

Homo-Diels-Alder reaction of a very inactive diene, bicyclo[2,2,1]hepta-2,5-diene, with the most active dienophile, 4-phenyl-1,2,4-triazolin-3,5-dione. Solvent, temperature, and high pressure influence on the reaction rate

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Abstract

Solvent, temperature, and high pressure influence on the rate constant of homo-Diels-Alder cycloaddition reactions of the very active hetero-dienophile, 4-phenyl-1,2,4-triazolin-3,5-dione (1), with the very inactive unconjugated diene, bicyclo[2,2,1]hepta-2,5-diene (2), and of 1 with some substituted anthracenes have been studied. The rate constants change amounts to about seven orders of magnitude: from $3.95 \cdot 10^{-3}$ for reaction (1+2) to $12200 \text{ L mol}^{-1} \text{ s}^{-1}$ for reaction of 1 with 9,10-dimethylantracene (4e) in toluene solution at 298 K. A comparison of the reactivity ($\ln k_2$) and the heat of reactions ($r-nH$) of maleic anhydride, tetracyanoethylene and of 1 with several dienes has been performed. The heat of reaction (1+2) is $-218 \pm 2 \text{ kJ mol}^{-1}$, of 1 with 9,10-dimethylantracene $-117.8 \pm 0.7 \text{ kJ mol}^{-1}$, and of 1 with 9,10-dimethoxyanthracene $-91.6 \pm 0.2 \text{ kJ mol}^{-1}$. From these data, it follows that the exothermicity of reaction (1+2) is higher than that with 1,3-butadiene. However, the heat of reaction of 9,10-dimethylantracene with 1 ($-117.8 \text{ kJ mol}^{-1}$) is nearly the same as that found for the reaction with the structural C=C counterpart, N-phenylmaleimide ($-117.0 \text{ kJ mol}^{-1}$). Since the energy of the N=N bond is considerably lower (418 kJ/bond) than that of the C=C bond (611 kJ/bond), it was proposed that this difference in the bond energy can generate a lower barrier of activation in the Diels-Alder cycloaddition reaction with 1. Linear correlation ($R = 0.94$) of the solvent effect on the rate constants of reaction (1+2) and on the heat of solution of 1 has been observed. The ratio of the volume of activation (V^\ddagger) and the volume of reaction (V_{r-n}) of the homo-Diels-Alder reaction (1+2) is considered as "normal": $V^\ddagger/V_{r-n} = -25.1/-30.95 = 0.81$. Copyright © 2012 John Wiley & Sons, Ltd.

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Keywords

4-phenyl-1,2,4-triazolin-3,5-dione, activation volume, bicyclo[2,2,1]hepta-2,5-diene, heat of reaction, homo-Diels-Alder reaction, rate constants, reaction volume