Subsection: Organic Chemistry. Registration Code of Publication: 8-14-4-29 Publication is available for discussion in the framework of on-line conference "Butlerov readings". http://butlerov.com/readings/ Contributed to editorial board: December, 2008.

Kinetic parameters of the reactions of molecular decomposition of unsaturated acids

© Tamara S. Pokidova, and Evgeniy T. Denisov*⁺

Institute for Problems of Chemical Physics at RAS. Chernogolovka, 142432. Moscow Region. Russia. Fax: +7 (496) 524-96-76. E-mail: det@icp.ac.ru

*Supervising author; ⁺Corresponding author

Keywords: reaction rate constant, method of intersecting parabolas, molecular decomposition, molecular addition, β , γ -unsaturated acids, reaction enthalpy, activation energy.

Abstract

Experimental data on molecular decomposition of β_{γ} -unsaturated acids of different structure into olefine and CO₂ have been analyzed with the use of the method of intersecting parabolas. Kinetic parameters characterizing such decomposition have been calculated and factors exerting influence on activation energy of such parameters have been defined. Activation energies and constants of reaction rates of such decomposition have been calculated for 25 acids. Comparison of activation energies of thermoneutral decomposition of unsaturated acids (E_{e0}), peroxyesters and carboxylic radicals with the formation of CO₂ has shown that for such compounds it is directly proportional to the number of bonds, participating in the reaction (E_{e0} /number of bonds = $33.3 \text{ kJ} \cdot \text{mol}^{-1}$). For the first time activation energies and constants of reaction rates of addition of CO₂. to olefines, reverse to acids decomposition, have been calculated.