ANNALS OF CHEMISTRY

INERT

IN the age of convenience packaging, few items have scored a greater success in the marketplace than aerosol sprays. The phenomenal growth of the aerosol industry began in the early nineteen-fifties, when chemists at E. I. du Pont de Nemours & Company hit upon an ideal propellant-a mixture of two gases that could be confined under low pressure in tin-plate or aluminum cans-and Robert H. Abplanalp invented a massproducible plastic-and-metal valve that could dispense the contents of the cans at the touch of a fingertip. Cheap, lightweight cannisters soon supplanted the cumbersome and expensive steel containers that had housed aerosol sprays since the Second World War, and from then on the proliferation of aerosols proceeded at an incredible rate. In 1947, four and a half million cans of the old-style aerosols-mainly insecticides-were manufactured and sold. By 1954, the annual production of aerosols had jumped to a hundred and eighty-eight million cans-a hundred million of them being more or less equally divided between insecticides and shaving lathers. In 1958, the production of aerosols soared past the five-hundred-million mark, with hair sprays taking over as the leading item. And in 1968, when two billion three hundred million aerosols were turned out, the total of a decade before was nearly equalled by the production of hair sprays alone.

By 1970, practically every product that was conceivably sprayable either had been packaged or was being considered for packaging in aerosol form. As a result, more than three hundred different uses have been devised for aerosols, which dispense everything from baby powder, slip preventive for bathtubs, breath sweeteners, and cheese spreads to cooking-pan coatings, nasal sprays, oven cleaners, rug shampoo, shoe polish, telephone disinfectant, waxes, weed killers, and whippedcream substitutes. With the exception of a few failures, among them toothpaste and chocolate syrup, most of the new aerosol products-lavishly advertised and imaginatively marketedhave gained wide acceptance by the public. Today, with personal products such as deodorants, hair sprays, and shaving lathers accounting for fifty per cent of the take, aerosols are a threebillion-dollar-a-year industry in the United States. They are also virtually ubiquitous. In 1973, two billion

nine hundred and two million three hundred and forty thousand aerosols were manufactured and sold in this country—enough to provide about fourteen for every citizen of the land—and the 1974 total was more than three billion, which amounted to about fifty per cent of the total world production. Small wonder that the average American family is estimated to possess between forty and fifty cans of aerosol in various parts of the house.

Though some consumer groups and medical researchers had reservations about this fantastic propagation of aerosol sprays, the matter caused no real stir until last year, when it became known that the propellant most commonly used in them-the same mixture of gases that had enabled the du Pont people to start the aerosol boom some twenty years ago-might be seriously threatening the environment. The first hint of this was received in 1970, when Dr. James E. Lovelock, a biospheric chemist at the University of Reading, in England, detected one the gases-trichloromonofluoromethane-in the ambient air over western Ireland. Because he knew that the other gas-dichlorodifluoromethane-is far more stable, though less easily measurable, Lovelock assumed that it was present also, and in fact he later found this to be the case. (Both gases had been synthesized in 1928 by chemists in the General Motors research laboratories who were trying to find a non-toxic, non-flammable refrigerant; dichlorodifluoromethane has been widely used ever since as a coolant in refrigerators and air-conditioners.) When Lovelock subsequently took air samples from shipboard in the North and South Atlantic, in 1971, he discovered that trichloromonofluoromethane had pervaded the entire troposphere-the six-to-ten-mile-high portion of the atmosphere that lies between the earth and the stratosphere. At the time, he found no cause for alarm in his observations, for the simple reason that both gases-closely related compounds of chlorine, fluorine, and carbon, which are marketed by du Pont, their chief manufacturer, under the trade name of Freon-were known to be chemically inert. In fact, it was their chemical inertness that, to-



gether with a high volatility, had made them ideal as an aerosol propellant, which must vaporize at room temperature and not react with any of the ingredients it is designed to propel. As a result, Lovelock and other investigators at first regarded the omnipresence of chlorofluorocarbons in the troposphere as a harmless and potentially valuable tool for tracing air movement and wind direction.

