Chemists shed light on sun's role mixing up molecules

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(PhysOrg.com) -- University of Sydney scientists have discovered a startling new mechanism where sunlight can rearrange the atoms of molecules to form new chemical substances.

The research, by Professor Scott Kable, Dr. Meredith Jordan and collaborators at the School of Chemistry, is published in a recent issue of *Nature Chemistry*. It has implications for the extent that pollutants are dispersed across the Earth's surface, and how quickly they are removed.

Until now, chemical models of the atmosphere assumed a molecule emitted into the atmosphere stays fixed as that molecule, until it is either photolysed (broken up) by sunlight, or attacked by other molecules.

Professor Kable and Dr. Jordan have now overturned this theory using a common, small pollutant molecule, acetaldehyde, in a lab-based experiment that substituted a laser light for the sun.

"We chose a special variant of the acetaldehyde compound, where three of the four hydrogen atoms were replaced with 'heavy hydrogen' (called deuterium)," Professor Kable explains.

"While not changing any of the chemical or photochemical properties to any significant extent, this subtle chemical change did allow us to follow the photochemical reactions with much more detail."

Professor Kable says conventional atmospheric models predicted that

acetaldehyde should simply break in half when it absorbs light.

"Our experiments showed that the atoms in the molecules were instead extensively scrambling - specifically the hydrogen and deuterium atoms were scrambling - before the acetaldehyde broke apart."

Acetaldehyde is converted into various other chemical compounds during the scrambling process. The most important of these is an alcohol (vinyl alcohol) which has very different photochemical properties to acetaldehyde and is removed from the atmosphere by different processes.

"Our research shows that compounds such as acetaldehyde, when emitted to the atmosphere, will transform into other substances before the sun has a chance to destroy them," Professor Kable says.

"If molecules are being transformed by sunlight, then the chemistry of the atmosphere is much more complicated than we have considered up until now."

Although this work changes scientific understanding of how pollutants are dispersed through the atmosphere, Professor Kable is careful to note it won't change global warming models. "Nearly all carbon-based compounds in the atmosphere end up as CO_2 eventually. It won't change models of CO_2 loading in the atmosphere," he says.

More information: The article 'Near-threshold H/D exchange in CD3CHO photodissociation', by Meredith Jordan and Scott H Kable et al, is published in *Nature Chemistry*, 23 May 2011.

Provided by University of Sydney