Journal of Solution Chemistry 2012 vol.41 N3, pages 525-535

Anomalies in the change of volumetric parameters of the Diels-Alder reaction in solution

Kiselev V., Bolotov A., Shakirova I., Kashaeva H., Potapova L., Konovalov A.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

In this article negative values of the activation volume in retro-Diels-Alder reactions are interpreted in terms of the different possibilities of penetration of the solvent molecules into the sterically branched structures of the adduct and activated complex. Empty spaces, inaccessible to penetration of solvent molecules, lead to increases of the molar volume of the screened adducts in solution and, consequently, to a less negative value of the Diels-Alder reaction volume. The values of partial molar volumes of anthracene, maleic anhydride and the adducts cyclopentadiene-maleic anhydride, anthracene-maleic anhydride and anthracene-tetracyanoethylene, in several solvents, were calculated from the solution density data. © Springer Science+Business Media, LLC 2012.

http://dx.doi.org/10.1007/s10953-012-9808-5

Keywords

Diels-Alder reaction, Intramolecular holes, Partial molar volume, Reaction volume, Solvent effect