INITIAL STAGES OF ACETYLENE PYROLYSIS. FORMATION OF VINYLACETYLENE

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Abstract: A novel mechanism of initial stages of acetylene pyrolysis is proposed based on nonempirical quantum-chemical computations and analysis of the literature on the topic. The mechanism can account for experimental results from an unified standpoint. The mechanism relies on the transformation of linear structure of acetylene into a transoid structure under the vibrational excitation of 10 kcal/mol that has been discovered by the present authors' group. It was shown that this structure corresponded to singlet diradicaloid. Reaction of diradicaloid with acetylene molecule or another diradicaloid results in *trans*-1,4-diradical. The proposed mechanism of vinylacetylene formation consist of 6 stages with 5 intermediates (*trans*- and *cis*-1,4-diradicals, cyclobutadiene, tetrahedrane, and bicyclo[1.1.0]butane-2,2-diyl). The set of products of acetylene pyrolysis, received by multiples of the C_2H_2 units, the observation of induction period and NO sensitivity, and also results obtained in C_2H_2–C_2D_2 pyrolysis can be explained in the framework of the mechanism.

Keywords: acetylene; pyrolysis; vinylacetylene; mechanism; diradical

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Received November 1, 2014

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