

Kinetics and thermochemistry of the unusual [2 π + 2 σ + 2 σ]-cycloaddition of quadricyclane with some dienophiles

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Abstract

Copyright © 2017 John Wiley & Sons, Ltd. Kinetic parameters of the unusual [2 π + 2 σ + 2 σ]-cycloaddition reactions of quadricyclane (1) with tetracyanoethylene (2), 4-phenyl-1,2,4-triazoline-3,5-dione (3), N-phenylmaleimide (4), and diethyl azodicarboxylate (5) are determined experimentally. Additionally, the enthalpies of 1 + 2 reaction in 1,4-dioxane solution (-236.6 ± 1.0 kJ mol $^{-1}$) and 1 + 3 reaction in toluene (-255.0 ± 2.8 kJ mol $^{-1}$) are determined calorimetrically and shown to be the largest in absolute magnitude among all known cycloaddition reactions involving these dienophiles. Solvent effect on the rate of 1 + 3 reaction in 11 solvents is studied and found to be moderate and similar to that of the conventional Diels-Alder and ene reactions. The difference in the reaction rate constants of 1 with different dienophiles can be up to 9 orders of magnitude and is mainly caused by the difference in activation enthalpies. This difference is not correlated with the standard enthalpies of reactions and is likely the result of high sensitivity of the [2 π + 2 σ + 2 σ] reaction rates to the energy of donor-acceptor interactions between the reactants.

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Keywords

4-phenyl-1,2,4-triazoline-3,5-dione, quadricyclane, rate constants, reaction heat, tetracyanoethylene, [2 π + 2 σ + 2 σ] reaction

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