



A theoretical study of the carbocation formation energy involved in the isomerization of α -pinene

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ABSTRACT

α -Pinene isomerization starts with the formation of the pinanyl carbocation, which then undergoes rearrangement into two different isomers. One isomer yields monocyclic rings as final products, such as limonene, α -terpinene, and terpinolene while the other isomer yields bicyclic compounds, including camphene. In this Letter, a computational study is carried out in order to find the optimal temperature and solvent for the promotion of the second path considering that the bicyclic compounds are of greater economical interest. The energies of formation of the carbocations at different temperatures were calculated in vacuum and in solvents using the PBEPBE/6-31+G(d,p) model chemistry.

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1. Introduction

Monoterpenes such as α -pinene are chemical compounds of economic significance for the pharmaceutical and perfume industries. Camphene particularly, an intermediate in camphor production [1,2]. The industrial isomerization of these compounds is usually performed with the help of acidic catalysts, also α -pinene conversion increases by acid treatment [3]. Currently, the catalyst of choice is TiO_2 acidified with H_2SO_4 , prepared 'in situ' because of commercial unavailability [4]. Camphene yields range from 35% to 45%, and an improvement in reaction selectivity is necessary.

α -Pinene isomerization starts with the formation of the pinanyl carbocation [5], which then undergoes rearrangement into two different isomers. One isomer yields monocyclic rings as final products, such as limonene, α -terpinene, and terpinolene. The other isomer yields bicyclic compounds, including camphene. The reaction pathway of α -pinene isomerization has been proposed by Allahverdiev et al. [6] and is shown in Figure 1. The box in Figure 1 is showing the energies of reaction calculated for the formation of isobornyl (ΔG_1) and menthenyl (ΔG_2) carbocations from pinanyl.

This Letter aims to establish the optimal temperature and solvent settings to promote camphene production and to inhibit the formation of monocyclic rings using theoretical methods, specifically by the determination of the carbocation formation and reaction energies of pinanyl, isobornyl, and *p*-menthenyl, both *in vacuo* and in solution, and under different temperatures.

2. Computational details

Carbocation conformations were optimized, and the geometry of minimum energy was found using the density functional theory (DFT) feature in GAUSSIAN 03 [7], the functional PBEPBE [8], and the 6-31+G(d,p) basis set. Frequencies were computed after the conformation optimization step, and thermodynamic quantities were obtained, including the formation energies for the main carbocations involved in α -pinene isomerization. Finally, values for the free energy were updated after the calculation of the thermal correction at different temperatures.

This procedure was performed *in vacuo* and was later repeated with octane and *p*-xylene as solvents. The polarized continuum model (PCM) was employed taking into account the IEF-PCM approximation (Integral Equation Formalism–Polarized Continuum Model) [9] because this generic approximation allows for the treatment of any solvent.

3. Results and discussion

According with the relevance of selectivity in the formation of the isobornyl and *p*-menthenyl cations, the energies of formation at different temperatures were obtained for each of the cations involved in this step of the process. Previously it was found by Allahverdiev and co-workers [10] that the selectivity is virtually independent of pressure and temperature, although the reaction rate depends on these parameters, but, in this work pinanyl was found to be the least stable, followed by *p*-menthenyl, and isobornyl was the most stable. The difference in the formation energy

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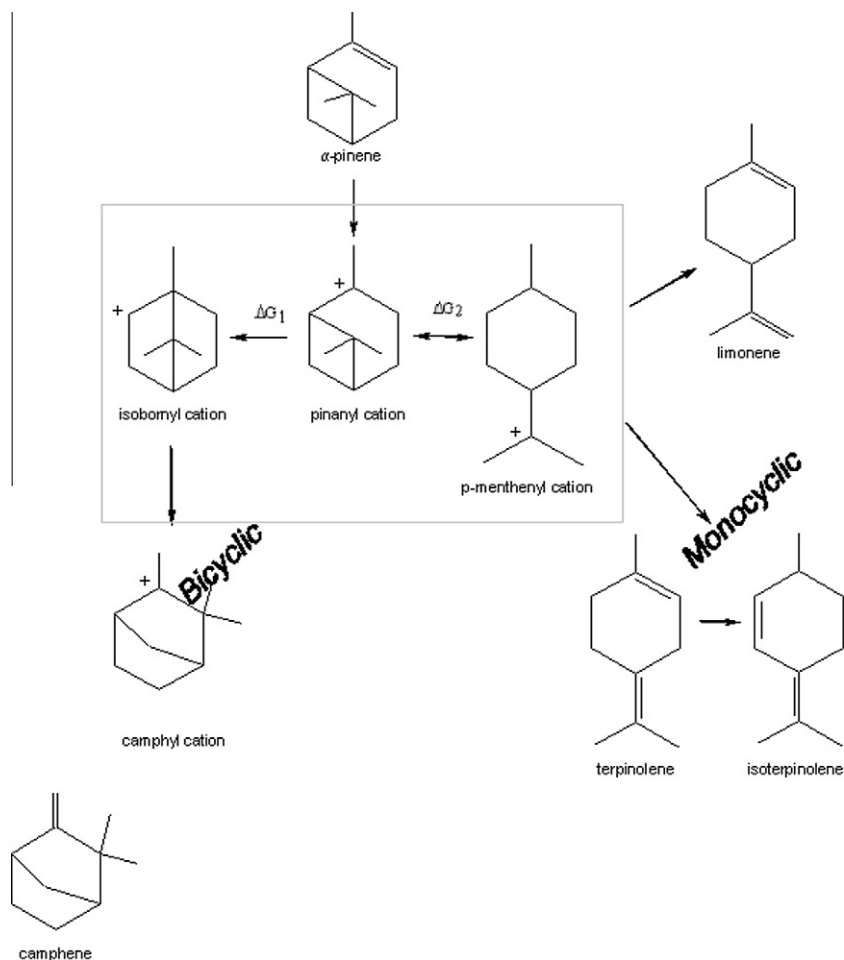