'HE assumption that chlorofluorocarbons would be innocuous in the environment because they were chemically inert might have gone unchallenged for some time if it had not been for Professor F. Sherwood Rowland, a member of the Department of Chemistry of the University of California at Irvine, who was a specialist in the chemistry of radioactive isotopes. Upon hearing that Lovelock had found chlorofluorocarbons to be everywhere in the troposphere, Rowland began to wonder where they were going and what would become of them. Since there appeared to be no particular urgency about the matter, he pondered it off and on for more than a year. Then, in the summer of 1973, he requested and received permission to investigate it from the Atomic Energy Commission, which had supported his work since 1956. On October 1st, he and Dr. Mario J. Molina, a photochemist from Mexico City, who had recently completed his Ph.D. studies at the University of California at Berke-/ ley and had just joined Rowland's research group, set out upon the trail of the chlorofluorocarbons, never suspecting that before the end of the year it would lead them to contemplate the possibility of an end to life on earth.

To begin with, the two men were aware that chlorofluorocarbons, like all molecular gases, could be decomposed upon photolysis by short-wavelength ultraviolet light from the sun. They also knew that such decomposition would have to occur high in the stratosphere-from fifteen to twenty miles above the surface of the earth. Below that, almost all short-wavelength ultraviolet light is intercepted and absorbed by a fragile layer of ozone-a gas formed by the action of sunlight on oxygen-which shields the planet from harmful solar radiation. Because they were sure of the existence of a photolytic sink in the stratosphere-"sink" is a term that scientists apply both to the processes by which chemicals are de-

stroyed and to the places in which this breakdown occurs-the first question that Rowland and Molina asked themselves was whether there might be other methods or locations for the disposal of chlorofluorocarbons. Since Lovelock's measurements had indicated that the total amount of trichloromonofluoromethane in the troposphere was about equal to the total amount of it ever manufactured, this seemed unlikely, and after further study the two men came to the conclusion that the compounds, because of their relative insolubility in water, could not be removed and absorbed by natural sinks such as rainfall or the oceans, and, because of their chemical inertness, could not be broken down rapidly by any other known mechanisms in the troposphere. Thus, they presumed that the several million tons of chlorofluorocarbons estimated to be floating about in the troposphere would survive long enough to rise into the stratosphere. Rowland and Molina were aware that the upward diffusion of chlorofluorocarbons-as of any gas not lighter than air-would be very slow; in fact, after completing their next set of calcula-

tions they were able to estimate that the average molecule of chlorofluorocarbon would wander aimlessly, rising and falling between troposphere and stratosphere in the manner of a yo-yo, for between forty and a hundred and fifty years before it encountered shortwavelength ultraviolet light and decomposed. They also estimated that by this time, if chlorofluorocarbons continued to be manufactured and used as propellants and refrigerants at the 1972 worldwide rate of almost a million tons a year, the several million tons of the compounds pervading the troposphere would increase to nearly a hundred million tons, and the decomposition of chlorofluorocarbons in the stratosphere would increase correspondingly.

The significance of this increase became apparent late in November of 1973, when Rowland and Molina undertook to examine the consequences of the long-delayed but inevitable encounter between chlorofluorocarbons and ultraviolet light. The two men had known all along that as soon as a molecule of chlorofluorocarbon decomposed it would release atoms of chlorine. They now determined that, with-

in a second or two, each atom of chlorine (a highly reactive chemical) would seek out and react with a molecule of ozone (an extremely unstable substance), and that this, in turn, would initiate an extensive and complex catalytic chain reaction in which, over a period of a year or so, as many as a hundred thousand molecules of ozone could be converted into molecular oxygen and eliminated from the stratosphere. Uneasy at finding that a single atom of chlorine was capable of such destruction, Rowland and Molina returned to their earlier calculation that nearly a hundred million tons of chlorofluorocarbons could be expected to build up in the troposphere within the next century or so, and estimated that enough chlorofluorocarbon molecules would thereafter be decomposed annually in the stratosoheric sink to unleash five hundred thousand tons of chlorine atoms, Chlorine in this amount, they concluded, was sufficient to roughly double the depletion of ozone known to occur naturally each year, chiefly through a catalytic chain reaction initiated by oxides of nitrogen released into the stratosphere as a result of bacterial action in the ocean and in the soil. The chlorine would thus bring about a situation in which ozone would be destroyed much faster than under normal conditions.

