

steric effect

The effect on a chemical or physical property (structure, rate or equilibrium constant) upon introduction of substituents having different steric requirements. The steric effect in a reaction is ascribed to the difference in steric energy between, on the one hand, reactants and, on the other hand, a transition state (or products). A steric effect on a rate process may result in a rate increase ('steric acceleration') or a decrease ('steric retardation'). (The adjective 'steric' is not to be confused with stereochemical.) Steric effects arise from contributions ascribed to strain as the sum of (1) non-bonded repulsions, (2) bond angle strain and (3) bond stretches or compressions. For the purpose of correlation analysis or linear free-energy relations various scales of steric parameters have been proposed, notably A values, Taft's E_s and Charton's ν scales.

In a reactant molecule RY and an appropriate reference molecule R⁰Y, the 'primary steric effect' of R is the direct result of differences in compressions which occur because R differs from R⁰ in the vicinity of the reaction centre Y. A 'secondary steric effect' involves the differential moderation of electron delocalization by non-bonded compressions. Some authors make a distinction between 'steric' effects attributed to van der Waals repulsions alone, and 'strain' effects, attributed to deviations of bond angles from 'ideal' values.

See: Taft equation, van der Waals forces

Source:

PAC, 1994, 66, 1077 (*Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)*) on page 1168