Researchers discover new class of chemical reaction

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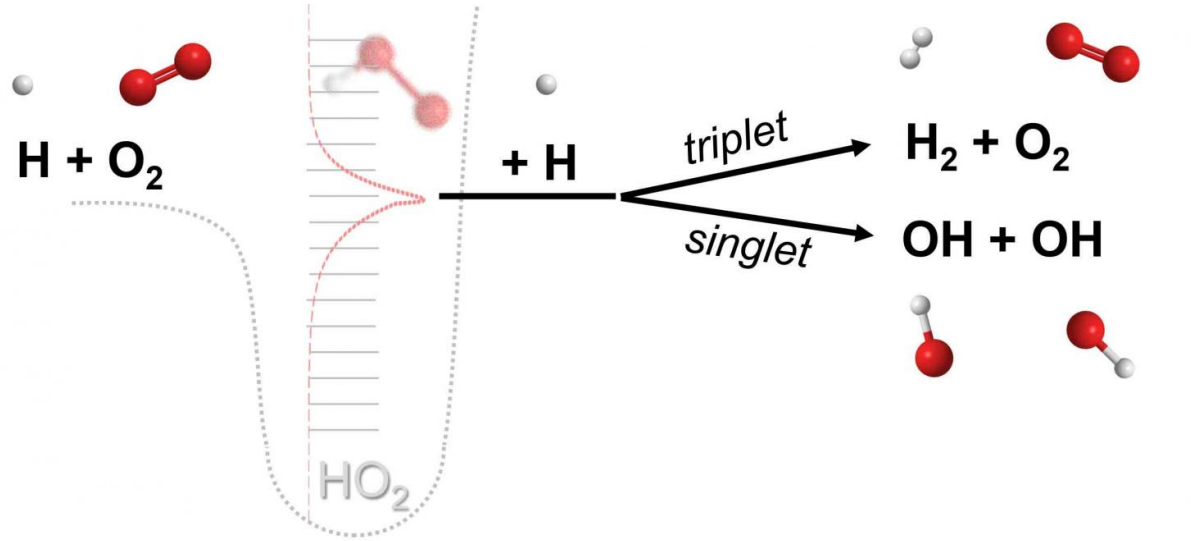

A chemical reaction where three different molecules (e.g. H, O2, H) each participate in the breaking and forming of chemical bonds. The reaction is mediated by an ephemeral collision complex (HO2**) formed from the collision of two molecules (H, O2) which then reacts upon colliding with a third molecule (H). Data from advanced computations reveal that reactions of this class, hypothesized nearly a century ago and then later assumed to be unimportant, are major chemical pathways. Credit: Michael P. Burke/Columbia Engineering

A new study led by Michael P. Burke, assistant professor of mechanical engineering at Columbia Engineering, has identified the significance of a new class of chemical reactions involving three molecules that each

participate in the breaking and forming of chemical bonds. The reaction of three different molecules is enabled by an "ephemeral collision complex," formed from the collision of two molecules, which lives long enough to collide with a third molecule.

This fourth class, which the researchers have named "chemically termolecular reactions," was first hypothesized by Cyril Hinshelwood and Nikolay Semenov in their studies of chain reactions in the 1920s and 30s (they won the 1956 Nobel Prize in Chemistry for this work). For decades, researchers have considered these reactions unimportant—if they even occurred at all—and until now, no one has studied them. Burke, who explores a variety of problems at the interface between fundamental physical chemistry and practical engineering devices, decided to investigate these reactions after realizing that common combustion situations, such as those encountered in many engines, have sufficiently high fractions of highly reactive molecules known as free radicals to make these reactions possible. The new study is published today in *Nature Chemistry*.

"Combustion has always been a launching point for understanding all sorts of other chemical mechanisms," says Burke, who is also a member of the Data Science Institute. "Potentially there could be innumerable reactions from this new class that impact how we model gas phase chemistry, from designing new types of engines to understanding the planetary chemistry responsible for cloud formations, climate change, evolution of pollutants, even perhaps the sequence of reactions that could impact the conditions for extraterrestrial life. Our discovery opens up a whole new world of possibilities."