At the time Rowland and Molina reached this conclusion-it was a few days before Christmas-they had no easy way of determining exactly how much of the ozone layer might eventually be destroyed. However, a rough calculation led them to estimate that a loss of from twenty to forty per cent was within the realm of possibility. This was a disconcerting prospect, to say the least, since the work of previous investigators had demonstrated that such a reduction would cause a tremendous increase in the kind of solar radiation known to be most detrimental to plant and animal cells. Rowland and Molina thus came to the further chilling conclusion that if chlorofluorocarbon propellants and refrigerants continued to be used at present rates, chlorine might one day take over chemical control of the stratosphere, with consequences that could conceivably disrupt, if not destroy, the biological systems of the earth. Moreover, they realized that even if the use of the two gases were to cease at once, destruction of part of the ozone layer-though the full effect would not actually be felt for a decade or twowas foreordained by the fact that the chlorofluorocarbons already in the troposphere were inexorably seeping up



"The long and short of it is I found it just about impossible to come by fifty grand legitimately."

THE ISLAN PORTER

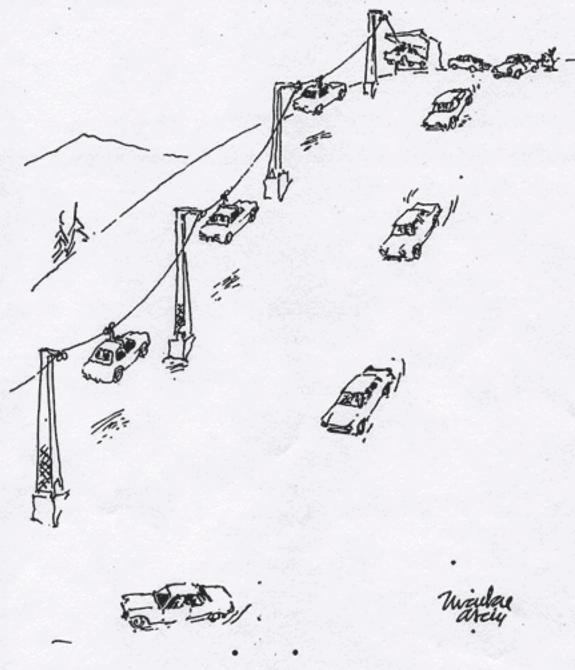
into the stratosphere. In effect, they had discovered a

planetary time bomb.

Since Rowland and Molina were not specialists in atmospheric chemistry, they initially reacted to their theory with disbelief, assuming that somewhere in their calculations they had made a simple mathematical mistake. But when they reviewed their work they were unable to find any error. At that point, seeking outside advice, they paid a visit to Dr. Harold S. Johnston, a professor of chemistry at the University of California at Berkeley, who in 1971 had been the first scientist to call attention to the threat posed to the ozone layer by oxides of nitrogen released from the exhaust of supersonic transports. Dr. Johnston not only confirmed their conclusion that large amounts of ozone could be destroyed through a chain reaction initiated by tiny amounts of chlorine but also informed them that similar theories had recently been worked out by several different groups of atmospheric scientists who were conducting research for the Department of Transportation's Climatic Impact Assessment Programa three-year, twenty-milliondollar study that had been set up in 1971 to investigate the effects of nitrogen-oxide and sulfur-dioxide emissions from

the SSTs. According to Johnston, these scientists had undertaken to examine the potential role of chlorine in the stratosphere because they were aware that the use of ammonium perchlorate in the fuel of the National Aeronautics and Space Administration's proposed space shuttle would result in the release of hydrogen chloride from its exhaust. But they knew of no existing major sources of chlorine in the stratosphere, and so they had not considered their findings immediately important. The irony of this was heightened when Johnston told Rowland and Molina that recent work in England had indicated that the chain reaction triggered by free chlorine atoms could destroy ozone six times as efficiently as the one initiated by nitrogen oxides.

