NEWS CHEMISTRY

New class of 'ozone-safe' refrigerants may have unexpected downside

Hydrofluoroolefins could exacerbate global warming, though real-world implications are unclear

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A worker washes windows next to air conditioning units—a typical user of refrigerants—at an apartment building in Tokyo. TORU HANAI/BLOOMBERG VIA GETTY IMAGES

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Call it a case of unintended consequences. In 2013, a new class of chemical refrigerants—used to cool everything from homes to freezers—replaced the ones that were destroying the ozone layer. But a study published this week finds that some of the new compounds, known as hydrofluoroolefins, (HFOs) can create fluoroform, a gas that has a global warming potential 14,800 times worse than carbon dioxide.

Still, the actual implications of the work—published in *the Proceedings of the National Academy of Sciences*—are unclear, says Stephen Montzka, an atmospheric scientist at the U.S. National Oceanic and Atmospheric Administration who was not involved in the research. The amount of fluoroform produced by HFOs is minute, he notes, so they still have a lower global warming potential than chemicals used in the past.

Refrigerants have come and gone seemingly as often as the seasons. First came ammonia and other toxic substances. Then supposedly safer chlorofluorocarbons (CFCs) in the 1930s. Four decades later, scientists realized that CFCs break down ozone, and the 1987 Montreal Protocol called for a ban. Hydrofluorocarbons (HFCs) were next. They're easier on ozone, but they can linger in the atmosphere for up to 260 years, and they trap heat with infernal proficiency. The Kigali Amendment to the Montreal Protocol, passed in 2016, aims to phase out 80% of hydrofluorocarbons by the late 2040s, creating the need for a new, fourth generation of refrigerants.

Enter HFOs. They have gained popularity because they break down in the atmosphere in a matter of days, giving them little chance to trap heat. The volatile "olefin" part of the chemical reacts with hydroxyl radicals, highly reactive oxidants known to degrade air pollutants. This reaction rapidly degrades HFOs, earning them a low global warming potential from the Intergovernmental Panel on Climate Change. To make that calculation, the agency evaluates how much heat a substance traps and how long it lasts in the atmosphere compared with carbon dioxide.

But, "The world is actually more complicated than that," says Max McGillen, an atmospheric chemist at CNRS, France's national research agency. No one looked at what happens if the olefin reacts with ozone instead of hydroxyl radicals, he says. The neglected interaction can produce fluoroform, a chemical that lingers in the atmosphere for 270 years and traps lots of heat.

In the new study, McGillen and his colleagues tested how five different HFOs reacted with ozone in a 123-liter stainless steel cylinder. After letting the chemicals interact in the chamber for up to 2 days, the team took samples and injected them into a gas chromatography mass spectrometer. The machine identifies the different gases produced by the chemical reaction and measures the amount of each. Three of the five HFOs produced small amounts of fluoroform.

The researchers then modeled how this chemical reaction could play out in the atmosphere using a global simulation that mimics the physics and chemistry of our planet. The vast majority of the HFO molecules are likely to react with hydroxyl radicals and dissipate, McGillen says. Nevertheless, depending on the specific compound, 0.13% to 2.96% of it is likely to react with ozone, the researchers report.

"We're the first people to actually recognize this chemistry," McGillen says.

The main reason the percentage is so small, he notes, is that only 10% of Earth's ozone is dispersed in the lower atmosphere, where an HFO leaking into the air would have the chance to react with it. The rest is concentrated much higher in the stratosphere, in a layer no thicker than two pennies, where an HFO is unlikely to reach, McGillen says.

Although the discovery is concerning, McGillen says, "It's not something to get too alarmist about." More HFOs need to be tested, he says.

Regardless, "It is very important to examine the environmental fate of substances emitted into the atmosphere—by all mechanisms," says Mark McLinden, a chemical engineer at the National Institute of Standards and Technology who was not involved in the study. "So kudos to the authors."

Curiously, McGillen says, one of the most widespread HFOs the team analyzed did not produce fluoroform. However, other studies have raised a flag about its ability to degrade into the "forever chemical" trifluoroacetic acid (TFA) and pollute drinking water. In addition, the European Union plans to ban most HFOs over the next decade.

"I would hope that chemical companies might take note of this chemistry," McGillen says. "It identifies the need to really assess the fate of these chemicals that are being produced in a more holistic way."

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