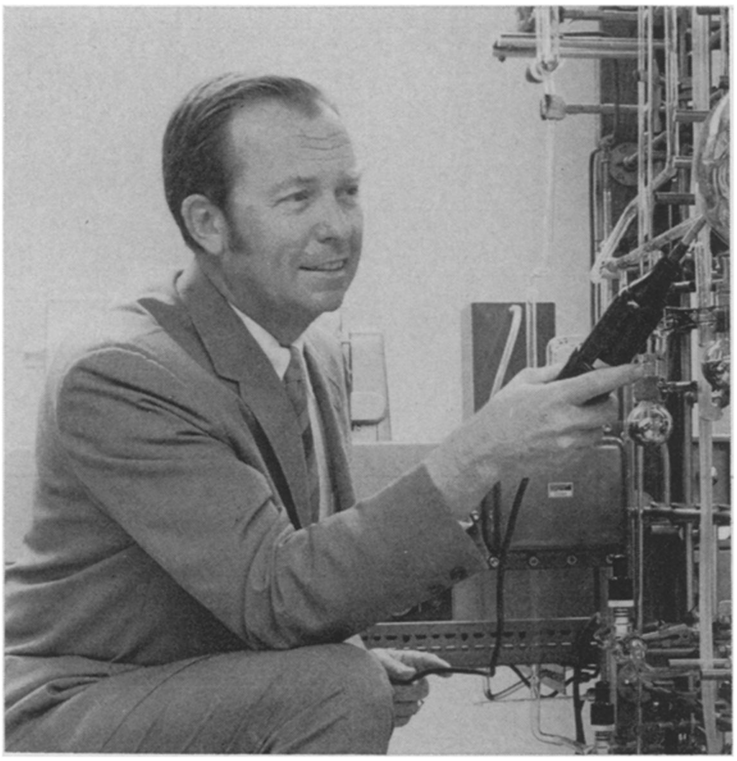
SINGLET OXYGEN

Another pollution culprit

Chemists suspect that an active breed of oxygen is a harmful air pollutant

by Edward Gross



University of California, Riverside

Pitts: Singlet oxygen may be crucial in specific cases.

General recipe for a 20th century urban atmosphere: Begin with pure air. From millions of autos, take several thousand tons of nitrogen oxides yearly. Sift in sulfur oxides from burned fuel oil. Sprinkle liberally with hydrocarbons, carbon monoxide and ozone. Season with aldehydes, ketones and peroxides. Garnish with soot particles from incinerators. Let simmer in direct sunlight.

After a few hours, a choking eye-searing and poisonous haze called photochemical smog will be ready for consumption.

Chemists know many of the ingredients of the toxic brew and even some of the major reactions, but there is still much to learn about what happens chemically in that turbulent soup. Before 1967, only a handful of scientists—even air pollution experts—considered as significant the role of something called singlet oxygen.

Even today, it is a relative stranger, but it is becoming more prominent. In October, 135 U.S. and foreign scientists gathered in New York for the first international conference on the role of singlet oxygen in the environment. A few years earlier, the meeting's sponsor, the New York Academy of Sciences, would have been lucky to have attracted a tenth of that number.

Singlet oxygen is molecular oxygen in an excited, or higher-energy state. A source of energy is sunlight, and energy is the reason for the emerging concern. In terms of electronic structure, singlet oxygen is characterized by a pair of electrons spinning in opposite directions. By contrast, in the normal or ground-state condition of molecular oxygen the electrons spin in the same direction. The result of these spins, when acted upon by a magnetic field and observed on a spectrometer, is three distinct spin states for the ground state (also called a triplet state) and one spin state for the singlet.

The presence of that single state opens an atmospheric Pandora's box. Its higher energy makes singlet oxygen a potential reactive species, since to get rid of its excess energy and return to the ground state it could enter readily into reactions with other substances.

