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Thermochemistry of monoterpene β-ocimene

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Abstract: Monoterpenes are the second group of volatile organic compounds (VOC) most emitted into the atmosphere by biogenic sources.[1,2] The atmospheric decomposition reaction can lead to the formation of O_3, which in the troposphere is a greenhouse gas. [3] However, there is not much information on the properties of monoterpenes present in the atmosphere, being necessary further investigations. The β-ocimene is a monoterpene having two stereoisomeric forms, *trans*-β-ocimene ((E)-3,7-dimethyl-1,3,6-octatriene) and *cis*-β-ocimene ((Z)-3,7-dimethyl-1,3,6-octatriene) to whom, according to our knowledge, there are not studies on its structural and thermochemical properties. Thus, in this study, we have characterized structurally and determined the thermochemical properties of the *trans*-β-ocimene and *cis*-β-ocimene. Conformational analyses were performed to obtain the most stable conformation for the stereoisomers of β-ocimene. Geometric optimization and harmonic vibrational frequency calculations were done at the MP2/6-311G(d,p) level of theory. Single point calculations were also carried at the MP2/cc-pVDZ, MP2/cc-pVTZ e MP2/cc-pVQZ, with the objective of approaching of a complete basis set (CBS) limit. In order to obtain a high level of electronic correlation, were also performed single point calculations at the QCISD(T)/6-311G(d,p) level of theory, from which, through the use additivity approximation, the QCISD(T)/CBS level of theory was obtained. For the determination of the thermodynamics properties, isodesmic reactions were used, in which the values of the standard enthalpy of formation and standard Gibbs free energy of formation for the other species involved in the reaction are known, which allowed to calculate the values for the standard enthalpy of formation and standard Free Gibbs energy of formation of the species under study. The most stable geometries for *trans*-β-ocimene and *cis*-β-ocimene are presented in the Figure 1.

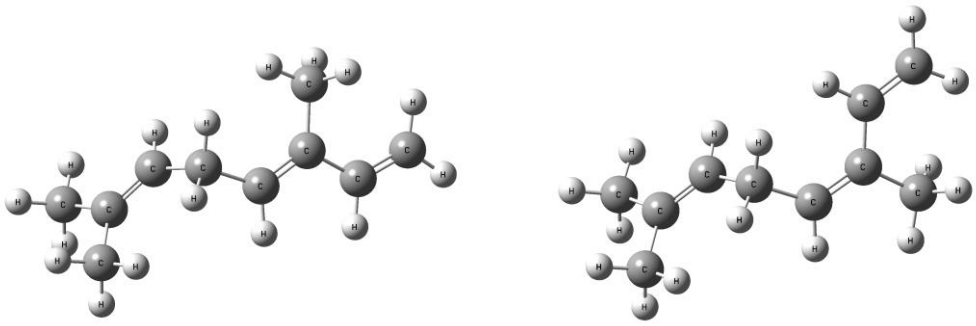

Figure 1: Most stable geometries for *trans*-β-ocimene and *cis*-β-ocimene, respectively.

The values obtained for the standard enthalpy of formation and standard free Gibbs energy of formation of the *trans*-β-ocimene and *cis*-β-ocimene are presented in Table I. To the best of our knowledge, it is the first determination of these thermochemical data. Of these data, we can conclude that by a difference of 0.342 kcal/mol between standard Gibbs free energies of formation, we can consider that *trans* and *cis* stereoisomers are in equilibrium in the atmosphere.

Table 1. Standard Enthalpy and Gibbs free energy of formation in kcal/mol (298 K and 1 atm).

Species	ΔH_f°	ΔG_f°
trans-β-ocimene	17.09	63.37
cis-β-ocimene	17.43	63.71

The most stable conformer and the standard enthalpy and Gibbs free energy of formation para *trans*-β-ocimene and *cis*-β-ocimene were determined using a high level of theory. To the best of our knowledge, it is the first determination of these thermochemical data, which may be useful in later studies of atmospheric decomposition.

Key-words: *ab initio*, thermochemistry, atmospheric chemistry, VOC, ocimene.

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