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A sequence of chemical reactions that may play role in ozone depletion over the Antarctic has been demonstrated in the laboratory by JPL chemists.

Reporting their work in the Friday (Nov. 27) issue of Science, team led by Dr. Mario J. Molina described how they staged series of reactions that could explain how the so-called ozone hole may be caused in large part by chlorine in the atmosphere from chlorofluorocarbon products.

In their experiment they specifically showed how chlorine is liberated from an inert form, hydrochloric acid, and converted to form that is easily broken down by sunlight -- paving the way for it to attack ozone.

The ozone hole, first reported by British scientists in 1985, is seasonal drop in the protective layer of ozone over the Antarctic that has occurred each southern spring for the past several years. It has been the subject of two research expeditions -- the National Ozone Expedition in 1986 and the Airborne Antarctic Ozone Experiment in 1987 -- mounted by NASA in conjunction with the National Oceanic and Atmospheric Administration, the National Science Foundation and the Chemical Manufacturers Association.

According to Molina, scientists have debated three chief groups of theories of what causes the hole. One, the dynamic theory, is that the hole is caused naturally by movements of air. second set of theories has centered on nitrogen oxides of natural origin as key agent in an ozone- destroying process. The third family of theories implicates chlorine, the source of which is the release of manmade chlorofluorocarbons.

Based on the two Antarctic expeditions, Molina added, preliminary data show that natural or dynamic forces alone could not cause the hole, although it appears they play an important part. Theories involving nitrogen oxides also were ruled out by the expedition data.

Even if chlorine is the key agent, however, atmospheric scientists have not understood fully how it destroys ozone. By developing and testing theory that demonstrates part of such chemical chain, Molina and his colleagues believe they may have an explanation that best fits the data from the 1987 expedition.

Their laboratory experiments, conducted before the 1987 expedition, predicted that hydrochloric acid (HCl) and chlorine nitrate (ClONO₂) can react in ice particles of Antarctic stratospheric clouds to form molecular chlorine (Cl₂) and nitric acid (HNO₃). The molecular chlorine absorbs light very efficiently, causing it to split into chlorine radicals that can attack ozone. The nitric acid is retained in the ice particles.

In the JPL group's scenario, some of the chlorine then form chlorine monoxide (ClO), which in turn reacts with other chlorine monoxide to form combined molecule, or dimer, Cl₂O₂. Normally this reaction does not occur at other latitudes of the Earth because chlorine monoxide usually combines with nitrogen dioxide (NO₂) to form chlorine nitrate. Expedition researchers in 1987, however, found high

quantities of ClO and low quantities of NO₂ at the South Pole, which suggests that the dimer formation reaction is taking place.

The Cl₂O₂ then undergoes series of further reactions which may eventually result in the release of two single chlorine atoms. These can then react with ozone (O₃) to create chlorine monoxide (ClO) and oxygen (O₂). The net result is that two ozone atoms have been turned into oxygen, and chlorine monoxide is left to start the process again.

While at the University of California at Irvine in the 1970s, Molina was one of two chemists who originally called attention to the possible role of chlorofluorocarbons in destroying ozone, an important atmospheric blanket that screens the Earth from ultraviolet light. His group's current paper, however, describes chemical reactions peculiar to the Antarctic because of temperature and chemical conditions there.

Molina co-authored the Science paper with National Research Council resident fellow Dr. Tai-Ly Tso; Dr. Luisa T. Molina; and NRC resident fellow Dr. Frank C-Y. Wang.

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