As might be expected, Rowland and Molina came away from their meeting with Johnston fully convinced of the magnitude and urgency of the prob-



lem they had uncovered, and of the necessity of publishing their data as quickly as possible. During the first week of January, 1974, Rowland wrote an article describing their findings and sent it off to Nature, the international scientific journal, which is published in England. For the next eight months, the dissemination of their theory about the calamitous effect of chlorofluorocarbons upon ozone seemed to rival the slowness with which the gases themselves were diffusing upward into the stratosphere. To begin with, the editors of Nature were obliged to wait until the data had been evaluated by referees, and therefore did not get around to publishing the article until June 28th. A press release based on the article was sent out by the public-information office of the University of California at Irvine, and was picked up by the Los Angeles Times, the San Francisco Examiner, and several other California newspapers. Unaccountably,

however, though the release was sent to the Los Angeles bureaus of the New York Times, the Wall Street Journal, the Christian Science Monitor, the National Observer, Time, and Newsweek, the story did not appear in any of those publications. As a result, word of Rowland and Molina's ominous findings did not become public knowledge on the East Coast until the two men reported them in person on September 11th at a meeting of the American Chemical Society being held in Atlantic City.

By that time, Rowland and Molina had calculated that if chlorofluorocarbon production continued to increase at the present rate of ten per cent a year until 1990 and remained constant thereafter, between five and seven per cent of the ozone layer would be destroyed by 1995, and between thirty and fifty per cent of it would disappear by the year 2050. To underscore the gravity of even a five-per-cent deple-

tion, they cited studies indicating that the resulting increase in ultraviolet radiation would, after 2050, cause forty thousand additional cases of skin cancer each year in the United States alone. They went on to warn that greater losses of ozone could cause other serious biological damage, such as genetic mutation and crop damage, and might even shift stratospheric temperatures sufficiently to create changes in the world's weather patterns. To point out the irreversible aspect of the problem, they predicted that if nothing was done over the next decade to prevent further release of chlorofluorocarbons, the vast reservoir of the gases that would have built up in the meantime would provide enough chlorine atoms to insure continuing destruction of the ozone layer for most of the twenty-first century. Not surprisingly, they told the members of the Chemical Society that in their opinion the advantages of using chlorofluorocarbon propellants and re-

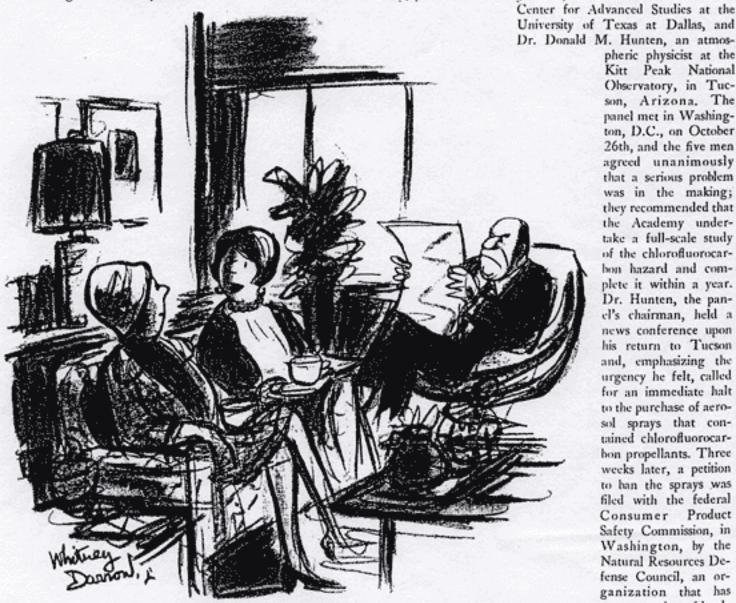
serious hazards they posed to the climate of the world and to the health of its inhabitants. And they urged that the compounds be banned.

