Cyclic and Acyclic NN Bonds in Reactions with Some Alkenes and Dienes

Kiselev V., Kornilov D., Konovalov A. Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2017 Wiley Periodicals, Inc., A Wiley Company. The kinetics of the Diels-Alder (DA) reactions of 4-phenyl-1,2,4-triazoline-3,5-dione 1, trans-diethyl azodicarboxylate 2, and tetracyanoethene 3 with 1,3-cyclohexadiene 4, cycloheptatriene 5, 1,3-cycloheptadiene 6, cyclooctatetraene 7, and 1,3-cyclooctadiene 8 in a range of temperatures and pressures has been studied. Values of the enthalpy, entropy, and volume of activation, as well as the enthalpy and volume of reaction have been obtained. Observed reaction rates of 5+1 and 7+1 have been compared with the known rate of norcaradiene 17 formation in the equilibrium $5 \rightleftharpoons 17$, and that of bicyclo[4,2,0]-octa-2,4,7-triene 20 in the equilibrium $7 \rightleftharpoons 20$. The kinetic data show that the rate of formation of 17 from 5 is much greater than the loss rate of dienophile 1 in reaction of 5+1. In contrast, the formation rate of tautomer 20 is less than the loss rate of dienophile 1 in reaction of 7+1. This reflects that the consecutive reaction of $5 \rightarrow 17$ (+1) $\rightarrow 15$ is possible whereas the consecutive reaction of $7 \rightarrow 20$ (+1) $\rightarrow 22$ does not occur as the only way.

http://dx.doi.org/10.1002/kin.21094