



# ATMOSPHERIC OZONE

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## INTRODUCTION

This account is my personal perspective on atmospheric ozone and on some of the events that have advanced this field of science. My point of view is that of a physical chemist, in particular that of a photochemist. Some of this review is along an unusual line for the *Annual Review of Physical Chemistry*, in that I illustrate the mechanics by which new scientific developments interact with society, business, and politics. I quote conversation in the interdisciplinary Tower of Babel. For the physical chemist who is not expert in atmospheric sciences, I plant a number of educational packages between the anecdotes.

## BRIEF HISTORY OF OZONE SCIENCE TO 1960

### *Experiments and Observations (1)*

In 1774, Joseph Priestley and Carl Wilhelm Scheele independently discovered oxygen. Christian Friedrich Schönbein discovered ozone in 1839, named it after the Greek verb *ozein* (to smell), and developed starch-iodide paper, which he used to estimate the ozone concentration in air at several places in Europe. The structure of ozone was presumed to be  $O_3$  in 1864 and quantitatively proven to be  $O_3$  in 1898.

In the laboratory during 1880 and 1881, Sir Walter N. Hartley observed that ozone strongly absorbs ultraviolet radiation between 200 and 300 nm and concluded that this absorption band was responsible for the observed sudden cut-off of solar ultraviolet radiation below 300 nm. About the same time, J. Chappuis discovered very weak diffuse optical absorption bands by ozone in the visible spectral region. Examining the spectrum of Sirius in 1890, W. Huggins found sharp ultraviolet absorption bands between

320 and 360 nm; in 1917, these bands were found to be caused by atmospheric ozone.

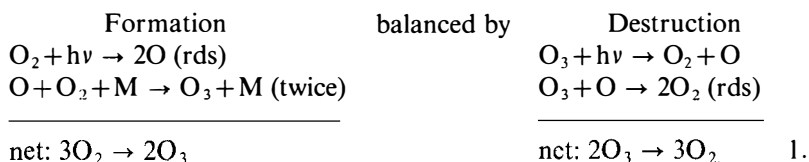
G. M. B. Dobson developed (1924–1928) a spectrometer that measured ozone by taking the ratios of pairs of lines in the ultraviolet spectral region. He used this instrument for routinely measuring the atmospheric ozone column. In 1929, Dobson established a network of ozone measuring stations in Switzerland, England, New Zealand, California, India, and Egypt. The station in Arosa, Switzerland, has been measuring atmospheric ozone continually since 1929. F. W. P. Götz derived the “Umkehr” method of obtaining the vertical distribution of ozone, by using the spectra of scattered radiation from the overhead sky through sunrise and sunset. He showed that the maximum concentration of ozone occurred at an average altitude of about 22 km (1929–1934).

Ozone scientists, including Dobson, set up a large network of Dobson instruments during the International Geophysical Year (1957/1959). For the first time, they obtained a comprehensive picture of how the ozone column varies with season and latitude in the Northern Hemisphere. Since the International Geophysical Year, approximately one hundred Dobson stations have been in operation, with an irregular distribution over the world and with temporal variation in their number and location. Although the Dobson instrument represents simple technology, it appears to be capable of accurately measuring the ozone column, if it is carefully recalibrated from time to time and if it is operated by skilled, dedicated technicians.

The high technology era of stratospheric ozone slowly began in the 1950s. Using V-2 rockets captured after World War II, F. S. Johnson and coworkers (1952) measured the vertical profile of ozone up to 70 km altitude, and later rocket flights measured the distribution of solar radiation above the atmosphere. In 1956, S. Fred Singer proposed to measure the vertical profile of ozone from future satellites by using backscattered ultraviolet solar radiation, in effect the Dobson method from above the stratosphere. This proposal was demonstrated to be feasible on a satellite flight in 1966. Following a circumpolar orbit, the Nimbus 7 satellite, launched in 1978, carried a solar backscattered ultraviolet instrument, which operated for more than a decade. Every day, it measured the ozone column and a low resolution ozone vertical profile throughout the sunlit globe, but its problems with degradation of optical components in space were solved only in the late 1980s (2).

