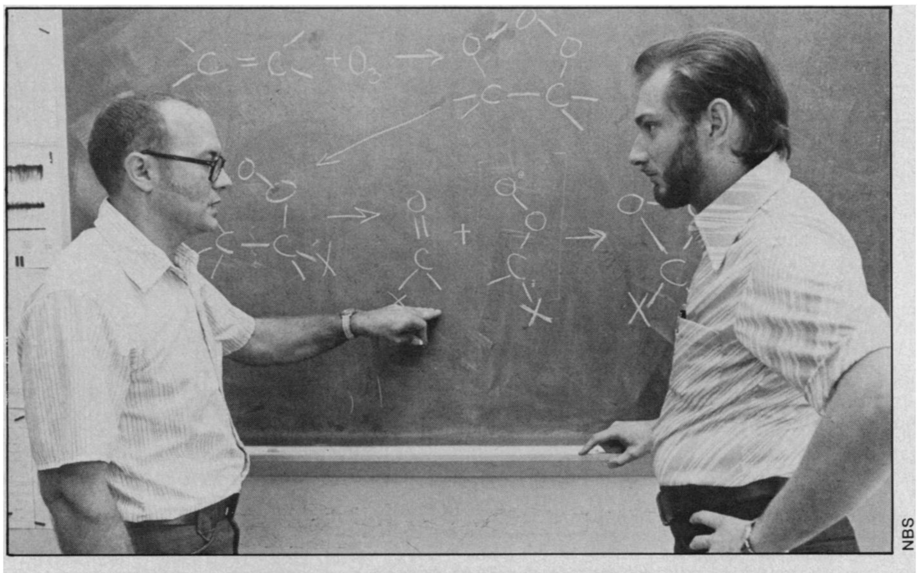
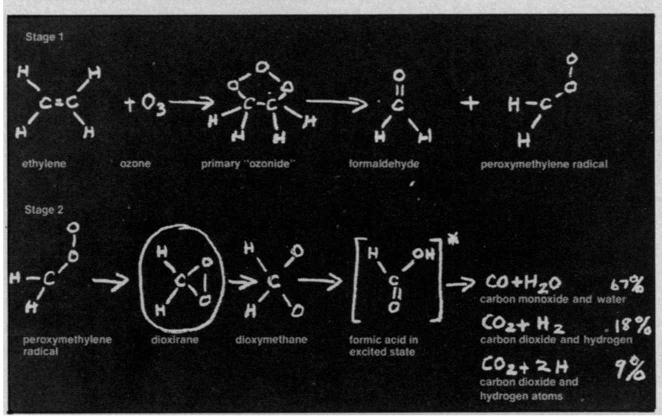
SCIENCE NEWS OF THE WEEK

Dioxirane: Nonradical Route to Smog

Carbon, oxygen and hydrogen are the basic elements of organic chemistry. Because there are various different ways that they can bond to each other, they, along with other elements, can build up the thousands of often highly complex compounds that make organic chemistry a difficult study. A new class of organic compounds is always interesting to pure chemists, and it becomes even more interesting than usual to applied chemists when the first member of the new class is a substance that plays an important intermediary role in the reactions that make photochemical smog.

Such a compound is dioxirane (made of two hydrogen atoms, one carbon and two oxygens), which was recently discovered at the National Bureau of Standards in Gaithersburg, Md. What makes dioxirane different from other compounds made of those atoms is a ring formed by the carbon and the two oxygens. (The two hydrogens are bonded to the carbon outside the ring.) What makes dioxirane of practical importance is that it appears in the reactions of olefins, which are found in automobile exhaust, and ozone, which is in the atmosphere. The discovery of dioxirane supports a model of smog chemistry that differs from the commonly accepted one. The difference may ultimately affect the way emission-control devices are designed.





Suenram and Lovas (above) discuss the olefin-ozone reaction in which dioxirane is formed (left).

The formation of dioxirane in the ozone-olefin reaction has been determined in two different ways. F. J. Lovas and R. D. Suenram found it by microwave spectroscopy during a study of the reaction at low temperature. Richard I. Martinez, Robert E. Hule and John T. Herron detected it by mass spectrometry, also at low temperatures. Both papers are in the Nov. 1 CHEMICAL PHYSICS LETTERS.

"The identification of dioxirane in ozone-olefin reactions comes as somewhat of a surprise since this reaction sequence has been studied intensively by a variety of techniques for many years, and in all the previous work dioxirane has never been detected," Lovas and Suenram write. The reason appears to be that dioxirane is an unstable compound that quickly collapses to its non-ring form, the dioxymethane radical. The low temperatures at which the present experiments were done made the ring form last long enough to be found.

The particular reaction studied is that of ozone with ethylene. This reaction occurs in two stages: In the first stage ethylene and ozone combine to yield a primary ozonide, which decomposes into formaldehyde and a peroxymethylene radical. In the second stage, according to the generally accepted model, the peroxymethylene radical decomposes into various free radicals that consume the formaldehyde made in the previous stage and yield carbon monoxide, carbon dioxide and water as the final products.

A first experiment by Herron and Huie confirmed that stage one of the reaction takes placed as modeled, but when they compared the reaction rates and the relative abundances of final products with a computer program of the model developed by their colleague, Robert Brown, they found a discrepancy in the second stage. According to what comes out of their experiment, the decomposition products of the peroxymethylene radical had to be 90 percent molecular fragments and only 10 percent free radicals. They concluded, therefore, that stage two had to happen differently.

Meanwhile, Suenram and Lovas were studying the reaction at a temperature of -196° C, and discovered their evidence for the existence of dioxirane. Though the discovery was a surprise experimentally, it was not unheralded theoretically. In 1975, W. R. Wadt and W. A. Goddard III had proposed a mechanism for stage two that postulated the existence of dioxirane, and in their paper, Lovas and Suenram point out that their result supports that proposal. According to the Wadt-Goddard model, phase two goes as follows: The peroxymethylene radical changes to dioxirane; dioxirane changes to dioxymethylene, and that becomes an excited state of formic acid. (All the foregoing species are made of the same atoms. What changes is the arrangement and bonding.) Finally the formic acid breaks down into carbon monoxide and water (67 percent) or carbon dioxide and hydrogen (18 percent) or carbon dioxide and two hydrogen atoms (9 percent).

Martinez, Huie and Herron then did another experiment at low temperature that confirmed the presence of dioxirane in the reaction. Though dioxirane is unstable, Suenram suggests that now that its existence and method of production have been shown, "chemists should be able to synthesize and isolate some of the larger, more stable derivatives and study the chemistry of this new class of compounds." Suenram and Lovas have also studied the reactions of other terminal olefins (those with a carbon-carbon double bond) with ethylene and found that dioxirane appears in them. □