Since it almost certainly exists in the urban atmosphere, scientists now reason that it must react with pollutants to play a role in smog formation, as well as produce its own harmful biological effects.

Researchers emphasize, however, that the elimination of singlet oxygen will not end air pollution. Its importance cannot be measured in terms of tons of pollutants converted, says Dr. James N. Pitts Jr., professor of chemistry at the University of California at Riverside.

"I'm not saying it's the major source of air pollution," he explains. "I'm not saying it's the reason we have air pollution. But it could be among the most critical contaminants in terms of specific reactions. Its health effects could be serious and they warrant detailed examination."

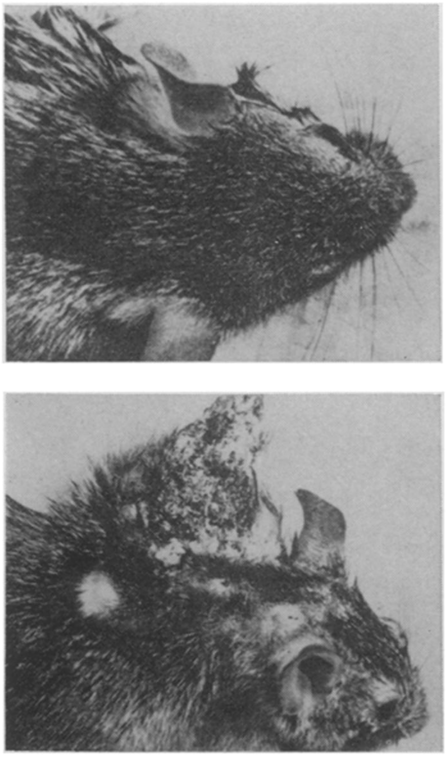
Dr. Pitts ranks singlet oxygen as a secondary pollutant, one not directly emitted in the air but formed by chemical and photochemical processes. One obvious reason for its not being a major source of air pollution is its quantity in the air. Dr. R.H. Kummler of General Electric's space sciences laboratory in Philadelphia estimates that the singlet oxygen concentration in the air is at most two hundredths of a part per billion, and a thousandth of that at a minimum.

Though it may exist in the lower atmosphere, its lifetime is estimated at only 0.1 second before its extra energy is released by quenching in collisions with atmospheric substances. This may seem like a short life, but in relation to other particles whose lifetimes are measured in thousandths and millionths of a second, it is long enough to enter into reactions that are biologically and environmentally significant.

Because of its relatively brief life, singlet oxygen wasn't discovered in the atmosphere until 1958, when electronic telemetry equipment in rockets detected its presence in the upper atmosphere, where it exists for a longer time because there are fewer molecules to quench it. It still has not been detected in the lower atmosphere, because of interference from other air pollutants and scattered sunlight.

