

Snipping carbon rings and chains

A lot of good chemistry goes up in smoke when fossil fuels are burned. Large amounts of methane are flared off at petroleum digging sites and most of the petroleum itself eventually is ignited as fuel. Chemists are now looking for ways to use these materials more efficiently, converting them to substances amenable to further chemical manipulation into such complex materials as drugs.

Fossil fuels as they come out of the ground are rings or chains of linked carbon atoms surrounded by hydrogens. Some of these molecules contain double bonds and are easy for chemists to use. But the others, called alkanes, consist of only single bonds that are very stable and thus resistant to chemical change.

"If you ask how to cut a sausage, the first thing to do is break the skin. You want to do it specifically, with a pair of scissors, not with a battering ram," Robert H. Crabtree of Yale University said at the meeting in Washington, D.C., of the American Chemical Society. Crabtree was the first to demonstrate several years ago that special metal catalysts could selectively remove hydrogens from hydrocarbon molecules. A variety of methods have since been developed by other research teams, and several groups now report ways to approach the more difficult task of breaking carbon-carbon links after the hydrogens are gone.

Special complexes of metal atoms are the scissors for breaking the carbon-hydrogen and carbon-carbon bonds of hydrocarbons in solution. Chemists have performed such reactions on metal surfaces for several years, but these activations require high temperatures and break bonds at random, rather than selectively.

Crabtree and colleagues now use as catalysts exotic metals — platinum, iridium and rhenium — bonded to chemical groups, called ligands, such as the phosphorus-containing triphenyl phosphene. These groups keep the metal from precipitating out of the solution.

The trick to breaking up hydrocarbons is to use a limited amount of ligand, so that some binding sites on the metal remain free. These active sites then can bind to the hydrocarbon's hydrogen and carbon atoms, breaking the bonds between them. In the work of Crabtree's group, one metal molecule will have up to four free active sites. But Robert G. Bergman and colleagues at the University of California at Berkeley leave only one active site free.

Both Crabtree and Bergman find that, in some molecules, the active sites will break a carbon-carbon group also. "These are rather special systems designed to present the carbon-carbon bond in a favorable light," Crabtree says.

Mimicking biology is another approach

to the breaking of hydrocarbon bonds with metal catalysts. John T. Groves of the University of Michigan at Ann Arbor uses synthetic catalysts resembling the molecules in liver that convert hydrocarbons into alcohols for excretion. These catalysts have an oxygen attached with a double bond to a metal surrounded by ligands. The oxygen is inserted into the hydrocarbon between the hydrogen and carbon atoms, making a single band with each.

While the activation of hydrocarbons is now accepted among chemists, the mechanism remains controversial. "This chemistry is so new we are still trying to understand why it takes place," Bergman says.

"We have demonstrated that these reactions can work, in principle," Crabtree concludes. He says other chemists in industry are already examining potential applications. — J.A. Miller

Soil and land biota give, not take, CO₂

In the continuing attempt to improve calculations of the various sources and sinks for carbon dioxide (CO₂), a team of biologists has come up with estimates showing that soil and terrestrial biota contribute carbon to the atmosphere rather than store it. The finding throws a new and potentially significant factor into an already complicated equation.

Researchers from the Ecosystems Center at the Marine Biological Laboratory (MBL) in Woods Hole, Mass., and from the Complex Systems Research Center at the University of New Hampshire in Durham, estimate that between 1860 and 1980 soil and biota released from 135 to 228 billion tons, or gigatons, of carbon into the atmosphere. In 1980 alone, they calculate, between 1.8 and 4.7 gigatons were released, with 80 percent of this quantity due to deforestation, particularly in the tropics.

It has been estimated previously that over the last 120 years, CO₂ in the atmosphere has increased by no less than 15 percent, and maybe by as much as 30 percent. Some modelers have assumed that soil and biota are a sink for carbon because the build up in CO₂ would stimulate storage of carbon in soils and in plants by increasing photosynthesis. However, the researchers note that temperature, water and nutrient supply are much more important than the availability of CO₂ in setting the rate of photosynthesis, and that "the general warming of the past century would probably cause a loss of carbon stored on land."

The researchers found that when an ecosystem such as a forest is disturbed through clearing for agriculture and pasture, or for cutting and regrowth of forest, the carbon in the upper meter of soil is reduced by as much as 50 percent as the microbes oxidize the carbon. "The biota is a source of carbon dioxide and not a sink," says John Hobbie of MBL. "A lot more carbon is coming into the atmosphere than the geochemists thought, so the models don't balance anymore."

The researchers base their findings, to be published in *SCIENCE*, on three sources of information: rates of clearing for agriculture gathered by the United Nations Food and Agricultural Organization since 1949; an independent estimate of rates of clearing of tropical forests; and on the as-

sumption that in tropical regions, agricultural expansion since 1950 has occurred at a rate proportional to population growth. They do not consider the contribution of undisturbed ecosystems because in general, these are assumed to contain a steady amount of carbon.

Combustion of fossil fuels, the other major source of carbon, still adds more CO₂ to the atmosphere than the biota and soil, but the amount has been declining since the oil shortage in 1973. The researchers express cautious optimism that changes in rates of reforestation also could help slow down the increase in CO₂. — C. Simon

New tests seek out seafood toxins

According to an old adage, a diner does well to avoid seafood during months lacking "r," when humans are most apt to fall prey to the chemical warfare of the sea. Last week, at the meeting of the American Chemical Society in Washington, D.C., government officials joined scientists to discuss the newest findings in the distribution and chemistry of seafood toxins. In particular, two researchers announced the development of kits that commercial and recreational fishermen could use to test seafood for toxins at the site of the catch.

The main plagues of the seafood industry — ciguatera fish poisoning and paralytic seafood poisoning (PSP)—stem from dinoflagellates, single-celled organisms that make up the dreaded red tide. Summer upwellings bring nutrients to the ocean's surface, providing a fertile home for the tiny poison-producers, upon which bony fish and shellfish feed.

Though many marine organisms can eat and accumulate the toxins without ill effect, humans are not so lucky. Both ciguatera and saxitoxin (the main poison implicated in PSP) interrupt transmission of nerve impulses by keeping sodium ions from moving through cell membranes.

Edward P. Ragelis of the Food and Drug Administration (FDA) estimates that every year, between 10,000 and 50,000 fish eaters get ciguatera, an often chronic, occasionally fatal disease characterized by diarrhea and temperature reversal (patients