Photochemical Smog: Is It Safe to Treat the Air?

"We treat water to prevent the formation of various toxic substances. We treat soil for that and other reasons. Why not treat the air to prevent the formation of photochemical smog?" That is the question asked by Julian Heicklen of Pennsylvania State University. He argues that minute concentrations of free-radical scavengers could be added to the air over large cities on days when smog formation is most likely. These scavengers would break the lengthy free-radical chain reactions that produce photochemical oxidants such as ozone.

Heicklen's proposal is extremely controversial among atmospheric scientists. Many, if not most, atmospheric scientists say they are unalterably opposed to the concept of adding anything to the atmosphere. Most consider this proposal a prime example of technological optimism—using one technology to correct the side effects of a second one, and thereby introducing a completely new, and potentially more serious, set of side effects.

There has been little public discussion of Heicklen's proposal, perhaps because most scientists and nearly all the media have apparently written him off as a basically harmless, albeit fixated, crank. But Heicklen's latest accomplishment may bring the proposal into the public spotlight. He and his colleagues, Jehuda Neumann, Hava Steinberger, and Menachem Luria of the Hebrew University of Jerusalem, have apparently convinced officials of that city to permit a test program there provided that the program's safety can be demonstrated.

The idea of using free-radical scavengers is not particularly new. At least 15 years ago, M. Levine of the Lockheed Aircraft Corporation in Los Angeles proposed that iodine vapor could be used for that purpose. But most scientists were dismayed by the prospect of exchanging a brownish haze for a purplish one, and the idea received little consideration. At that time, furthermore, the mechanism of formation of photochemical smog was not well understood, and it was difficult to predict exactly what might happen if a scavenger were released into the atmosphere.

By 1969, the general mechanism for formation of photochemical smog had been worked out by a number of investigators, including Heicklen. The primary reactions were shown to be photocatalyzed interactions between hydrocarbons and nitric oxide (NO) leading, through a lengthy chain reaction, to the formation of ozone (O_3) and nitrogen dioxide (NO_2). Heicklen and his co-workers began experimenting with various free-radical scavengers and found that they could inhibit the chain reaction.

If, for example, one part of diethylhydroxylamine [$(C_2H_5)_2NOH$, or DEHA] is added to a photoreactive mixture of four parts ethylene and two parts nitric oxide, Heicklen, Leonard Stockburger III, and B. K. T. Sie have found that the oxidation of ethylene is decreased by a factor of 5 and the oxidation of nitric oxide is reduced by a factor of 20. The only by-products formed which are not already in the air are ethanol and nitroethane ($C_2H_5NO_2$, which is formed by the direct reaction of DEHA with ozone). Diethylamine hydrogen sulfite, a complex of DEHA and sulfur dioxide, is formed on surfaces but not in the air. Much smaller quantities of DEHA can be used in the atmosphere, Heicklen argues, because the oxidation of nitric oxide needs to be reduced by only about a factor of 2 to 4 to prevent smog formation. This smaller requirement results from the diurnal nature of smog formation.

In most large cities, the primary reactants for smog production are produced by automobiles during the morning rush hour. If these reactants are trapped by an air mass, or inversion layer, over the city, the formation of photochemical oxidants proceeds throughout the morning, peaking early in the afternoon. In the afternoon, the important wavelengths in sunlight are filtered out and the oxidant level abates. Inhibition of the chain reaction during the early morning hours, Heicklen contends, would thus prevent smog formation the entire day. The scavenger would not even need to be added every day. In Los Angeles, for example, there are only about 70 days of moderate to severe smog each year. In Washington, D.C., there are only five to ten.

Heicklen, Alice Gitchell, and Romulus Simonaitis initially tested aniline and similar compounds and presented their preliminary results in 1973, only to be met with a mixture of apathy and scorn. One of the few who did not scoff was Leslie A. Gillette, president of the Organic Chemicals Division of Pennwalt Corporation, Philadelphia. Gillette wrote Heicklen and sent him a sample of DEHA, a Pennwalt product that has been used effectively as a free-radical scavenger in the production of certain polymers. All of the company's experience, Gillette told Heicklen, suggested that there was little risk involved with use of this clear, volatile liquid. Heicklen and R. K. M. Jayanty tried it and found that it was as effective as aniline and surpassed only by *N*-methylaniline.