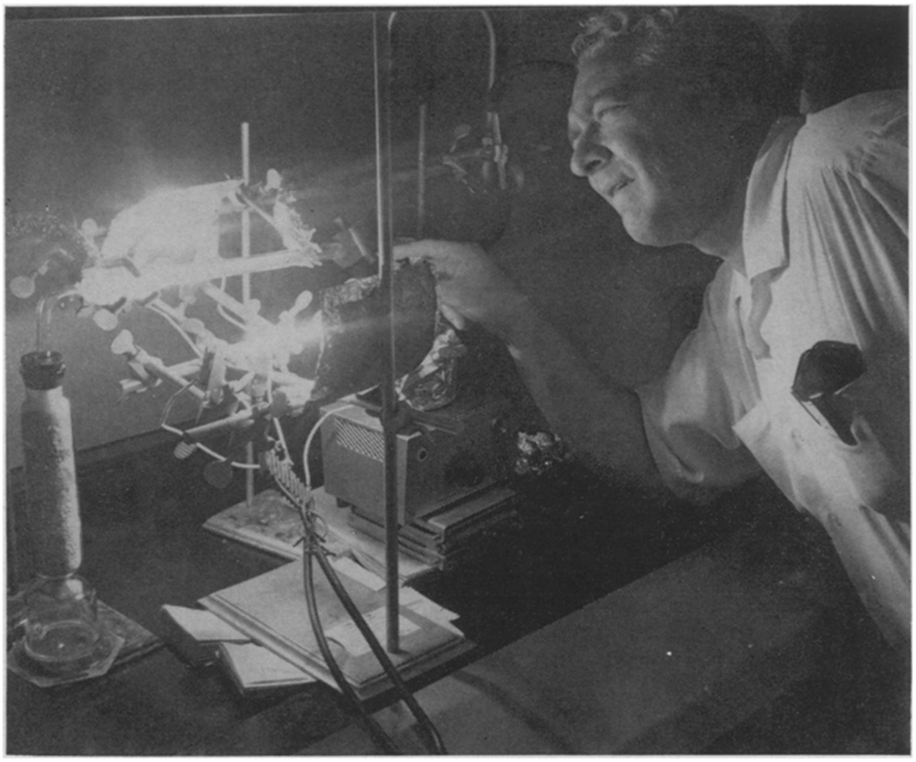
Its presence in the lower atmosphere was postulated as early as 1960 but not much attention was paid to the idea since the only way scientists could envision singlet oxygen being produced was by the direct irradiation of ordinary oxygen by sunlight, a process that could not produce significant amounts.

So there the idea sat until 1967, when Dr. Pitts and his co-workers at Riverside showed that singlet oxygen could be produced in a much more efficient way. They suggested that a



A.U. Khan & H.J. Lipner

Singlet oxygen: Possible cancer link.



Robert Petterson

Petterson: Making enough cheaply would open the way to detailed studies.

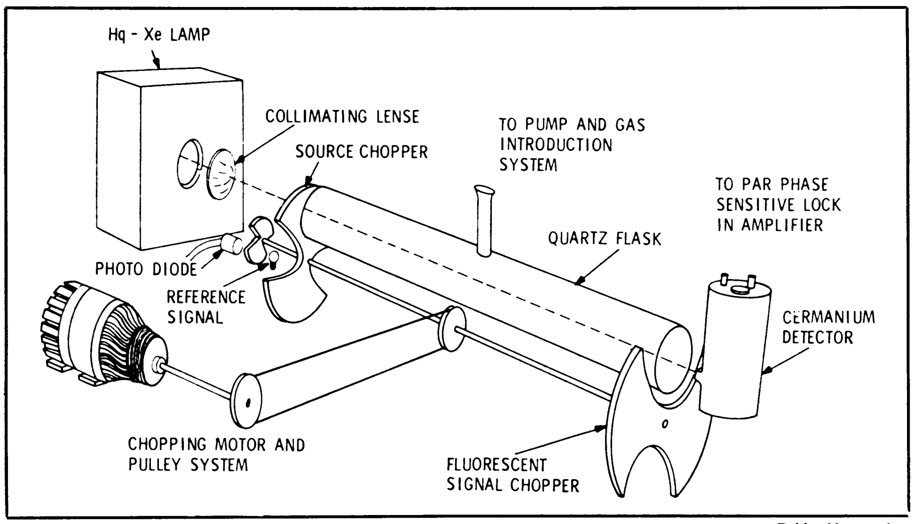
wide variety of atmospheric pollutants could absorb energy from sunlight. If regular molecular oxygen quenched these known, excited compounds, then it could absorb their energy and be converted to singlet oxygen that could go on to trigger further chemical reactions.

This proposal of electronic energy transfer gave new meaning to singlet oxygen since there were enough pollutants to produce significant quantities down an excitation chain.

Today, chemists recognize several additional ways to produce singlet oxygen. In the first, ozone, a molecular form of oxygen with three atoms instead of two, is photolyzed, or broken down by light, into singlet oxygen and oxygen atoms. In the two remaining processes, energy transfer and chemi-excitation, no light at all is needed except to make ozone in the first place.