Figure 1. α -Pinene reaction pathway and energies of reaction calculated for the formation of isobornyl (ΔG_1) and menthenyl (ΔG_2) carbocations.

between pinanyl and isobornyl was 8 kcal/mol while 5 kcal/mol was the difference relating pinanyl and *p*-menthenyl for *in vacuo* calculations, as shown in Figure 2. These relations were conserved for calculations in solvent media.

In experimental works was found that main transformations of α -pinene were thought to occur through addition of H^+ to α -pinene

with the formation of a pinylcarbonium ion, which is the sole precursor for all products [11]. Considering that monocyclic and bicyclic ring production is defined in this step of the process, so the reaction energies of formation for isobornyl (ΔG_1) and *p*-menthenyl (ΔG_2) were analyzed. The temperature dependence of the reaction energies is shown in Figure 3 for calculations performed both

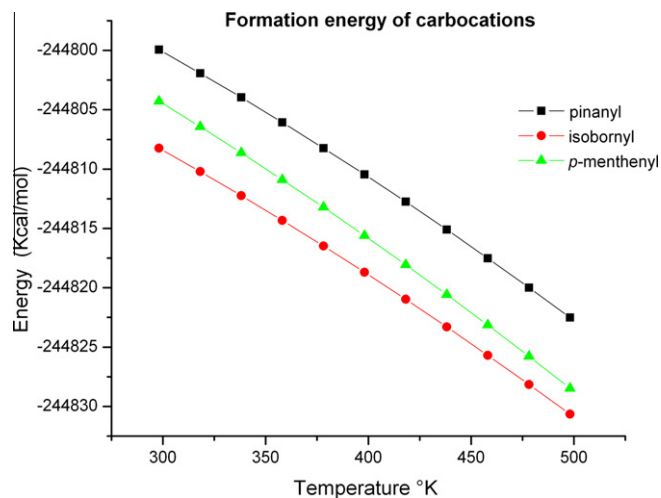


Figure 2. Formation energies for isobornyl and *p*-menthenyl cations derived from pinanyl.

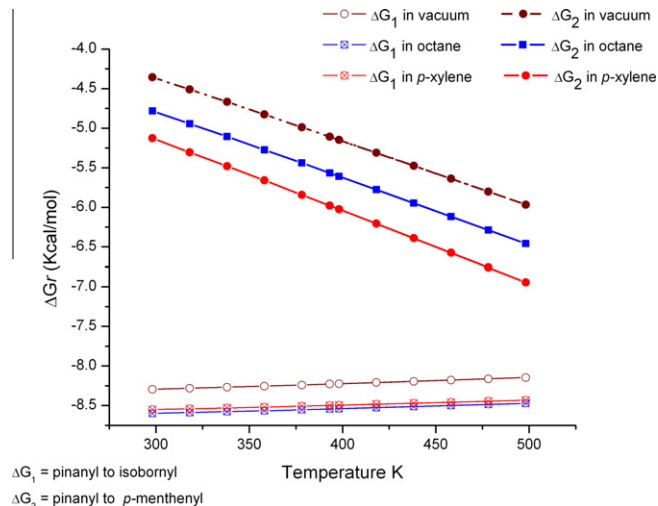


Figure 3. Temperature dependence of the free energies of reaction for carbocation formation.

in vacuo and in solution. The difference in the reaction energies, $\Delta G_2 - \Delta G_1$, decreases as the temperature increases based on calculations performed under the assumption of both *in vacuo* and in-solution conditions.

The effect of temperature on the reaction results decreases the difference in the reaction energies of the cation formation. Atalaya and Gündüz found that the selectivity of camphene was increasing with catalyst supported on natural zeolite without heat treatment. The experiments were carried out at constant temperature of 373 K [12]. This confirms the need for more active catalytic methods than the conventional one based on TiO_2 .

An analysis of the reaction energies shows that the formation of the isobornyl cation is thermodynamically more stable than the formation of *p*-menthenyl by 3.9 kcal/mol *in vacuo*. However, this difference in the energies of reaction is diminished when in the presence of the studied solvents.

4. Conclusions

Ebmeyer et al. have reported that the formation of isobornyl and *p*-menthenyl are equally favorable (1.8 kcal/mol) [5]. In this Letter, the formation of the isobornyl cation was 4.06 kcal/mol and was more favorable than the formation of *p*-menthenyl.

The reaction should be performed at a lower temperature. According to the results found in this work, the catalysis that promotes the reaction at lower temperatures will result in a higher selectivity toward the product of greater commercial interest, i.e., camphene.

The presence of the solvent facilitates formation of the *p*-menthenyl cation, although it also favors the formation of the isobornyl cation. Hence, the reaction can be performed without the presence of a solvent.

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