An updated understanding of how to synthesize value-added chemicals

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Researchers have long been interested in finding ways to use simple hydrocarbons, chemicals made of a small number of carbon and hydrogen atoms, to create value-added chemicals, ones used in fuels,

plastics, and other complex materials. Methane, a major component of natural gas, is one such chemical that scientists would like to find to ways to use more effectively, since there is currently no environmentally friendly and large-scale way to utilize this potent greenhouse gas.

A new paper in *Science* provides an updated understanding of how to add functional groups onto simple hydrocarbons like methane. Conducted by graduate students Qiaomu Yang and Yusen Qiao, postdoc Yu Heng Wang, and led by professors Patrick J. Walsh and Eric J. Schelter, this new and highly detailed mechanism is a crucial step towards designing the next generation of catalysts and finding scalable approaches for turning greenhouse gases into value-added chemicals.

In 2018, a paper published in *Science* described a mechanism for adding functional groups onto methane, ethane, and other hydrocarbons at room temperature using a cerium-based photocatalyst. The ability to use earth-abundant metals like cerium to create value-added chemicals was an exciting prospect, the researchers say. However, there were aspects of this study that Schelter and his group, who have been working with cerium for a number of years, wanted to understand more thoroughly.

"There were some things in the original paper that we thought were interesting, but we didn't necessarily agree with the conclusions based on the data that they were reporting," Schelter says. "We had an idea that what was happening in terms of the mechanism of the reaction, the steps that were involved, and the catalyst that was operative for their chemistry was different from what they were reporting."

To run the experiments and collect the data they would need to support a new hypothesis, Schelter and Walsh applied for a seed grant from the University of Pennsylvania's Vagelos Institute for Energy Science and Technology. This funding supported a new collaboration between Schelter and Walsh, allowing the researchers to purchase specialized

equipment and hire Yu Heng Wang, a former Penn postdoc who is now an assistant professor at National Tsinghua University in Taiwan.

Thanks to the Vagelos Institute support, the Schelter and Walsh groups were able to combine their complementary expertise in inorganic and organic chemistry and to conduct experiments to obtain data required to propose a new mechanism. This included synthesizing new chemicals, studying reaction rates, looking at how the photocatalyst reacted with different isotopes, and computational analysis. The researchers also isolated the proposed reaction intermediate and were able to obtain its crystal structure, an additional challenge considering that many of the compounds in this study were highly air- and moisture-sensitive.

"We are using conventional techniques to understand the system better and to give a clear mechanism," Yang says about their approach. "Here, we are mostly using the inorganic perspective with different techniques to understand the mechanisms of the organic reaction. So, it's a collaboration of inorganic and organic perspectives to understand the mechanism."

After more than two years of work, the researchers were able to propose a revised mechanism that highlights the essential role of chlorine atoms. While the previous study implicated an alcohol-based intermediate, this latest study found that chlorine radicals, atoms with unpaired electrons that make them highly reactive, form a selective chemical "trap" in the photocatalyst that can give rise to different products.

"I think the hardest part was to understand why the reactivity was happening, and we had to approach that with some unconventional thinking of these intermediate complexes," says Walsh. "The behavior of the intermediates fits a pattern that people attribute to a radical based on oxygen, but in fact it's really a chlorine radical that's the active species, activating the alcohol to make it look like it's a radical derived from the

alcohol."

Having a detailed understanding of this chemical reaction is a crucial step towards improving existing catalysts and making these and other chemical reactions more efficient. "In order to rationally develop the next generation of catalysts, we have to understand what the current generation is doing," says Walsh. "With this information, we and others can now build on this revised mechanism and reaction pathway to push the science forward."

And while there is more work to be done towards finding a fast, scalable reaction for methane transformation, having a detailed understanding of the mechanisms that drive this specific reaction is essential to both reducing greenhouse gas emissions and being able to use methane to create value-added products, the researchers say.

"Chemistry is at its most elegant when we can refine knowledge through expanded insight," says Schelter. "The contribution here is about getting the right model and using it to advance to the next generation of catalysts that will be even better than the current one."

More information: "Photocatalytic C–H activation and the subtle role of chlorine radical complexation in reactivity" *Science* (2021). science.sciencemag.org/cgi/doi … 1126/science.abd8408

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