Thematic Section: Quantum-Chemical Research. **Full Paper**
Subsection: Physical Chemistry of Polymers. *Reference Object Identifier* – ROI: jbc-01/17-49-2-25
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/17-49-2-25
Submitted on February 24, 2017.

Quantum-chemical study of the fracture reaction of the deformed polyethylene chain

© **Boris E. Krisyuk**,[1,2]*+ and **Eldar A. Mamin**[2,3]
[1] *Laboratory of Kinetic of Thermal Transformations. The Institute of Problems of Chemical Physics of the Russian Academy of Sciences. Academician Semenov Ave., 1. Chernogolovka ,142432. Russia. Phone: +7 (916) 601-63-14. E-mail: bkris@mail.ru*
[2] *Department of Chemistry and Physics. Plekhanov Russian University of Economics. Stremyanny St., 36. Moscow, 117997. Russia. Phone: +7 (499)237-93-02. E-mail: @mail.ru*
[3] *Laboratiry of Physics and Chemistry of Synthetic and Nature Polymer Blends. N.M. Emanuel Institute of Biochemical Physics of the Russian Academy of Sciences. Kosygina St., 4. Moscow, 119334. Russia. Phone: +7 (915) 018-05-71. E-mail: yeldar443@mail.ru*

*Supervising author; +Corresponding author

Keywords: quantum-chemical calculation, reaction of the rupture of stressed macromolecule, the sensitivity of the rate constant to deformation.

Abstract

A model is proposed for reactions of thermal decay of the polyethylene chain in the presence of a tensile force acting along the axis of the molecule. The reaction of an isolated chain is studied with the molecule of octane as a model of polymer molecule. It was shown previously that eight carbon atoms are sufficient for the solution of such tasks. The deformation was introduced to the model by fixing the distances between the terminal carbon atoms different from that in equilibrium. At a fixed length of the molecule (L) the reaction coordinate, the length of the middle C-C bond (R) was scanned. Thus a section of the potential energy surface of the reaction at $L=const$ was obtained. From the set of cross-sections at different L parameters of the initial and transition states for the reaction of free molecules were obtained. This calculation takes into account that the original molecule is a singlet, whereas the products are two radicals, using the method of splitting the molecules into fragments, which is implemented in GAUSSIAN-09. On the basis of the quantum-chemical calculations by the methods B3LYP, LC-ωPBE, MP2, CCSD(T) using basis sets 6-31+G*, 6-31+G** was estimated the sensitivity of the reaction to strain. The parameter characterizing sensitivity of the reaction to deformation (strain) is the elongation of the model molecule in the transition state. All methods showed that the chain rupture of the polyethylene occurs when the elongation on the order of 1 Å. The calculation results show that in all cases, the rupture of molecules such as polyethylene is accelerated by the action of tensile deformation. The results obtained confirm the known data on the nature of the influence of deformation of reaction center upon the activation energy of the elementary processes. This is illustrated by the data obtained for the rupture of octane representing a fragment of polyethylene chain. Stretching of the chain brings the reagent closer to the transition state and thus reduces the activation energy (in this case, the dissociation energy of the activated bond).

