Generalized Polany-Semenov relation applied to monomolecular decays of olefins and vinyl ethers

© **Alexander A. Kunitsa**,[+] and **Alexander F. Shestakov**
Institute of Problems of Chemical Physics RAS. Akad. Semenov St., 1. Chernogolovka, 142432.
Moscow region. Russia. Phone: +7 (496) 522-17-63. E-mail: aakunitsa@gmail.com

_____
*Supervising author; [+]Corresponding author

Keywords: monomolecular reactions, generalized Polany-Semenov relation.

Abstract

In this paper, with the help of special reaction coordinate transformation two-parametric non-linear correlation equations were obtained, which relate activation energies and heat effects of monomolecular decays of olefins and vinyl ethers. These equations allow to approximate the results of quantum chemical barrier calculation with mean-square error less than 1 kcal/mol. It was shown that to achieve the accurate description of experimental barriers it is necessary to calibrate one of the correlation equation parameters using the known experimental data or the results of exact calculations.