38g Theoretical Study of the Decomposition Mechanism of a Free Radical Initiator and Solvent Effects on the Reaction

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The decomposition mechanism of diethyl peroxydicarbonate (DEPDC), a free radical initiator for a polymerization reaction, is studied with density functional theory. Cage effect and diffusivity of initiators in solvents are investigated using molecular dynamics simulations. Results show that the decomposition reaction is not homolytic. The calculated activation energy of each decomposition step differs from experimental values which are based on a one-step decomposition assumption. The differences between the effects of supercritical CO2 and conventional solvents on the above initiator decomposition are discussed.