

Theoretical Study of the Reactivity of C2 - C5 Alkenes Towards Ozone.

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Abstract: Ozonolysis is an important process for the chemical removal of volatile unsaturated organic specie from troposphere. The reaction proceeds via ozone attack to the unsaturated bond forming a molozonide, which rapidly decomposes to carbonyl products. As the first step is highly exothermic, molozonides are formed with excess internal energy and the consecutive step is generally fast, so that the addition step is the rate controlling. This first step, in turn, is better described by a submechanism taking into account the reversible formation of a pre-barrier intermediate, followed by the addition [1]. The search for a theoretical method to accurately describe the ozonolysis reaction is a topic of interest worldwide, with main concern about the description of the kinetics of different unsaturated species towards ozone and the observed trends in their compared reactivity. In this context, this work aims to the study of the ozonolysis reaction path of some alkenes of low molecular weight (C4 and C5). Our goals are the search for the stationary points in the reaction paths and the prediction of the barrier heights from theoretical methods. Density Functional Theory has been used in all calculations, adopting the BHandHLYP, wB97X and M06-2X functionals and the augcc-pVTZ basis set. The selected alkenes were: 1-butene, Z-2-butene, E-2-butene and isobutene (C4) and 3-methyl-1-butene, 2-methyl-2-butene, E-2-pentene and Z-2pentene (C5). 2.3-dimethyl-2-butene (C6) has also been included in our list. Each optimized geometry has been validated by vibrational frequencies calculations, observing that stationary points corresponding to reagents and intermediates showed only real vibrational frequencies, whereas, for the saddle points, a single imaginary vibrational frequency was expected. BHandHLYP results for the reaction barriers (electronic energy differences between the saddle point and the reactants, corrected by zero point energies) were, for 1-butene, Z-2-butene, E-2-butene and isobutene: 4.91, 3.53, 4.10 and 5.55 kcal mol⁻¹, respectively. For 2-methyl-2-butene and 3-methyl-1butene, the calculated barriers were 4.30 and 6.17 kcal mol⁻¹, respectively. Including the thermal and entropic contributions, the values for the Gibbs free energy of activation (298 K) were: 15.99, 14.35, 14.97, 16.74, 15.91 and 17.42 kcal mol⁻¹ (1-butene, Z-2butene, E-2-butene, isobutene, 2-methyl-2-butene and 3-methyl-1-butene, respectively). From these data, and adopting the conventional transition state theory, the rate coefficients at 298 K were calculated, being (in cm³ molecule⁻¹ s⁻¹): 9.60x10⁻¹⁹ (1butene), 1.51x10⁻¹⁷ (Z-2-butene), 5.37x10⁻¹⁸ (E-2-butene), 2.69x10⁻¹⁹ isobutene,



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 1.10×10^{-18} (2-methyl-2-butene) and 8.62×10^{-20} (3-methyl-1-butene). These results are smaller than the experimental results by factors ranging from about 10 to 370. The ratios between the rate coefficients for the ozonolysis of each alkene and the rate coefficient for the propene ozonolysis (calculated at the same theory level) are in agreement with the experimental data. It is concluded that although small adjustments in the theoretical model are still necessary to guarantee the accurate prediction of the rate coefficients of the C4 and C5 alkenes, the model suggested from the BHandHLYP data is already enough accurate for the prediction of reactivity trends of the different alkenes towards ozone .

Key-words: Ozonolyses, alkenes, molozonide, rate coefficients **Support:** This work has been supported by CNPq and FAPERJ **References:**

[1] R. C. de M. Oliveira, G. F. Bauerfeldt, J. Phys. Chem. A, 119, 2802 (2015).