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

Kiselev V., Kashaeva E., Shihab M., Potapova L., Iskhakova G.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

The influence of the temperature and external pressure on the rate of the Diels-Alder reaction between 9,10-dimethylantracene 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