References

[1] V.A. Shershnev, N.N. Volkova, G.I. Dzhardimalieva, B.E. Krisyuk. Mechanically stressed structures and thermal degradation kinetics of zinc and cobalt acetylenedicarboxylates dehydrates. *Butlerov Communications.* **2014**. Vol.40. No.12. P.133-140. ROI: jbc-02/14-40-12-133
[2] S.H. Johes, E. Whittle. *Int. J. Chem. Kinet.* **1970**. Vol.2. P.479.
[3] A.A. Popov, G.E. Zaikov. *J. Macromol. Sci., Rev. Macromol.* **1988**. Vol.27. P.379.
[4] B.E. Krisyuk, A.A. Popov, E.T. Denisov. *Vysokomolekulyarnie Soedienia.* **1988**. Vol.30. P.1736. (russian)
[5] B.E. Krisyuk, V.V. Cheremisyin. *Vysokomolekulyarnie Soedienia.* **1992**. Vol.34. P.973. (russian)
[6] B.E. Krisyuk. *J. Molec. Struct. THEOCHEM.* **2004**. Vol.677. P.77.
[7] A.A. Popov, Rappoport N.Y., Zaikov G.E. Oxidation of oriented and tensed polymers. *Moscow: Chem.* **1987**. (russian)
[8] A.A. Popov, S.K. Rakovsky, D.M. Shopov, L.V. Ruban. *Izvetiya Academii nauk SSSR Seria Khimicheskaya.* **1976**. No.5. P.982. (russian)
[9] Sway M. *Indian J. Chem*. **1990**. Vol.29. P.748.
[10] K. Al-Niami, K.A. Holbrook, G.A. Oldershaw. *J. Chem. Soc. Faraday Trans.* **1989**. Vol.85. No.2. P.1601.

[11] N.J. Bunce, M. Hadley. *J. Org. Chem*. **1974**. Vol.39. No.15. P.2271.
[12] S.M. Handford-Styring, R.W. Walker. *Phys. Chem. Chem. Phys*. **2001**. Vol.3. P.2043.
[13] J. Ribas-Arino, D. Marx. *Chem. Reviews*. **2012**. Vol.112. P.5412-5487.
[14] M.K. Beyer, H. Clausen-Schaumann. *Chem. Reviews*. **2005**. Vol.105. No.8. P.2921-2948.
[15] A.M. Saitta, M.L. Klein. *J. Chem. Phys*. **1999**. Vol.111. P.9434.
[16] A.M. Saitta, M.L. Klein. *J. Amer. Chem. Soc*. **1999**. Vol.121. P.11827.
[17] B.E. Krisyuk, E.V. Polianczyk. *Int. J. Polym. Mat.* **1993**. Vol.23. No.1-2. P.1.
[18] B.E. Krisyuk, E.V. Polyanchik. Calculation of sensitivity to deformation of acid hydrolysis reactions of polyamide and polyester. *Chemical Physics*. **1993**. Vol.12. No.2. P.253-259. (russian)
[19] B.E. Krisyuk. *Vysokomolekulyarnie Soedienia A*. **1997**. Vol.39. No.3. P.500-504. (russian)
[20] S.N. Zhurkov, V.E. Korsukov. *J. Polym. Sci.* **1974**. Vol.12. P.385.
[21] S.N. Zhurkov, V.E. Korsukov. *Fizika Tverdgo Tela.* **1964**. Vol.15. P.2071-2080. (russian)
[22] B.E. Krisyuk, A.V. Mayorov, V.A. Ovchinnikov, A.A. Popov. Quantum-chemical modeling of the reaction route of butene-2 with ozone. *Butlerov Communications.* **2011**. Vol.28. No.17. P.11-16. ROI: jbc-02/11-28-17-11
[23] E.A. Mamin, B.E. Krisyuk, A.V. Maiorov. Comparison of reactivity of fluoro- and chlorosubstituents of ethylene with ozone. *Butlerov Communications.* **2013**. Vol.36. No.10. P.73-80. ROI: jbc-02/13-36-10-73
[24] B.E. Krisyuk, A.V. Mayorov, V.A. Ovchinnikov, A.A. Popov. Vliyaniye deformatsii na reaktsionnuyu sposobnost svyazi s=s v reaktsii s ozonom. *Khimicheskaya fizika.* **2010**. Vol.29. No.10. P.18-25. (russian)
[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox. Gaussian 09, Revision C.01. Gaussian, Inc., Wallingford CT, **2009**.
[26] A.A. Granovsky. Firefly version 8.0.0, *http://classic.chem.msu.su/gran/firefly/index.html*
[27] J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery. General Atomic and Molecular Electronic Structure System. M.W. Schmidt, K.K. Baldridge. *J. Comput. Chem.* **1993**. Vol.14. P.1347-1363.