The Breakdown of Vinyl Ethers as a Two-Center Synchronous Reaction

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Abstract—The experimental data on the molecular decomposition of vinyl ethers of various structures to alkanes and the corresponding aldehydes or ketones in the gas phase were analyzed using the method of intersecting parabolas. The enthalpies and kinetic parameters of decomposition were calculated for 17 reactions. The breakdown of ethers is a two-center concerted reaction characterized by a very high classical potential barrier to the thermally neutral reaction (180–190 kJ/mol). The kinetic parameters (activation energies and rate constants) of back reactions of the formation of vinyl ethers in the addition of aldehydes or ketones to alkanes were calculated using the method of intersecting parabolas. The factors that influenced the activation energy of the decomposition and formation of ethers were discussed. Quantum-chemical calculations of several vinyl ether decomposition reactions were performed. Ether formation reactions were compared with the formation of unsaturated alcohols as competitive reactions, which can occur in the interaction of carbonyl compounds with alkenes.

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