In the energy transfer mechanism, ordinary oxygen contacts ozone and absorbs enough energy to became singlet oxygen. In the chemi-excitation method, an organic molecule reacts with ozone, breaking it down into singlet oxygen.

The last two reactions, since they can occur without light after the ozone is made, have special significance for processes inside the human body. For example, a person could breathe in ozone, which is not only a pollutant but is sometimes used in hospitals as a disinfectant and deodorizer, and have it react with the right organic compound to produce singlet oxygen. From



R.H. Kummler

Flow tube apparatus: Testing reactions between pollutants and singlet oxygen.

there, the singlet oxygen could attack the biochemical machinery of the cell.

Dr. Robert W. Murray of the University of Missouri suggests that ozone has been taking the blame for singlet oxygen. "What is being attributed to ozone may in part be due to singlet oxygen," he says, and he is presently exposing tobacco seedlings to singlet oxygen to see if indeed it is toxic.

In addition, scientists at the Atomic Energy Commission are coming to suspect singlet oxygen as an intermediary in radiation damage, with implications for cancer therapy (SN: 12/21, p. 614). The work of Dr. Ahsan Ullah Khan of Florida State University indicates a possible connection between cancer and singlet oxygen. Dr. Khan, after painting the skins of rats with a known carcinogen, exposed some to ordinary light and kept some in the dark. The light-exposed rats had twice as much skin cancer as those protected from the light.

Dr. Khan has worked out a possible mechanism to explain this occurrence involving excitation, quenching, singlet oxygen formation and a subsequent attack on DNA or an enzyme to produce cancer.

Dr. Pitts sees still another place where singlet oxygen can be a culprit. He thinks that the air pollutant PAN (peroxyacetylnitrate), can result from auto exhaust, and plant and animal tis-

. . . singlet oxygen

sue could be broken down in the body by water to produce singlet oxygen, which in turn might do damage to the life system.

But the implications for singlet oxygen go further than isolated reactions. It may be at the heart of most reactions in which light degrades materials, from plastic decomposition to sunburn to the spoiling of cooking oils. "In any known sensitized photo-oxidation reaction, singlet oxygen seems to be the most probable reaction intermediate," says Dr. Anthony M. Trozzolo of Bell Telephone Laboratories in Murray Hill, N.J.

The major obstacle to pinning down the effects lies in its short lifetime. A way must be found to produce a continuous stream of it at atmospheric pressure so its effects on plants and animals can be observed. At present a microwave generator is used to produce it, but the method requires low atmospheric pressure.

To overcome this problem, Dr. Robert Petterson of Loyola University in New Orleans is developing an apparatus that he hopes will be so simple and cheap that "high schools could make singlet oxygen with this rig." The machine consists of two chambers, a light one where a crystalline sensitizer is irradiated in the presence of oxygen, and a dark one where the singlet oxygen is detected or where a test subject could be placed, all at normal atmospheric pressure.

But so far, so bad.

"The kind of results we're getting aren't good," complains Dr. Petterson. "We're not getting enough singlet oxygen. We hope we can soup it up with more powerful lights and get more through."

In the meantime, the U.S. National Air Pollution Control Administration, because requests for research grants to study singlet oxygen are mounting, wants to know more about it. The NAPCA sent Dr. J.A. Hodgeson to the New York conference. Dr. Hodgeson, who is doing singlet oxygen research himself, evaluated the conference disclosures on singlet oxygen: "From what I have seen here, I don't think singlet oxygen is the predominant intermediate in smog formation. I thing it could be important in atmospheric reactions with specific pollutants and may be of some biological importance. It certainly is worth investigating."

Dr. Hodgeson feels that more must be known about its existence and concentration in the atmosphere, and that means more research. But at a time when NAPCA itself is cutting back on air pollution research funds, the task will not be easy. □