

CHEMICAL PHYSICS

PINNING DOWN TRANSIENTS

Fast diffraction method probes short-lived intermediates in solution

AT A TOWN HALL MEETING, talking about transients conjures up images of fly-by-night residents of dubious character. To chemists, however, the term brings to mind short-lived species that are often invoked in theoretical reaction models but tough to pin down in the lab. The fleeting chemical entities don't hang around long enough to be studied by conventional means. But by using ultrafast diffraction methods, an international team of scientists has just succeeded in elucidating structures of transient species present in reactions of haloalkanes.

Hytcherl Ihee, an assistant chemistry professor at Korea Advanced Institute of Science & Technology in Daejeon, and his coworkers in Korea, France, and

Italy report direct experimental evidence for $\text{CH}_2\text{ICH}_2\cdot$, a solution-phase bridged radical species formed during dissociation of 1,2-diiodoethane (*Science*, published online July 14, dx.doi.org/10.1126/science.1114782).

The study broadens the range of liquid-phase samples that can be probed with time-resolved X-ray diffraction methods and may lead to similar studies of complex biomolecules in solution, the researchers say.

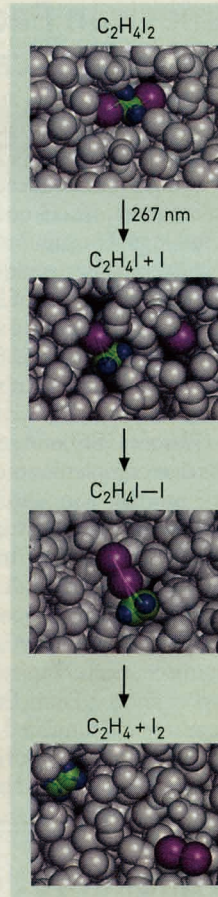
The bridged structure of the iodoethane radical, as opposed to bent alternatives in which iodine is bonded to only one carbon atom, was first hypothesized more than 40 years ago to explain the stereochemical outcome of free-radical addition reactions involving halogenated alkanes. Un-

FALLING TO PIECES Time-resolved diffraction studies show that the bridged intermediate, $\text{C}_2\text{H}_4\text{I}$ (second panel from top), forms within picoseconds of exciting the parent molecule, $\text{C}_2\text{H}_4\text{I}_2$. Dissociation to C_2H_4 and I_2 is complete after about 1 μs .

til now, the species has not been detected directly.

To examine the reaction dynamics, Ihee and coworkers used a pump-and-probe method, in which the analyte is excited with short bursts of ultraviolet laser light and then interrogated with X-ray pulses of picosecond duration from a synchrotron source.

The group finds that just picoseconds after firing the laser, diiodoethane is stripped of one of its iodine atoms. The product, $\text{CH}_2\text{ICH}_2\cdot$, adopts the bridged structure with a triangular C-I-C frame. Then within nanoseconds, $\text{CH}_2\text{ICH}_2\cdot$ binds to an iodine atom to form an isomer of diiodoethane, $\text{C}_2\text{H}_4\text{I-I}$. Finally, roughly 1 μs after the laser pulse excites the molecules, the isomer dissociates into C_2H_4 and I_2 . —MITCH JACOBY



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ORGANIC SYNTHESIS

Pyridines Yield To Diels-Alder

With the help of a little electronic tug from tungsten, chemists from the University of Virginia have managed to persuade pyridines to undergo a Diels-Alder reaction (*J. Am. Chem. Soc.* **2005**, *127*, 10568). The reaction methodology offers synthetic chemists a promising new route to the complex isoquinuclidine core common to a number of medically relevant compounds, according to the report.

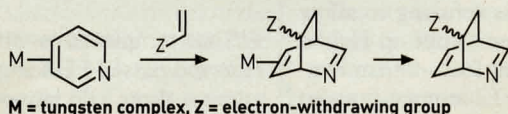
Diels-Alder reactions with pyridines are virtually unknown because the heterocycles' aromatic stabilization makes them inert to this type of cycloaddition reaction. Chemistry professor W. Dean Harman, grad students Peter M. Graham and David A. Delafuente, and coworkers reasoned that a π -basic metal, like tungsten, could coordinate one of the heterocycle's double bonds and

disrupt its aromaticity, effectively making the pyridine into a diene.

Harman previously used this strategy to coax benzene into undergoing Diels-Alder reactions. Pyridines, however, present an additional obstacle: Metals tend to coordinate to the heterocycle's nitrogen atom rather than its double bonds. Harman's group gets around this problem by using 2-substituted pyridines, such as 2-(dimethylamino)pyridine and 2,6-lutidine. "We played the trick of blocking the nitrogen from binding to the metal," Harman explains.

After coordinating to a π -basic tungsten complex, the once-inert pyridines undergo cycloaddition with electron-deficient alkenes under mild conditions. Harman's group observed that only one regioisomer of the bicyclic product is formed and that the reaction is somewhat stereoselective.

The new methodology may lead to many new reactions with π -bound heterocycles, Harman points out. His group is currently trying to make the reaction general for all pyridines. "I expect that we're going to have access to a number of reactions with heterocycles that haven't been observed before," he says. —BETHANY HALFORD



SURRENDER Coordination to a tungsten-centered base increases the Diels-Alder reactivity of the heterocycle. After cycloaddition, a single-electron oxidant cleaves the tungsten complex from the isoquinuclidine core.