Pennwalt subsequently supported Heicklen's research for 2 years with a grant of about $70,000 while he proved to his own satisfaction that the concept was viable. But he ran into barriers when he tried to convince others. He went to the Environmental Protection Agency (EPA), for example, and asked them to issue a protocol describing the tests that would be necessary to certify that DEHA is safe. But EPA, according to Wilson Talley, does not have a legislative mandate to develop such protocols and does not certify products. EPA officials also indicated that they would not look favorably on projects designed to add additional chemicals to the air. Talley concedes, though, that EPA has no authority to prevent injection of DEHA into the air unless it can definitely prove that the chemical is hazardous. If, however, the federal Toxic Substances Act should be passed by Congress, the agency would then have the power to require proof of safety before DEHA could be released into the atmosphere.

Heicklen has contacted a number of other agencies and individuals, including the National Academy of Sciences, the Council on Environmental Quality, and even President Ford, in an effort to enlist more cooperation from EPA. In each case, however, the effort was without success. Pennwalt finally dropped its support of the research last year when it became clear that EPA would not provide assistance. But the company did enter an agreement with Heicklen to provide DEHA for his research. The contract also calls for a small commission for Heicklen on any future sales of DEHA for use in air pollution prevention—an aspect that troubles many of Heicklen's peers.

Heicklen's first sympathetic hearing came while he was on sabbatical at the Hebrew University of Jerusalem. Neumann and Steinberger saw merit in the proposal and pointed out that Jerusalem has many features that would make it nearly ideal for a test. Virtually the only source of pollutants in the city is automobile traffic. The meteorological conditions are nearly ideal. Almost every morning in August, there is a low inversion layer over the city until about 11 o'clock. Pollutants from the morning traffic react during the morning and a peak in ozone concentration is reached about noon; in the afternoon, the pollutants are dispersed by winds.

The concentrations of photochemical oxidants are highly reproducible and are closely correlated with traffic levels. The periods before and after the proposed 3- to 5-day experiment could thus serve as a control. The final advantage is that Jerusalem is a small target. Nearly 80 percent of its traffic occurs within an area of about 9 square kilometers. DEHA would be applied at a rate of about 50 kilograms per square kilometer to produce a concentration of about 50 parts per billion (ppb), assuming a 300-meter inversion layer. (Inversion layers can be as high as 1000 meters in other cities, and a proportionately higher amount of DEHA would be required.)

The three investigators, joined now by Luria, approached the Israel Ministry of Health, whose approval would be required if the test were conducted, and this May received a reply suggesting that approval for the test might be granted if its safety can be demonstrated. Officials of the ministry refused, however, to specify precisely what demonstration of safety they will accept. In effect, they told the four to perform whatever tests they think adequate and return with the results. If they then approve the test, Heicklen has arranged for Pennwalt to provide DEHA for it and for the Interscience Research Foundation in the United Sates to underwrite the test's cost, about $15,000.

Pennwalt has done some toxicity studies which suggest that DEHA presents a very low risk. The company contends that the chemical could pass the safety tests required by the Food and Drug Administration for food additives. Short-term inhalation studies of massive doses of DEHA in rodents have shown no ill effects, and the company has observed no health effects related to DEHA in the 10 years it has made the chemical.

Heicklen, James F. Meagher, and James Weaver began toxicology studies last year. They and Richard Latt of Pennsylvania State University exposed rats to DEHA at a concentration of 9 parts per million (ppm)—about 200 times the maximum amount that would be used in smog prevention—for 72 hours per week the first 3 months and 40 hours per week thereafter. They have also exposed the rats to the vapor of diethylamine hydrogen sulfite and to about 10 ppm nitroethane. So far, the investigators have exposed 154 animals, some for as long as 12 months, and the only unusual pathology they have observed is a malignant skin tumor on one animal. Critics argue that they have not observed nearly enough animals to reach any significant conclusions about the safety of the chemicals, but Heicklen argues that they have studied about half as many as are used in carcinogenicity testing.

Heicklen has also enlisted Marvin Legator of the University of Texas Medical Branch at Galveston to test DEHA for mutagenicity. Legator has used several standard tests for mutagenicity, but the chemical has demonstrated no mutagenic activity. Some mutagenic activity was displayed, however, by urine from some animals exposed to the three chemicals, suggesting that DEHA might be metabolized into a mutagen. The amount of activity varied widely from animal to animal, though, so the significance of these results is not yet clear. Legator also examined urine from a student of Heicklen's who had been exposed to about 1 ppm of DEHA for 4 hours; no mutagenic activity was observed.