HE information presented by Rowland and Molina in Atlantic City touched off a chain reaction of its own. Within two weeks, their findings were confirmed by an announcement of similar findings by Dr. Paul Crutzen, a meteorologist working with the National Center for Atmospheric Research and the National Oceanic and Atmospheric Administration, both in Boulder, Colorado. They were also confirmed by two of the scientific groups that had been investigating the problem of ozone depletion for the Climatic Impact Assessment Program. One of these groups was led by Dr. Ralph J. Cicerone, a physical chemist at the University of Michigan's Space Physics Research Laboratory; the other was headed by Dr. frigerants scarcely seemed worth the Michael B. McElroy, professor of at-

mospheric science at Harvard University's Center for Earth and Planetary Physics. The calculations of both indicated that chlorofluorocarbons would, if anything, destroy ozone even faster than Rowland and Molina had estimated.

Coming hard on the heels of a disclosure by Dr. Fred C. Iklé, director of the Arms Control and Disarmament Agency, that nitrogen oxides released by the heat of thermonuclear explosions in warfare would destroy a large part of the ozone layer, these alarming predictions received wide coverage in the press and aroused considerable public concern. There was already a great deal of concern in the scientific community. In mid-September, the National Academy of Sciences appointed a special five-man panel to assess the situation and recommend a course of action. In addition to Professors Rowland, Johnston, and Me-Elroy, its members included Francis S. Johnson, executive director of the Center for Advanced Studies at the University of Texas at Dallas, and

> pheric physicist at the Kitt Peak National Observatory, in Tucson, Arizona. The panel met in Washington, D.C., on October 26th, and the five men agreed unanimously that a serious problem was in the making; they recommended that the Academy undertake a full-scale study of the chlorofluorocarbon hazard and complete it within a year. Dr. Hunten, the panel's chairman, held a news conference upon his return to Tucson and, emphasizing the urgency he felt, called for an immediate halt to the purchase of aerosol sprays that contained chlorofluorocarbon propellants. Three weeks later, a petition to han the sprays was filed with the federal Consumer Product Safety Commission, in Washington, by the Natural Resources Defense Council, an organization that has won a number of landmark court cases involving environmental



"I always like a midweek holiday. Then there's a three-day gap between Harvey's holiday depression and his usual Sunday low."

problems. Among other things, the Council's petition cited recent measurements taken from high-altitude aircraft by Philip W. Krey, of the Atomic Energy Commission's Health and Safety Laboratory, in New York City, which showed that chlorofluorocarbon molecules had already risen into the lower stratosphere, twelve miles above the earth.

MEANWHILE, the aerosol industry had been developing its own response to the situation. In September, when chlorofluorocarbons first broke into the headlines, spokesmen for the du Pont Company, which had been aware of the findings of Rowland and Molina for more than six months, contented themselves with pointing out that the calculations were hypothetical-that no real proof existed to demonstrate that the two gases could rise into the stratosphere, let alone that they could lead to the destruction of ozone. Subsequently, Dr. Raymond L. McCarthy, technical director of the company's Freon Products Division, announced that industry-sponsored studies involving both direct measurement of chlorofluorocarbons in the troposphere and observation of their chemical reactions in chambers designed to simulate high-altitude conditions would be undertaken by scientists at several universities. According to Dr. McCarthy, these studies would take three years to complete, and would be coordinated by a trade group known as the Manufacturing Chemists Association. Nineteen producers of chlorofluorocarbons, including the six American manufacturers-du Pont, the Allied Chemical Corporation, the Union Carbide Corporation, the Pennwalt Corporation, the Kaiser Aluminum & Chemical Corporation, and Racon, Inc.-would finance the studies. Mc-Carthy said that pending the first results of the industry-sponsored research there was no dependable evidence that chlorofluorocarbons posed a hazard to ozone, or, for that matter, that the chlorine chain reaction worked out by Rowland and Molina and other investigators could occur at all. He added that it would be an injustice if hypothesis were to serve in the meantime as a basis for judgment and action. Nevertheless, during the month of November the sale of aerosol products dropped by seven per cent, and rumors soon began circulating that du Pont had halted construction on a new chlorofluorocarbon-manufacturing plant, in Corpus Christi, Texas.

