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Diffusion control of the Diels-Alder reaction rate at elevated pressures

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Abstract

The influence of the temperature and external pressure on the rate of the Diels-Alder reaction between 9,10-dimethylanthracene and maleic anhydride was studied in the series of solvents with wide intervals of viscosity (0.3-43.2 mPa s), dielectric constant (2-38), and internal pressure (3-8.8 kbar). At a standard pressure these properties of the solvent exert a weak and irregular effect on the reaction rate constant and activation enthalpy and entropy. The effect of the external pressure on the rate constant was studied in a high-pressure (up to 1 kbar) optical cell in acetonitrile and silicon oil and in a barostat cell (up to 6 kbar, toluene, silicon oil). Close values of the activation volume were obtained in all solvents. In toluene the reaction rate increases smoothly in the whole pressure interval. In more viscous silicon oil a similar dependence is observed up to 3 kbar, and the reaction rate decreases sharply with the further increase in the pressure and viscosity because of the diffusion control of the process.

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Keywords

Activation volume, Diels-Alder reaction, Diffusion control, External pressure, Kinetics, Viscosity effect