Society Will Evaluate Results

Legator is continuing the studies in order to get a better understanding of what is happening. When the final results are available, Heicklen plans to submit them to the Environmental Mutagen Society for evaluation. He is also trying to get the National Cancer Institute (NCI) to undertake much more expensive, 2-year studies to screen the chemicals for carcinogenicity—although many scientists argue that the mutagenicity tests are an accurate predictor of carcinogenicity.

Whether or not this particular chemical is proved safe, Heicklen argues that his proposal has several advantages compared to catalytic converters on automobiles for controlling smog. Chemical prevention would, for example, also control stationary sources of emissions. The importance of this is illustrated by considering again the case of Los Angeles. By 1990, stationary sources there are expected to produce as much oxides of nitrogen as was produced by automobiles in 1971. Even in the unlikely event that all automobile emissions were curtailed, photochemical smog might still be as prevalent then as it is today.

Chemical prevention could also be less costly and more energy efficient. A National Academy of Sciences report predicts that installation of catalytic converters on all automobiles will cost $23.5 billion per year and produce an annual fuel penalty of 25 billion gallons; inflation since the report was issued has brought the figure closer to $32 billion. Heicklen argues that this is a case of massive overkill. He contends that the emission controls provide a significant benefit only in large cities, and then only for 30 to 60 days per year. For most of the country, most of the days of the year, the economic and fuel penalties are being paid without receiving benefits in return.

Chemical prevention of smog, in contrast, could be used only when and where it is needed, and thus would cost only about $200 to $600 million per year. Some critics, such as Paul Altshuller of EPA, argue that Heicklen's estimates are unrealistic, and that the actual cost might be as much as ten times higher. But even the higher estimate would still be small compared to the cost of catalytic converters. It seems highly unlikely, though, that Congress will reverse its position requiring control of automobile emissions. DEHA might nevertheless still be useful as a stopgap measure until all new cars have adequate emission controls. It might also be used in cities where smog remains severe despite controls on automobiles.

Heicklen contends that the catalytic converters are a much worse example of a technological fix than chemical prevention: he and other scientists argue that the oxidative catalysts in the converters will transform part of the sulfur in gasoline into sulfuric acid. If all cars in the Los Angeles basin were equipped with catalytic converters, Heicklen argues, the ambient concentration of sulfuric acid in the atmosphere from that source alone would be between 1 and 10 ppb.

Sulfuric acid is known to correlate with respiratory disease in humans at concentrations above 2.5 ppb, and is lethal to 50 percent of a population of guinea pigs after 8 hours exposure to a concentration of 4 to 12 ppm. He thus argues that even a slight risk from DEHA would be preferable to the known risk from sulfuric acid or from the smog itself.

Heicklen seems to have anticipated many potential objections to chemical prevention. Use of DEHA would not, for example, control carbon monoxide in the air. But this could be accomplished by installing afterburners on cars, he argues, at only 10 percent of the cost of catalytic converters. And for most cities, this might not even be necessary, since they are already close to meeting EPA standards and some scientists think those standards are unrealistically low.

Dispersal might also be a problem but Heicklen thinks DEHA could be dispersed by evaporation from cannisters placed throughout the city or possibly sprayed from moving vehicles or aircraft. If a test is conducted in Jerusalem, DEHA will probably be sprayed from a truck patrolling the highways. Altshuller and others argue that Heicklen has not given enough consideration to whether the chemical would reach a great enough height to be effective. But Heicklen contends that if DEHA is released near highways, it will be transported anywhere the pollutants are carried.

Another potential problem might be the effect of DEHA on other living organisms, but Heicklen argues that there is no evidence to support such a possibility. In fact, Pennwalt is currently studying application of DEHA to the surfaces of plants as an antioxidant to prevent damage from ozone. The only major question now, he feels, is its potential toxicity to man, and that is something that can be determined only through more extensive testing.

The reaction among Heicklen's peers is mainly negative. Many, in fact, seem to want to dismiss the proposal out of hand. It is often dismissed with a vehemence that seems inappropriate in a scientific discussion, although many of the arguments unquestionably deserve further consideration. Among the foremost critics are James N. Pitts, Jr., of the University of California at Riverside, Jack Calvert of Ohio State University, and Altshuller. That their views represent those of the majority is demonstrated by a recent incident that followed Heicklen's presentation of the proposal at a scientific meeting. Heicklen's paper received only scattered applause, but Pitts' impassioned response from the audience received vigorous applause.

