

FINDING TRANSITION STATES ALGORITHMICALLY FOR AUTOMATIC REACTION MECHANISM GENERATION

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We present an automatic procedure to generate the transition state geometries required for automatic calculations of reaction rates via TST, in the context of automatic kinetic model building software.

Software such as Reaction Mechanism Generator (RMG) can automatically build detailed kinetic models containing thousands of intermediate reactions and species. Each family of reactions has an associated reaction template, which is applied via graph theory to ensure all possible reactions are included. RMG is best at predicting gas phase pyrolysis and combustion of relatively simple hydrocarbons. When the kinetic data used to estimate reaction rates are sparse, or reactions do not follow simple trends (eg. due to steric effects) the rate estimates suffer. This may be addressed by calculating kinetic parameters via transition state theory (TST), which requires the automatic location of transition state (TS) geometries on a vast scale.

Reaction families are grouped by molecularity, as each group will require a different method. The bimolecular hydrogen-abstraction family is tackled first. The crucial step is to locate the 3D geometry of the TS. We use distance geometry to generate structures that are likely to be either side of the TS on the minimum energy pathway, then a double-ended search (e.g. QST2) to locate the TS from these structures. The distance geometry method requires upper and lower bounds on interatomic distances at the target geometries (either side of the TS). For stable structures, these interatomic distances can be predicted from the bonding and hybridization using software such as RDKit. We take these distances for the reactants and products, and modify them to approach the TS. To a first approximation this alteration depends only on the reaction family; further refinement depends on the functional groups reacting. By studying reactions between specific radical–molecule pairs, we have identified trends in interatomic distances based on functional group, thus allowing us to make better TS geometry estimates based on molecular structure.

The TS estimate is refined by a surface walking saddle point optimization at a higher level of theory, then checked using an intrinsic reaction coordinate (IRC) search to ensure it connects the desired reactants and products. This procedure has been automated for inclusion in the automatic reaction mechanism generator RMG. We test the approach on a set of hydrogen abstraction reactions with known transition state geometries.