Experimental and theoretical study of the kinetics and mechanism of the reaction of chlorine atoms with $CH_3CHClCH_3$ and $CD_3CDClCD_3$

Autorzy

Dariusz S. Sarzyński

Łukasz Fojcik

Zdzisław Latajka

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Streszczenie

The overall rate constants for H-abstraction (k_H) from $CH_3CHClCH_3$ and D-abstraction (k_D) from $CD_3CDClCD_3$ by chlorine atoms in the temperature range 298–528.5 K were determined and are described by the expressions: $k_H = (3.52 \pm 0.21) \times 10^{-11} \exp(-184 \pm 19/T)$ cm^3 $molecule^{-1}$ s^{-1} and $k_D = (1.91 \pm 0.16) \times 10^{-11} \exp(-185 \pm 31/T)$ cm^3 $molecule^{-1}$ s^{-1} respectively. The results of the experiment show that the value of the kinetic isotope effect (k_H/k_D) for the overall rate constants is temperature independent and is equal to 1.85 ± 0.17. A theoretical examination of these reaction mechanisms revealed some unusual properties, such as negative values of the activation energy for the H-abstraction reaction from the secondary carbon atom. Moreover, it was proved that in the radical process of H-abstraction from the primary carbon atom of 2-chloropropane the created R–Cl···Cl complex is the most stable structure responsible for the value of the activation energy of this transformation.

Adres publiczny

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https://www.acs.org/content/acs/en.html