Pitts' primary objection to Heicklen's proposal is that the effects of DEHA and its oxidation products on humans are not known. He is particularly concerned that DEHA is structurally similar to the notorious carcinogen diethylnitrosamine $[(C_2H_5)_2N\text{–}NO]$, and thus potentially quite dangerous. Legator's failure to find mutagenic activity, however, would seem to suggest that the resemblance between the two compounds is only superficial. Pitts argues, and Heicklen agrees, that very detailed studies of the effects of DEHA should be conducted before direct exposure of the general public is seriously considered.

Pitts also argues that extrapolation of Heicklen's results in the smog chamber to real urban atmospheres is questionable. He and Altshuller argue that the principal effect of a free-radical scavenger would be simply to delay formation of smog, and thus simply move the problem downwind. The pollutants that did not react to form ozone over the initial city would react later to form it over the suburbs, over a rural area, or perhaps even over another city. Altshuller notes that this has already happened as a result of automobile emission controls that reduce emissions of hydrocarbons, but not of nitrogen oxides. Rural ozone levels are high in some areas already, and use of DEHA might simply make the situation worse. Calvert is also concerned that DEHA might undergo unforeseen reactions downwind to produce even worse pollutants.

Pitts contends, furthermore, that exposure of everyone in a city to DEHA would be an abridgement of individual rights, since there would be no way to avoid it short of leaving the city. He rejects the analogy to treatment of water with chlorine or fluoride. In these cases, he contends, the benefits are clearly identified and the risks are equally well identified, whereas neither the benefits nor the risks are clear with chemical prevention of smog. Heicklen says that the exact same arguments can be applied against catalytic converters.

Finally, Pitts says, there is a very clear moral issue involved, since the project would involve exposing the whole population of a city to a chemical with demonstrated side effects. But it may be that the issue is not all that clear. The use of DEHA would require the same kind of delicate balancing of risks and benefits that is required, for example, for drugs, food additives, chlorine in water, or even catalytic converters. And this may be a problem that cannot be settled until those risks and benefits are more clearly defined.

There seem to be very few scientists occupying the middle ground. One of the few is Sidney Benson of the University of Southern California. Benson concedes that, at first, he thought the idea sounded "pretty idiotic." And even now he thinks that there must be a much greater investigation of potential hazards before any experiments are conducted in the atmosphere. But he thinks Heicklen has given careful consideration to most of the problems involved and has given a satisfactory response to the most important criticisms. He thinks that the concept might possibly be sound and that, at the very least, more research should be undertaken to identify and quantify the risks.

Many of the arguments may be moot. Until the question of mutagenic activity is resolved, there obviously will be no atmospheric tests. If the mutagenic question is resolved satisfactorily, it will still probably be necessary to test DEHA for carcinogenicity, and that would take at least 2 years. If DEHA is found to present a mutagenic hazard, then Heicklen must go back to square one with a new chemical. He already has a candidate, a DEHA analog that would probably not be metabolized. But Heicklen does not have the research funds to begin again with a new chemical and the disqualification of DEHA might, to the immense relief of many other scientists, sound the death knell for the concept as well.—THOMAS H. MAUGH II

Coal Research (III): Liquefaction Has Far to Go

Liquefaction is perhaps the most difficult of coal conversion techniques. Not only is it technically demanding, requiring subtle rearrangements of coal's chemical structure to incorporate additional hydrogen, but liquefaction faces economic barriers to commercial use that may well prove more difficult to overcome than those of new gasification and direct combustion techniques. Nonetheless, liquefaction of coal will clearly be needed to supplement and then supplant petroleum—perhaps before too long, although there is debate about exactly when. Domestically, oil production has been declining since 1970 and imports have climbed to 40 percent of total consumption. Worldwide, consumption of oil exceeds the rate at which new supplies are being found. Coal is by far the largest potential source of substitute liquid fuels.

Liquefaction of coal in the true sense of that term is still an unattained goal. Existing commercial processes for converting coal to liquid fuels gasify the coal first and then synthesize a liquid product. The process is inherently inefficient, since it involves high temperatures and the breaking of all the carbon-carbon chemical bonds in the coal material before putting some of them back together again. Hence new methods for