

Thermochemistry of the atmospheric decomposition of β -ocimene initiated by OH radical

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Abstract: Volatile Organic Compounds (VOCs) are an important class of compounds emitted into the atmosphere, mainly by biogenic sources.[1] Under atmospheric conditions, they may react with OH and NO₃ radicals.[2] Reaction with OH radical occur mainly daytime and may lead to the formation of O₃, considered a greenhouse in troposphere, and atmospheric aerosols, which affect terrestrial albedo.[3] β -Ocimene is a monoterpene with two stereoisomeric forms: *trans*- β -ocimene ((E)-3,7-dimethyl-1,3,6-octatrieno) and *cis*- β -ocimene((Z)-3,7-dimethyl-1,3,6-octatrieno), and the presence of three instaurations provides the possibility of multiple reaction paths. The atmospheric decomposition of β -ocimene initiated by OH radical can occur by OH addition or hydrogen abstraction, and Figure 1 shows the different reaction positions (except carbons 3 and 6 for abstraction).

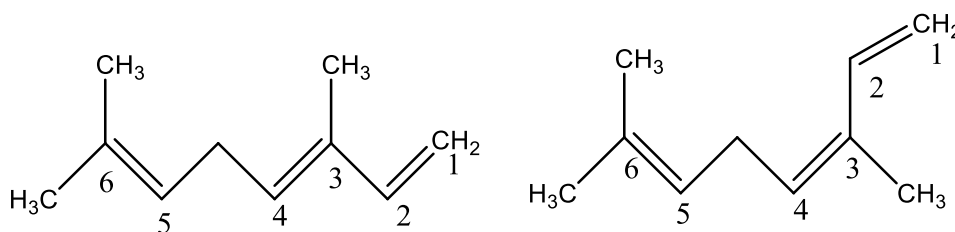


Figura 1: *Trans*- β -ocimene and *cis*- β -ocimene structures, respectively.

In this way, before a kinetic study, an analysis of the thermodynamic viability of these reaction paths is necessary and this is the proposal of this work. Geometry optimizations and harmonic vibrational frequency calculations were done at the MP2/6-311G(d,p) level of theory, in order to obtain the reaction enthalpy and Gibbs free energy for all reaction possibilities. Regarding the hydrogen abstraction, only the reaction path occurring in the carbon 5 is spontaneous, whose enthalpy and Gibbs free energy are, respectively, -6.00 and -5.97 kcal mol⁻¹ and -7.06 and -7.01 kcal mol⁻¹ for *trans* and *cis*- β -ocimene. On the other hand, all reaction paths for OH addition are spontaneous and exothermic, as can be seen in Table 1.

Table 1: Enthalpy and Gibbs free energy for OH addition to β -ocimene, at 298 K and 1 atm (in kcal mol⁻¹).

Reaction path	<i>trans</i> - β -ocimene		<i>cis</i> - β -ocimene	
	ΔH_R	ΔG_R	ΔH_R	ΔG_R
P1	-37.28	-27.46	-35.98	-25.68
P2	-24.32	-14.72	-24.15	-14.48
P3	-19.89	-8.73	-22.62	-11.89
P4	-42.06	-31.77	-40.08	-29.28
P5	-31.27	-21.57	-31.76	-21.52
P6	-33.36	-22.10	-32.96	-21.61

From these results, it can be observed that the addition path will predominate over the hydrogen abstraction, but the thermodynamics of the reactions of the two isomers is similar. Besides, position 3 is the least thermodynamically favorable. Furthermore, the most exothermic and exoergic path is the one through the carbon 4. According to our knowledge, this is the first determination of these values and these results may be useful for future kinetic studies of the atmospheric decomposition.

Key-words: *ab initio*, thermochemistry, atmospheric chemistry, OH radical, ocimene

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