Computer-generated isotope modeling for position specific isotope analysis

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Position-specific isotope analysis (PSIA) can give significant clues to the origins of molecules. On-line PSIA using pyrolysis and gas chromatography allows PSIA to be conducted with small quantities that may not be suitable for traditional NMR. However, this method requires a model to track isotope substitution through reaction pathways. The model is typically derived from a series of experiments using special isotopically-labeled reagents with known site specific enrichments.

We developed a computational method which has potential to replace these experiments which require expensive site-enriched reagents. The methodology uses the Reaction Mechanism Generator software to create kinetic models with atom-specific isotope tracking under pyrolysis conditions. In addition to tracking where each atom goes through each reaction, the computer program applies rudimentary heavy-atom kinetic isotope effect estimates to the rate coefficients.

A propane pyrolysis mechanism created with this framework replicated, within experimental uncertainty, the relationship necessary to map fragments to the parent molecule's position specific enrichment. This mechanism involved no tuning of kinetic or thermodynamic parameters to experimental data. Isotope tracking mechanisms created with this methodology have potential to estimate isotope scrambling, design experimental conditions, and estimate PSIA for new compounds. The code to generate and analyze these mechanisms is publicly available on the Internet for use and modification, so it can hasten the development of PSIA techniques without the use of special site-enriched reagents.