Emory chemists reveal challenge to reaction theory

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For nearly 75 years, transition-state theory has guided chemists in how they view the way chemical reactions proceed. Recent research by Emory University chemists is challenging the long-held theory, showing that in some cases chemical reactions can proceed via a path that completely bypasses the "transition state."

"Our understanding of chemical reactions rests on the notion of the transition state. If we think of reactions as occurring on an energy landscape, the transition state is the 'mountain pass' separating the reactants, and the resulting products from the reaction are valleys," says Joel Bowman, an Emory theoretical chemist and chairman of the chemistry department.

According to transition state theory, reactions proceed over this mountain pass, Bowman says, "but our results for a well-studied chemical reaction show that the reaction occurs during the transition state -- and also through a surprising second path that is not near this transition state region."

Bowman's research, done in collaboration with physical chemist Arthur Suits of Wayne State University in Detroit, was published in the Nov. 12 issue of the journal Science, and was highlighted in the Nov. 15 issue of Chemical and Engineering News.

Using high-powered computational work and detailed experimental studies, the scientists demonstrated that formaldehyde (H2CO) exposed to light rays (or photoexcited) can decompose to hydrogen and carbon monoxide via a path that skirts that reaction's well-established transition state entirely.

Using detailed pictures and measurements developed by Suits, Bowman performed high-level calculations to create a "movie" of this second pathway. The visual model reveals that one of formaldehyde's hydrogen atoms breaks off and roams around before bumping into the second hydrogen atom and forming a hydrogen molecule (H2). At no point in this second pathway does the reaction go through its transition state.

Formaldehyde decomposition has long been a model system for those studying transition-state theory because the reaction is simple enough to treat with high-level theoretical models, and the products are easily detectable. Bowman's research shows that such transition-state-skirting pathways may not be all that unusual in other chemical reactions.

"Although this discovery does not overturn traditional transition-state theory, our work is part of a growing body of evidence that is changing and expanding the way chemists and biochemists think about chemical reactions," Bowman says.

Source: Emory University Health Sciences Center

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