For example, space vehicles experience very high temperatures and radical fractions in their descent back to Earth. Burke speculates that this fourth class of reactions could impact the heat flux to the vehicle, with significant implications for the design of thermal protection systems to

keep astronauts and/or payloads safe when coming down to Earth.

Working with Stephen J. Klippenstein, (Chemical Sciences and Engineering Division, Argonne National Laboratory), Burke used state-of-the-art computational methods, combining quantum chemical computations that simulate the breaking and forming of chemical bonds among reacting molecules with kinetic-transport computations that simulate the reactions and movements of bulk gases that governs performance of engineering devices.

"The power of these state-of-the-art computational methods," says Burke, "is that they can provide a unique lens into harsh chemical environments ill-suited for experimental techniques for studying individual reaction dynamics. Our calculations are based on computational data produced from first principles: the Schrödinger equation, the fundamental equation of quantum mechanics. Combining these data with other physics-based models enables us to directly pinpoint the impact of just a single reaction out of many, in a way that is very difficult to do in the lab."

Using theoretical methods, including those they developed for this study, the researchers showed that these chemically termolecular (i.e. three-molecule) reactions not only are major chemical pathways but also impact flame propagation speeds, a measure of overall fuel reactivity that governs the performance, stability, and efficiency of many modern engines.

The chemistry of many systems, including combustion and planetary atmospheres, is governed by complex chemical mechanisms, where the overall conversion from a set of initial reactants to a set of final products goes though many intermediate chemical molecules with many individual chemical reactions occurring on the molecular level. Our current understanding of the complex mechanisms of combustion and

planetary atmospheres has been premised on the classes of reactions that are known to take place. Up to now, only three classes of reactions have been considered:

- Unimolecular reactions, where one reactant undergoes bond breaking and/or forming to yield different products
- Bimolecular reactions, where two reactants collide and then undergo bond breaking and/or forming to yield different products
- Termolecular association reactions, where two reactants collide to form a molecular complex with a new chemical bond between the two reactants and a third molecule, known as the bath gas, removes some of the internal kinetic energy of that molecule to stabilize it

The bath gas is usually considered an inert, or non-reactive, molecule that does not participate in any bond breaking or forming, but instead takes away some energy from the other molecular complex (which would have enough internal kinetic energy to decompose spontaneously if no energy were taken away).

If instead the molecular complex collides with a reactive molecule, then the third molecule can participate in the bond-breaking/forming process, yielding what Burke and Klippenstein call a "chemically termolecular reaction" product. "In our paper, we showed the importance of reactions involving H + O2 complexes with other radical species, e.g. H + O2 + H, in combustion environments," he notes. "However, given the fact that reactive molecules, like free radicals and molecular oxygen, are major constituents in combustion and certain planetary environments, there is significant potential for other chemically termolecular reactions to occur and to play a significant role in other environments."

William H. Green, professor of chemical engineering at MIT, says of the

study, "It has long been known that many gas phase association reactions have very low effective rates, because the initial energized adduct does not live long enough to be stabilized by collisional energy transfer, and just falls apart back to the reactants. This has led the field to think that these transitory adducts can be completely ignored. This article reveals that even if the unimolecular reactions of energized adducts are negligible, they can still participate in bimolecular reactions, with surprisingly important consequences."

Burke plans next to generalize these theories and methods for calculating chemically termolecular reaction rates to allow similar calculations in higher pressure environments, where collisions among molecules are even more frequent, important to cutting-edge engine designs. He will also explore the implications of the finding for other reactions and chemical environments, such as those involved in pollutant formation and reduction or the chemistry of planetary atmospheres.

More information: Ephemeral collision complexes mediate chemically termolecular transformations that affect system chemistry, *Nature Chemistry* (2017). DOI: 10.1038/nchem.2842

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