As the autumn wore on, it became

Neither the Administration nor Congress has yet come up with specific answers to these

questions. But the President's Council on Environmental Quality and the Federal Council for Science and Technology are sponsoring a broad interagency study of the situation, and during February two bills attempting to deal with the problem were introduced in the House of Representatives. Both bills avoid a politically unpalatable outright ban on chlorofluorocarbons by calling for additional studies to determine whether a chain reaction initiated by chlorine released from the gases is in fact destroying the ozone layer. These

obvious that the furor over chlorofluorocarbons would lead to a congressional inquiry, and on December 11th the Subcommittee on Public Health and Environment of the House Committee on Interstate and Foreign Commerce began two days of hearings to consider legislation that would regulate, and possibly ban, the manufacture of the gases. In an opening statement, the subcommittee chairman, Paul G. Rogers, a Florida Democrat, expressed grave concern over the problem, declaring that it was like a tale out of science fiction. "Since coming to the Congress, I have never begun hearings with such an cerie feeling," he said. "The idea that we may in fact be destroying the layer of atmosphere which protects us

recession.

from the sun's rays is both rather staggering and frightening."

As it happened, the legislation proposed to regulate chlorofluorocarbons was not reported out of the subcommittee, because the Ninety-third Congress expired eight days after the hearings were concluded. But the testimony of the witnesses on both sides of the issue, though it produced little information that had not already appeared in newspapers all across the country, had served to raise some difficult questions for the new Congress and the Administration to ponder, For example, who should assume the burden of furnishing absolute proof of whether chlorofluorocarbons pose a threat to the ozone layer? Who, for that matter, should determine whether

it is safe to wait for absolute proof to be established? What measures, if any, should be taken in the meantime to control the manufacture and use of the chemicals? Which agency should be given the power to enforce these measures? And which agency, then, should assume jurisdiction over the stratosphere?

studies are to be conducted over the next year or so by the National Academy of Sciences and by NASA. One of the bills-it has just been introduced in the Senate as well-would ban chlorofluorocarbons if their manufacturers fail to furnish proof within two years that the stuff is safe. The other bill would require that the administrator of the Environmental Protection Agency determine what constitutes a safe level of ozone depletion, and to what extent chlorofluorocarbon production should be regulated in order not to exceed it. Thus, both of the proposed laws would, in effect, grant industry's request for a delay in regulatory action. Indeed, it appears that the initial concern of the Congress over the threat that chlorofluorocarbons pose to the world's environment has been tempered by subsequent consideration of the adverse effects of regulatory legislation upon the national economy in a time of

Whether it is prudent, let alone safe, for Congress to try for a trade-off between these two priorities-the environment and the economy-remains a question. It also remains a question whether it is wise of Congress to assign a major role in determining the extent of the chlorofluorocarbon hazard to NASA, an organization that can surely be said to have a vested interest in the matter as a result of its billion-dollar-ayear space-shuttle program. It is equally questionable whether any legislation regulating the production of chloro-

fluorocarbons in the United States can be effective in preventing destruction of the ozone layer unless similar restrictions are imposed by the other chlorofluorocarbon-producing nations-including the Soviet Union, where the compounds are manufactured under the trade name Eskimon. For that matter, how can the E.P.A. administrator or anyone else determine a safe level of ozone depletion caused by chlorofluo-

rocarbons without taking into account the destruction of ozone that will be caused by supersonic transports? (According to a report released by the Department of Transportation just the other day, several hundred SSTs would reduce the ozone layer from ten to twenty per cent within five to ten years.) Or without taking into account the destruction of ozone that may be caused by other natural or man-made pollutants yet to be identified? While Congress and the Administration grope to find a way out of this murky situation, the problem, like the chlorofluorocarbons, remains in the air.

