

Theoretical Investigation of the Ozonolysis Mechanism of Monoterpenes: Reaction Path and Rate Coefficients

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The atmospheric chemistry of biogenic non-methane hydrocarbons has received special attention, since the emissions of volatile organic compounds (VOCs) from vegetation are the major source of reactive species in the atmosphere and the estimated worldwide emissions range from 825 to 1150 Tg carbon per year. In this group of biogenic volatile compounds, the monoterpenes alpha-phellandrene, beta-phellandrene and terpinolene are included [1]. The unsaturated terpenes are oxidized in the troposphere by either OH (daylight), NO₃ (nighttime) and O₃ (daylight and nighttime). Ozonolysis plays important role in atmospheric chemistry, being a chemical process of strong contribution to the removal of such compounds from troposphere [2]. Furthermore, the ozonolysis reaction also contributes to the formation of OH radicals [3]. Thus, it is important to understand the ozonolysis mechanisms of monoterpenes in the troposphere. The ozonolysis reaction is described by the reversible formation of a pre-barrier complex followed by the ozone addition and molozonide formation, as previously suggested [4]. The aim of this work is to evaluate the ozonolysis reaction of the monoterpenes alpha-phellandrene, betaphellandrene and terpinolene, based on the Criegge mechanism, through calculations of accurate kinetic parameters by theoretical methods. Stationary points (pre-barrier complexes, saddle points and products) have been located adopting the B3LYP, BHandHLYP and M06-2X functionals, with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Reaction paths have also been calculated at the same theoretical level. All the theoretical calculations (geometry optimization, vibrational frequencies, reaction path and scans) have been performed using the Gaussian 09 program [5]. The rate coefficients have been calculated at the canonical variational transition state theory level, using the kcvt program [6]. Both upward and downward ozone addition paths have been considered. As each monoterpene shows two unsaturated bonds, four pre-barrier complexes and four saddle points have been located for each monoterpene at each theoretical level. The B3LYP functional showed the worst performance, being unable to saddle points for alpha-phellandrene and terpinolene. At the locate some BHandHLYP/aug-cc-pVTZ level, pre-barrier complexes are stabilized by 0.83 - 1.32 kcal mol⁻¹ and saddle points are located in the range from 1.17 to 4.90 kcal mol⁻¹, above the isolated reactants. At the M06-2X/aug-cc-pVTZ level, pre-barrier complexes are stabilized by 3.54 - 5.43 kcal mol⁻¹ and saddle points are located in the range from 0.23 to 4.22 kcal mol⁻¹, under the isolated reactants. M06-2X/aug-cc-pVTZ level have predicted that pre-barrier complexes are located at lower energy values and also higher



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central barrier heights. As a global result, rate coefficients obtained from the molecular data obtained at the M06-2X level are higher than those obtained from BHandHLYP molecular properties. The results show and suggest that pre-barrier complexes are important to the kinetics of the global reactions. M06-2X room temperature rate coefficients have been found in reasonable agreement with experimental data (rate coefficients, at 298 K, for the ozonolysis of alpha-phellandrene, beta-phellandrene and terpinolene are: 2.04×10^{-14} , 1.21×10^{-15} and 3.75×10^{-14} cm³ molecule⁻¹ s⁻¹, respectively, and the corresponding experimental values [7-8] are: 2.97x10⁻¹⁵, 4.77x10⁻¹⁷ and 1.88x10⁻¹⁵ cm³ molecule⁻¹ s⁻¹). Both BHandHLYP/aug-cc-pVDZ and M06-2X/aug-cc-pVDZ levels could reasonably describe the ozonolysis of these terpenes, but only M06-2X/aug-ccpVTZ level could describe the ozonolysis and provide rate coefficients values in good agreement with the experimental values. The k_{predicted}/k_{experimental} ratio at M06-2X/aug-ccpVDZ level of alpha-phellandrene, beta-phellandrene and terpinolene are: 10, 148 and 18. At M06-2X/aug-cc-pVTZ level, the k_{predicted}/k_{experimental} ratio of alpha-phellandrene, beta-phellandrene and terpinolene are: 7, 25 and 20. The results show that k_{predicted}/k_{experimental} ratio are less sensitive to the relative energy of the pre-barrier complexes than to the location of the saddle point: by raising the relative energies of the saddle points in 1 kcal mol⁻¹, the k_{predicted}/k_{experimental} ratio is improved and the rate coefficients achieve excellent agreement with experimental values. Therefore, based on the Criegge mechanism, it can be concluded that the ozonolysis of monoterpenes is better described at M06-2X/aug-cc-pVTZ level and the kpredicted/kexperimental ration is mostly affected by the location of the saddle point, in comparison to the stabilization energy of the pre-barrier intermediates.

Key-words: alpha-phellandrene, beta-phellandrene, terpinolene, ozonolysis, rate coefficients.

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