

Martian organics and glow discharges

One of the major surprises of the Viking mission to Mars was the failure to detect even a trace, down to parts per billion or less, of organic materials in the material of the surface. Prior to Viking, many scientists believed—and still do—that carbon-rich meteorites should have left quantities of the stuff when they crashed into the planet in the past; some researchers felt that there was even visual evidence, such as surface features, photographed from orbit, that looked as though they had been shaped by water—a key ingredient in laboratory studies that have led to the ready formation of organic molecules. Yet no organics were found.

Various theories have since evolved to explain their absence. Ultraviolet light could break them up, although the thinnest of surface dust layers, or even a cloud, could effectively block most of the UV. Ozone, detected by Viking in the Martian atmosphere, could shield the Martian surface as it does the earth's, but it could also oxidize organics with which it came in contact. Analyses of results from the complex biology instruments on the Viking landers suggested to some researchers the presence of peroxides and superoxides, other ready sources of destruction. There has even been the suggestion that there might be Martian microorganisms that are "cannibals," consuming the organic remains of their ancestors and leaving a living population that is either too small or too localized for the Vikings to find.

But for all the facility of hindsight, as Viking project scientist Gerald Soffen points out, the missing organics were "really a shock"—so much so that scientists are still trying out new answers to the mystery. The latest suggestion, offered by A. A. Mills of the University of Leicester in England, not only adds to the list, but proffers some guidance for return missions to the red planet.

Mills proposes that during the huge dust storms that regularly swirl across the planet, friction within the dust clouds may build up electrostatic charges on individual particles, leading to "glow discharges" that effectively cleanse the particles of any organic matter. On earth, such built-up potentials are usually discharged by lightning, but the low Martian atmospheric pressure (less than one percent of earth's), says Mills, could let the more gradual glow discharges work. Terrestrial glow discharges are often seen in the upper atmosphere as auroras. The glow discharge, he points out, is "a very effective scavenger of even the most tenacious traces of organic matter from surfaces," particularly silicates, and, as such, is the conventional final stage in cleaning astronomical mirrors (in a near-vacuum chamber) for aluminizing.

In his laboratory, Mills tested the idea

by removing most of the air from a flask containing washed, oven-dried sand, then spinning the flask by hand to simulate a dust-storm's effect in building up friction among the grains. At a pressure of 0.1 torr (about 0.0001 atmospheres, which is equivalent to that high in the Martian atmosphere) a faint, greenish glow appeared, brightening and contracting as Mills bled in enough air to approximate the pressure near the surface, when ribbon-like discharges also began to show, finally dying out to mere sparkles at about 50 torr.

Glow discharges, he points out, also promote the dissociation of molecular gases into such products as ozone and atomic oxygen, which could contribute to the oxidation believed to be a factor in the reddish color of the Martian surface material. Hence, he suggests, future missions might do well to seek organic materials in the less reddish areas, as well as to attempt radiofrequency and electrostatic-field measurements in hopes of estimating the Martian glow-discharge potential. □

Cold studies specify light chemistry

Flash! The eye is quicker than the chemist. The first step in an eye's response to light at room temperature has been too rapid to examine, even in ultrafast studies with lasers (SN: 7/9/77, p. 26). In less than 6 picoseconds after it is hit by light, the visual pigment rhodopsin converts to prelumirhodopsin, first intermediate in the chemical sequence known as the visual cycle.

Now Kevin Peters and Meridith L. Applebury of Princeton University and Peter M. Rentzepis of Bell Laboratories have chilled the visual pigment and observed its reactions in slow motion with laser light. Even at a cool 4°K, the initial reaction is far from sluggish. Formation of prelumirhodopsin takes a mere 36 picoseconds, but permits chemists a long enough glimpse to detect important details of the process.

Color, or the light-absorption property, is the criterion chemists use to identify the substances of the visual cycle. Before exposure to light, rhodopsin is deep red;

it is sometimes called "visual purple." In contrast, if prelumirhodopsin were to last long enough to be seen, it would appear green-yellow. Peters and colleagues have evidence describing what structural difference in the chemicals produces these different absorption characteristics.

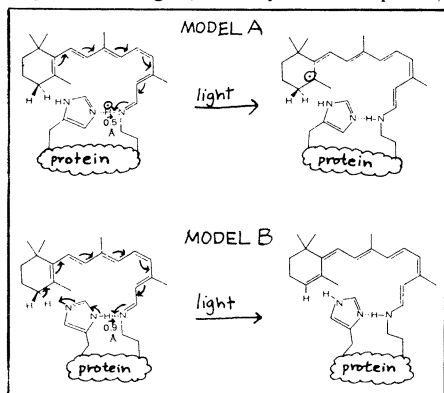
The initial transformation, from rhodopsin to prelumirhodopsin, adds a proton to a specific site, the researchers report in the August PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES. The speed of that reaction, as well as data from other laboratories, rules out an earlier suggestion that in the first step bulky sections of the rhodopsin rotate around a double bond.

The researchers pinpoint the crucial site as the junction between the protein portion of rhodopsin and its kinky light-absorbing tail. There, a nitrogen of the protein extends a double bond to a carbon atom of the tail. The researchers verified involvement of that site by comparing the response to light from slight variations of rhodopsin: one with a proton attached to that junction nitrogen, the other with a heavier deuterium nucleus bound there. The initial reaction of the protonated rhodopsin is about seven times as fast as that of the deuterated molecule, thus implicating the connecting site. The researchers are now working to distinguish between two plausible, detailed models. A likely source of the added protons, they suggest, is some amino acid (such as histidine) in the protein portion of the rhodopsin.

To describe the proton transfer further, the investigators invoke an axiom of quantum mechanics, appropriately called tunneling. Rentzepis explains that "classically" such a chemical reaction could never take place. The energy added to the system from the light is just not great enough to boost the molecules' state of excitation over the energy barrier separating it from the lower energy level of prelumirhodopsin. Yet the reaction does occur. "The barrier is too high to get over," Rentzepis says, "so the only way is to tunnel through."

Chemists have identified numerous inorganic examples of proton tunneling, but this is among the first in a biological system. The evidence for tunneling is that, as the temperature of the molecules is reduced, the reaction rate levels off, rather than dropping toward zero as the classical theory predicts.

Prelumirhodopsin was originally identified in low temperature studies. The combination of cold and ultrafast techniques may uncover even more short-lived compounds. In these studies Peters and colleagues observe a transient precursor to prelumirhodopsin (preprelumirhodopsin?) forming too fast to be monitored with the current methods. The researchers hypothesize that that precursor is the excited state of rhodopsin, after the molecule has absorbed energy from light, but before any chemical change occurs. □



Plausible proton shifts for initial vision step.