ONCERN over the potentially disastrous effect of chlorofluorocarbons in the stratosphere has tended to overshadow strong evidence that aerosol sprays are more immediately hazardous to the health of millions upon millions of people who have been inhaling them here on earth. For almost a decade, it has been known that chlorofluorocarbons in high concentrations could cause death from cardiac arrest. More recently, it has been reported that smaller doses of the gases can cause changes in the normal heart rhythm of human beings and can weaken heart muscle and lower blood pressure in test animals. For at least fifteen years, it has been suspected that the plastic resins in hair sprays cause a restrictive-lung-storage disease called thesaurosis, as well as abnormal lung cells that may be the precursors of lung cancer. These suspicions now appear to be confirmed by a study of five hundred cosmetologists in Utah recently conducted by Dr. Alan Palmer, an epidemiologist with the Department of Health, Education, and Welfare's National Institute for Occupational Safety and Health. Dr. Palmer's study found that nearly fifty per cent of the cosmetologists had symptoms of early obstructive lung disease such as asthma and emphysema. Even more ominous was the disclosure, in the spring of 1974, that vinyl chloride, a chlorinated hydrocarbon gas that had been used for twenty-five years in the manufacture of plastics and had been discovered to cause a rare type of liver cancer in workers who inhaled it, had also been employed for at least ten years as either a propellant component or a solvent in dozens of household aerosol sprays. (As with the chlorofluorocarbons, the labels of these aerosols listed vinyl chloride not by name but only as one of several "inert ingredients.") Incredibly, instead of following the lead of the Japanese government, which spent twenty-five million dollars to impound all aerosols containing this carcinogen, the Food and Drug Administration, the Environmental Protection Agency, and the Consumer Product Safety Commission—the three agencies responsible for regulating aerosol products to protect the public health in the United States-did little more than request that companies engaged in the manufacture of aerosols stop using vinyl chloride as a propellant in them. As a result, millions of spray cans containing a known cancer-producing

agent remained in stores and in households from one end of the country to the other even after it had been shown that with normal use-say, massacring a few bugs on the ceiling or giving style and body to a hairdo-it was possible to contaminate an average-sized room with up to four hundred parts of vinyl chloride per million parts of air. This level was eight times that known to cause liver tumors and other cancers in rats, and was soon judged by the Department of Labor's Occupational Safety and Health Administration to be four hundred times the safe level of exposure for workers.

In spite of extensive press and television coverage of the vinyl-chloride hazard during the spring and summer of 1974, there was no drop in the sale of aerosol sprays. Indeed, the average consumer's appreciation of the toxicity of aerosols apparently continued to be limited to a vague awareness of the warning that appears on virtually every aerosol can-"KEEP OUT OF REACH OF CHILDREN"-which, of course, is simply an evasion of the fact that there is no way to use a household aerosol in the presence of anyone, child or adult, and keep its contents out of the human lung. Ironically, it has taken a chance discovery by two chemists who were not even investigating within their usual field of research to bring home the full extent of the aerosol hazard. For by demonstrating that inert chlorofluorocarbons, instead of vanishing harmlessly into thin air, can scar the ozone layer Rowland and Molina have shown us that we may well have succeeded in inflicting a chronic and irreversible disease upon the atmosphere, which is the very lung of the earth. For better or worse, however, they have also provided us with a valuable lesson in the crucial necessity of testing potentially harmful substances-before putting them on the market-for their consequences both in the environment and upon the human beings who will come in contact with them. (Such testing might have begun some time ago if Congress had seen fit to agree upon the Toxic Substances Control Act, which, vigorously opposed by the Manufacturing Chemists Association and other industry groups, has twice passed both houses and then been allowed to die in conference.) In the meantime, as we await the results of studies yet to be undertaken and action yet to be decided upon, it appears that we can do little more than cross our fingers and hope that somehow or other Rowland and Molina will be proved -PAUL BRODEUR wrong.