Theoretical chemists find new dimension to rules for reactions

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Theoretical chemists at Emory University have solved an important mystery about the rates of chemical reactions and the so-called Polanyi rules.

The findings, published in the journal *Science*, reveal why a reaction involving methane does not conform to the known rules, a problem that has baffled physical chemists in recent years.

"We showed that a pre-reactive, long-range force can align the reaction of a chorine atom with methane, or natural gas, in a way that actually inhibits the reaction," says Joel Bowman, a professor of theoretical chemistry at Emory and the Cherry L. Emerson Center for Computational Chemistry. "We believe that the theoretical work that we did has extended and modified the Polanyi rules."

Bowman published the results with Gabor Czako, a post-doctoral fellow in theoretical chemistry who performed most of the complex computational and mathematical analyses that uncovered the results.

Long-range, their findings could play a role in the development of cleaner, more efficient fuels.

Understanding the dynamics of chemical reactions is key to driving reactions efficiently, whether in a laboratory experiment or in an industrial application. In 1986, John Polanyi shared the Nobel Prize in chemistry, in part by providing general rules for how different forms of energy affect the rates of reactions.

"The Polanyi rules tell you the best way to deposit energy in a simple molecule to make a chemical reaction occur," Bowman says. "It's a bit like knowing in advance how to invest $1,000 to maximize the return on investment."

Polanyi developed the framework based on studies of simple reactions of chlorine and fluorine atoms with hydrogen gas. As technology has advanced in recent years, some chemists began testing the Polanyi rules for more complicated reactions, and the rules appeared to break down. Most notably, sophisticated molecular beam experiments by Kopin Liu at the Institute of Atomic and Molecular Sciences in Taiwan showed that the reaction of halogen atoms with methane did not conform to the rules.

"Suddenly, the rules appeared to have changed, and no one could explain why," Bowman says. "We decided to roll up our sleeves and attack the problem theoretically."

Bowman and Czako drew from the computational power of the Emerson Center, specialized software and analytical techniques. They first created theoretical-computational simulations of the experiments done by Liu and others, and then described the results mathematically.

"Our calculations showed essentially an exact agreement with the experimental results," Bowman says. "When theory and experiment agree you're happy, but you still want to know why."

Determining why the reactions did not conform to the Polanyi rules was another complicated task, involving quantum mechanics and forces that govern the reaction down to the atomic level.

"As theoreticians, we're able to zoom in and look at the results of our calculations in a way that's virtually impossible in an experiment," Bowman says.

They identified a subtle interplay between the Polanyi rules and a pre-reactive long-range force of methane with chlorine. If you follow the Polanyi rules, this long-range force, or steric control, will misalign the reactants, preventing them from docking correctly and inhibiting a reaction. But if you apportion the energy in the opposite way to the rules, the misalignment is wiped out and the reaction occurs.

"This long-range force was playing a bigger role than was previously realized," Bowman says. "It can actually trump the Polanyi rules, at least in the reactions that Liu and we looked at. The Polanyi rules are certainly not all wrong, they just appear to be too simple to apply to more complex reactions."

The reactive properties of natural gas are of particular interest since it is an important fuel. Bowman and Czako are now applying their techniques to study the combustion of methane and oxygen, which produces carbon dioxide. "It's important to understand the dynamics of this reaction, because it might lead to more efficient ways to produce fuel, and a reduction in the levels of pollution emitted," Bowman says.

Provided by Emory University

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