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, CO_2

In the continuing attempt to improve calculations of the various sources and sinks for carbon dioxide (CO_2), 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, CO_2 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 buildup in CO_2 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 CO_2 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 assumption 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 CO_2 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 CO_2. — *C. Simon*

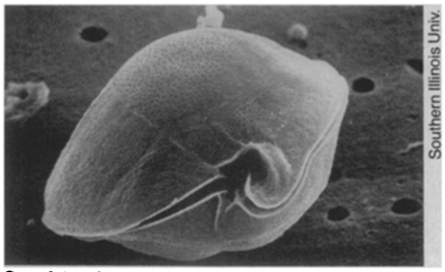
New tests seek out seafood toxins

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 ciguatoxin 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



Gambierdiscus toxicus, *a dinoflagellate implicated in ciguatera fish poisoning.*

perceive cold as hot and vice versa). PSP, while less common, is more deadly; its victims suffer usually fatal paralysis. Both toxins lack effective antidotes.

Currently, the only way to prevent harvesting of poisonous seafood is to close catch areas seasonally or in response to an outbreak of a toxin-related disease. "Ciguatera and PSP are major impediments to the development of the U.S. fishing industry," says Ragelis. "They also present a serious threat to communities on small isolated islands, where people depend on seafood for protein and bulk."

But quarantines do not prevent contaminated seafood from being caught. Improved methods of preserving and transporting foods have turned the problem of seafood toxicity into an epidemiologist's nightmare, and precipitated complicated legal liability battles. "It's like not having a traffic light at a dangerous intersection," says Ragelis. "We have no way to monitor the harvesting of toxic seafood, so people just keep getting hit."

But now, using the relatively new technique of enzyme immunoassay (EIA), two scientists are creating methods to screen seafood for toxins as it is caught. "We're working with the FDA to develop a pokestick for fish," says Yoshitsugi Hokama, a ciguatera researcher at the University of Hawaii in Honolulu. "Basically, a fisherman could poke a fish and dip the stick in a series of reagents. If the stick turns blue, you don't eat the fish." Meanwhile, Patrick E. Guire of Bio-Metric Systems, Inc. in Eden Prairie, Minn., has begun field-testing a dip stick that works on a similar principle to detect saxitoxin in pulverized samples of shellfish.

EIA utilizes enzymes and monoclonal antibodies, which react with the toxin, to turn color. While researchers have found this assay just as sensitive as more commonly used assays, they say that EIA provides a cheaper and easier way to detect the concentration of single, specific toxins in solution. However, scientists now believe that ciguatera and PSP are not caused by single toxins, but by several closely related poisons. To be effective, the chemical assay kit must be specific enough to detect only toxic chemicals, but not so specific that it misses potential poisons. Both Guire and Hokama hope to overcome the problem of specificity soon, and to have their kits ready for market within the next few years. *—S. Steinberg*

Gamma ray quasar could be a shock

Astronomers have been working with invisible forms of radiation, radio, X-rays and gamma rays for anything from a few years (gamma rays) to 50 years (radio). But still the first thing they do when they find a new source of such radiation is to look for a visible object to identify with it. It is still a reflex to use the visible sky as a reference.

CG 195+ 04 is the catalog designation of the second strongest unresolved source of high-energy gamma rays known in the sky. "Unresolved" means it may lie anywhere in, and possibly all over, a rather sizable "error box" that represents the uncertainty in the locating ability of its detector, the COS B satellite. The job of identifying CG 195+ 04 with a compact radio or optical object means finding a plausible candidate within that error box. Now an identification with a quasar designated 0630+ 180, which is both a radio and an optical object, is proposed.

If the identification is correct this would be the second quasar known to emit gamma rays and the most luminous source of high-energy photons (gamma rays and X-rays) known. It would also be an argument in favor of a new theoretical model of quasars proposed earlier this year and "the first step toward identifying a potential source of the nucleonic component of cosmic rays." The identifying observations are reported in the Aug. 15 ASTROPHYSICAL JOURNAL LETTERS by A.F.J. Moffat of the University of Montreal and the University of Bonn, West Germany; R. Schlikeiser and W. Sieber of the Max Planck Institute for Radioastronomy in Bonn; M.M. Shara of the Space Telescope Science Institute in Baltimore, R. Tufts of Cambridge University in England and H. Kühr of the University of Arizona's Steward Observatory.

The quasar was first discovered with the Effelsberg radio telescope near Bonn and then further studied with a radio telescope at Cambridge. Optical observations were done with the Smithsonian Astrophysical Observatory/University of Arizona Observatory Multiple Mirror Telescope on Mt. Hopkins in Arizona. Detailed studies of the quasar's radio and optical spectra were made and compared with other quasars to prove that it in fact is one. It qualifies in all respects except for its gamma-ray luminosity, which is "spectacular." According to these observers the ratio of gamma-ray luminosity to luminosity at other wavelengths for this quasar is 100 times that for 3C273, the only other quasar known to emit gamma rays.

To account for 0630+ 180's gamma-ray luminosity, Moffat et al. refer to the theoretical model they call "a proton quasar." A model of this kind was proposed in the ASTROPHYSICAL JOURNAL earlier this year (Vol. 265, p. 620) by R.J. Protheroe and Demetrius Kazanas of the NASA Goddard Space Flight Center in Greenbelt, Md.

The standard model of a quasar assumes that a black hole in its center pulls in matter from the surroundings. The kinetic energy gained by this matter as it falls is somehow converted to the radiation astronomers record. This conversion will happen only if for a while somewhere along the way the velocities of the infalling particles are made random (instead of all being continually directed toward the center).

The standard model proposes that forces existing in the neighborhood form the infalling matter into a disk, the so-called accretion disk, and bumping and grinding in this disk randomizes the velocities. Protheroe and Kazanas propose instead a shock front composed of protons with relativistic energies. Such high-energy protons would have enough momentum to resist the pull of the black hole's gravity for long enough so that the shock front would be able to maintain itself if it had a continual source of new protons (the infalling matter). Fighting gravity with its momentum, constrained from the outside by the ram pressure of the infalling matter above it, the shock front would sit as a spherical shell around the black hole at a radius of about 10^{17} centimeters, roughly a tenth of a light year.

Some of these energetic protons would interact with the other matter nearby and produce pions, which would then decay, producing gamma rays. Some of them might also leak out and become cosmic rays. The model was designed to explain the gamma rays from 3C273, which the accretion disk model would not provide. One of the criteria for its success, Protheroe and Kazanas wrote, would be a showing that other quasars emit gamma rays. If 0630+ 180 and CG 195+ 04 are the same object, at least one such is now known. But there's a big hitch.

The error box of CG 195+ 04 is so large that several other radio sources and at least one other (nonquasar) optical source lie within it. To settle the identification definitively will require a future gamma-ray telescope with much better resolution than COS B. *—D.E. Thomsen*

Organ transplant drug OK'd

A drug that reduces rejection of kidney, liver and heart transplants has been tentatively approved by the Food and Drug Administration. Cyclosporine is expected to improve the success rate of transplants between unrelated persons (SN: 3/5/83, p. 150; 9/29/79, p. 215). The drug will be marketed as "Sandimmune" by Sandoz Pharmaceuticals of East Hanover, N.J. It was approved via a streamlined process — the application, including 123 volumes of data, was received just nine months ago. □