the selectivity. Fig. 1 presents the reaction paths from pinene to *p*-cymene through the intermediate species. *p*-Cymene and heavy compounds are the more stable species in the reaction chain, but generally both are undesirable species.

The main products from α-pinene isomerization are obtained by two routes, one produces bi and tricyclic compounds like camphene, tricyclene and Δ^3-carene and the other route gives monocyclic compounds like limonene α-terpinene, γ-terpinene and terpinolene. This depends on the specific formed cation evolving after protonation of the α-pinene molecule. According to previous experimental work, besides α-pinene, camphene, limonene and α-terpinene, the reaction products include undesirable compounds like *p*-cymene, tricyclene and heavy weight compounds which together can amount more than 50% of the final products. Limonene formation is significant and once this molecule is formed, there is no possibility to transform it to camphene and only other monocyclic like α-terpinene, γ-terpinene, terpinolene and *p*-cymene can be produced. α-Terpinene can reach 20% of concentration during reaction and limonene and α-terpinene, during some stages of reaction can reach 50% of concentration [1]. Thus, the

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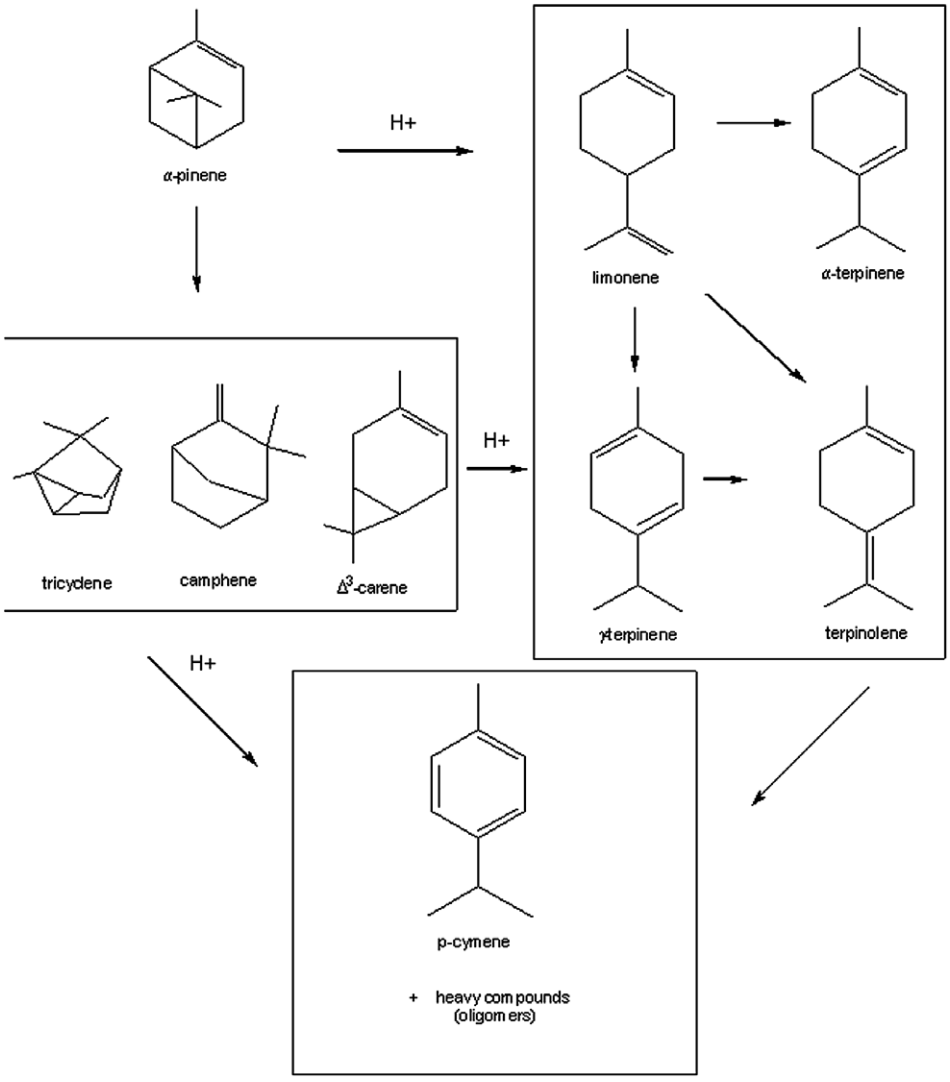

Fig. 1. Reaction paths of α-pinene.

understanding of reactivity of these two compounds can be useful to design new strategies to suppress or minimize its transformation and promote the camphene production. Information about the camphene reactivity could also be useful to propose strategies to inhibit its transformation to other compounds.

Taking in account the work of Ebmeyer [6] about that catalytic rearrangement as a key step in the production process, we also studied the energetically most favorable formation of the cations that are considered in the reaction pathway for the formation of monocycles, bi and tricycles. These are the pinayl, isobornyl and *p*-menthenyl cations. Fig. 2 shows the transformation scheme of α-pinene.

The reactivity of a molecular system can be studied from its electronic density or its electrostatic potential. The specific reaction sites in a molecule can be determined through local reactivity descriptors such as Fukui indexes ($f(\vec{r})$). The dependence of these locally values on the reaction coordinates makes these parameters useful for the prediction of the selective sites of a chemical reaction [7]. The analysis of reactivity descriptors was done by means of the density functional theory [8] using Gaussian 03 [9] and Materials Studio 4.1 [10], with the DMol3 module [11,12].

2. Theory and computational details

The density functional theory (DFT) provides a convenient conceptual reference for performing calculations of quantum-chemical parameters related to the global reactivity of a system, as well as the quantities that describe intermolecular reactivity or the selective sites of a molecule.

Global reactivity descriptors are important tools for obtaining information about the reactivity and stability of molecular systems [13]. In this work, the global chemical reactivity was determined by applying the following concept of electronegativity (χ) [14]:

$$\chi = -\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \tag{1}$$