

TUNNELING EFFECTS ON SIGMATROPIC HYDROGEN SHIFTS IN THE PHOTOREARRANGED INTERMEDIATES

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Sigmatropic hydrogen shift is one of the most important and elementary processes both in chemistry and biochemistry.

The rate constants for the 1,3- and 1,5-sigmatropic hydrogen shifts in the ground state of the photo-Fries rearranged intermediates of phenyl acetate produced by laser flash photolysis at 266 nm were directly measured in several solvents.^{1,2} The rate constant for the intramolecular 1,3-hydrogen shift (3.6 s^{-1}) is greater than that for the 1,5-hydrogen shift ($6.5 \times 10^{-2} \text{ s}^{-1}$) in the ground state in methylcyclohexane (MCH) at 293 K, contrary to the expectation by the Woodward-Hoffmann rule, showing that the heteroatom of the corresponding carbonyl oxygen plays an important role for the intramolecular hydrogen shifts. It is shown that the intramolecular 1,3-hydrogen (or deuterium) shift in MCH proceeds via tunneling processes at two vibrational energy levels: $E=0$ ($v=v_0$) and $E=E_v$ ($=3.9 \text{ kcal mol}^{-1}$ for the hydrogen shift or $4.4 \text{ kcal mol}^{-1}$ for the deuterium shift) ($v=v_1$) under the experimental condition. The temperature and isotope effects on the 1,3-shifts can be elucidated by the calculated rates according to the tunnel effect theory proposed by Formosinho. The enhancement of the rates for the 1,3- and 1,5-sigmatropic shifts in polar solvents, especially in alcohols, is caused intermolecularly by a basic catalysis of the solvents. It is shown that the 1,3- or 1,5-sigmatropic hydrogen shift proceeds via the intramolecular processes at a low concentration of phenyl acetate ($\sim 2 \times 10^{-3} \text{ M}$) in nonpolar MCH.

Similar tunneling effects on the 1,2-sigmatropic hydrogen shift of the photorearranged intermediate of N-acetyl pyrrole have been shown by means of laser flash photolysis at 266 nm.³

References

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