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Kinetics and mechanisms of the ozonolysis of 1,3-butadiene according to quantum chemical calculations

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Abstract

The mechanisms of the initial step of the ozonolysis of 1,3-butadiene in the *trans*-configuration were studied by density functional theory methods (DFT) B3LYP, double hybrid B2PLYP method based on both DFT and MP2 approaches and couple-cluster CCSD method. Two possible reaction channels were considered: concerted 1,3-cycloaddition of ozone to the double bond of 1,3-butadiene leading to the primary ozonide (Criegee mechanism) and stepwise addition by the biradical mechanism (DeMore mechanism). Predicted structures of intermediate and transition states, the energies of elementary steps, and activation barriers were reported. For the rate-determining steps of both mechanisms, the full geometry optimization of stationary points was performed at the b3lyp/aug-cc-pVDZ and b2plyp/aug-cc-pVDZ theory level. The rate constants and their ratio for reaction channels calculated for both mechanisms demonstrate that Criegee mechanism competes with DeMore one. The proportion of the competition is approximately 1:6 with the prevalence of Criegee mechanism. According to B2PLYP/aug-cc-pvdz, a total reaction rate constant is equal to 3664 L/mol·sec for both channels of the Ozone binding, whereas a total reaction rate constant calculated with CCSD/aug-cc-pvdz is equal to 2848 L/mol·sec.These results are in agreement with the experimental data ($3\cdot10^3$) and previous computational results.