

Chemists discover step in life process; imitate "nitrogen fixation" in lab

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Two chemists at the University of California, San Diego report they have succeeded in imitating in the laboratory a key life process called "nitrogen fixation", thus scoring a major advance toward understanding how the building blocks of all living cells are constructed.

Dr. Gerhard N. Schrauzer, UCSD professor of chemistry, and doctoral candidate Gordon Schlesinger said they have duplicated with simple chemicals the important functions of a complicated enzyme called nitrogenase, which acts as a catalyst in producing ammonia from nitrogen in the air.

They made the breakthrough after barely 10 months of experimentation, financed by a grant from the National Science Foundation. Investigators throughout the world have worked for many years on the same problem, and have not until now been able to imitate the biological process.

Nitrogen fixation is the process in which certain plants, with the aid of bacteria, convert nitrogen gas in the air to ammonia (NH₃). Ammonia is a primary material used in the construction of proteins, which in turn are the essential building blocks of all living cells.

Schrauzer said the experimental work completed to date is highly promising. "While we cannot foresee immediate industrial applications for our new catalyst system," he said, "we believe it will lead us to a deeper understanding of this enzyme and how it performs its job. Such knowledge could lead to an improved catalyst for industrial ammonia production. This would, in turn, help to increase the supply of this important, high grade fertilizer needed by the world's fast-growing population."

The heart of the UCSD chemists' system is a catalyst, or chemical reaction accelerator, made by combining salts of the metal molybdenum with sulfur-containing molecules in the presence of small quantities of iron. When a small quantity of this catalyst is placed in water and nitrogen gas at elevated pressure, and certain other ingredients are added, ammonia is slowly produced. The simple combination of chemicals comprising the UCSD catalyst contains only a dozen or so atoms, while the complicated enzyme which performs the same task in the living cell contains an estimated 100,000 atoms.

"Of course our catalyst system is still much less efficient at producing ammonia than is the enzyme," Schlesinger noted, "but we feel that we are following the same evolutionary process which was used by nature in developing and improving the nitrogenase enzyme. Nature must have started fixing nitrogen with simple, readily available materials and then evolved more efficient catalysts as life developed in complexity. And as we learn more about our catalyst and improve it, it is undergoing a kind of chemical evolution in the laboratory."

In the course of their research, Schrauzer and Schlesinger demonstrated that only molybdenum, of all the common metals, is efficient as a catalyst for nitrogen fixation. Molybdenum is known to be present at the heart of the nitrogenase enzyme along with small quantities of iron. "Thus," commented Schrauzer, "life on earth is totally dependent on this unusual metal." Until now many scientists have considered molybdenum to be a relatively uncommon and uninteresting metal.

In addition to promoting the utilization of nitrogen for biological purposes, the enzyme can catalyze chemical reactions involving other similar molecules, including acetylene, hydrogen cyanide, nitrous oxide, and hydrazoic acid. The UCSD chemists, in a striking demonstration of the validity of their catalyst system as a model for the enzyme, have also duplicated these reactions.

The basic principle of nitrogen fixation was noted as early as the time of the ancient Romans, who were aware that certain leguminous plants could restore and maintain soil fertility. In 1838 a French chemist, J.B. Boussingault, found that pea seedlings appeared to have an ability to extract nitrogen from the air. It was several decades, however, before it was discovered that pea seedlings do not perform the "fixing" process unaided, but work in a symbiotic relationship with certain microorganisms which form nodules on the plants' roots.

Early in this century, two German chemists, Haber and Bosch, developed an industrial process for combining nitrogen gas with hydrogen gas to make ammonia. But the essential secrets of the way in which nature makes ammonia from nitrogen continued to mystify scientists.

In the early 1960's, Du Pont investigators made a major advance by isolating the critical enzyme, nitrogenase. But they still did not know how the enzyme performed its job.

Then, last summer, Schrauzer and Schlesinger launched their experiments. Their efforts were crowned with success six months later when one of their catalysts first produced measurable quantities of ammonia in the laboratory.

Eighty percent of the air inhaled by humans is nitrogen gas. Inhaled, it does not undergo chemical reactions in the body (as does oxygen), and is exhaled unused. Only certain plants and bacteria possess nitrogenase, the enzyme required to form ammonia from nitrogen. The ammonia thus produced is then used by plants for the construction of proteins as a part of nature's nitrogen cycle.

Consuming these plants, animals break the plant proteins into simple units called amino acids, then re-form these acids into their own proteins. Humans, by consuming plant and animal proteins, thus obtain their protein supplies second or third-hand.

Thus the transformation of nitrogen into ammonia marks the beginning of protein production for eventual use by humans. In the natural decay process which completes the nitrogen cycle, bacteria re-convert animal and plant proteins into gaseous nitrogen, in which form it becomes available to begin the cycle anew.

Ammonia is best known to the average householder as a mild cleaning agent with a pungent odor. It is made industrially on a large scale for many uses, including explosives, plastics, fertilizers, adhesives, and dyestuffs. The chemical is manufactured under complicated conditions requiring temperatures as high as 800 degrees Fahrenheit and pressures up to 1,000 times higher than ordinary air pressure.

Nature, on the other hand, makes ammonia at room temperature and ordinary air pressure. And she makes ten times as much ammonia as does the chemical industry. Part of the challenge which has faced chemists has been to duplicate nature's ammonia-making process, and thus end the need for the costly high temperature and high pressure conditions required in commercial production.

Schrauzer, who was born in Germany in 1932, will soon become a naturalized U.S. citizen. He is an authority on vitamin B12, and in 1963 developed a simple model compound of this complicated cobalt-containing vitamin.

Schrauzer received his doctorate in chemistry in 1956 at the University of Munich, where he was a member of the University's faculty until 1964. He came to California in 1964, and joined the UCSD faculty as a full professor in 1966.

Schlesinger, who was born in Los Angeles in 1939, received his B.S. in chemistry from UCLA in 1962. At UCLA he won a fellowship from the National Science Foundation. Before enrolling at UCSD as a doctoral student in chemistry, he worked for seven years as an industrial physicist and chemical engineer. He is preparing his Ph.D. thesis on the subject of nitrogen fixation.