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Calculation of High Pressure Effects in Reactions of Hydrogen Transfer from Substituted Toluenes to Bromine Atom BRANDON WIEBE, University of the Fraser Valley, JACOB SPOONER, Simon Fraser University, NOHAM WEINBERG, University of the Fraser Valley; Simon Fraser University — A given reaction may proceed through several different mechanisms, each with its own transition state (TS). These TSs may have similar energies but different geometries and, as a result, different volumes. According to transition state theory, the activation volume ($\Delta V^{\neq}$) is the difference between the volume of the TS and the reactants. Experimentally, activation volumes can be obtained from the pressure dependences of the rate constants:

$$-RT(\partial \ln k/\partial P)_T = \Delta V^{\neq} = V^{\neq} - V^R$$

By comparing the calculated and experimental activation volumes, one can pick a TS of the right "size" and thus elucidate the reaction mechanism by identifying the most likely reaction pathway. It has recently been shown by our research group that molecular dynamics simulations provide a suitable tool for theoretical calculations of activation volumes. In this project we focus on the calculation of the activation volumes for a series of reactions in which an alpha-hydrogen is abstracted from a substituted aromatic hydrocarbon by bromine radical.

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