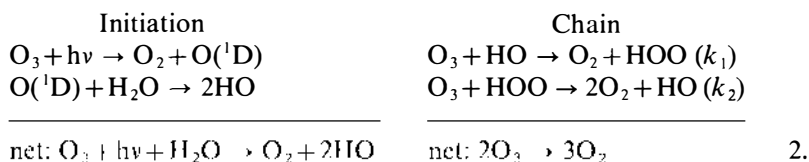
### *Theory of the Global Ozone Balance*

The first photochemical theory of stratospheric ozone was that of Sydney Chapman (1930):



Photolysis of molecular oxygen by solar ultraviolet radiation at wavelengths below 242 nm is the rate determining step (rds) in the formation of ozone. Visible, near ultraviolet, and far ultraviolet radiation dissociates ozone, and the products ( $O_2 + O$ ) almost always recombine as in the second formation step. On rare occasions, the atomic oxygen reacts with ozone to give a net destruction of two ozone molecules. In 1930, all physical and chemical constants needed to calculate the rates of the above processes had been measured, except for the distribution of solar ultraviolet radiation above the atmosphere. Chapman postulated that radiation from the sun corresponded to the Planck distribution at 6000 K. As calculated in 1931, the ozone vertical profile agreed well with the vertical profile of ozone observed by the Umkehr method at Arosa, Switzerland. When V-2 rockets were sent above the atmosphere in the 1950s, the observed ultraviolet radiation was more intense than that derived from a solar surface temperature of 6000 K, such that the calculated ozone column was about twice as large as that observed. During the 1960s, there was a search for "something else" that destroyed ozone.

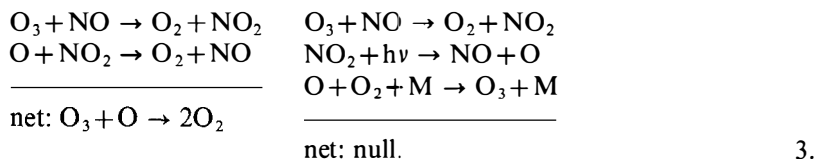
In 1958, Norrish and McGrath found greatly increased quantum yields when they added water vapor to ozone that was exposed to ultraviolet radiation. They proposed a catalytic chain reaction with unknown rate constants,  $k_1$  and  $k_2$ :



Ultraviolet radiation with wavelength less than 310 nm breaks ozone into molecular oxygen and electronically excited "singlet" atomic oxygen,  $O(^1D)$ , which is extremely more reactive than regular atomic oxygen,  $O(^3P)$ . Singlet atomic oxygen rapidly reacts with water to produce two hydroxyl radicals. An hydroxyl radical reacts with ozone to form the perhydroxyl radical, which in turn reacts with ozone to reform the hydroxyl radical; in one cycle of the chain, two molecules of ozone are destroyed. B. G. Hunt (1966) found that by assuming various values of  $k_1$  and  $k_2$ , he could obtain calculated values for the ozone vertical column larger and

smaller than those observed. He postulated values for these unmeasured rate coefficients, such that they gave the observed midlatitude ozone vertical column. Laboratory measurements (1972–1985) found Hunt's postulated values to be an order of magnitude too large.

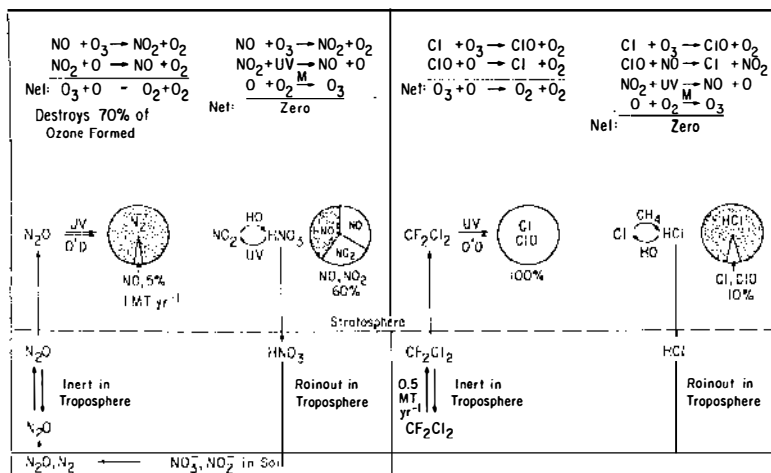
Murcray et al (1968) made the first observation of nitrogen oxides in the stratosphere, by measuring nitric acid vapor and detecting nitrogen dioxide by infrared spectroscopy. Continuing the search for something else that destroyed ozone, Paul Crutzen (1970) considered Murcray's observations and proposed ozone destruction by a catalytic cycle based on the oxides of nitrogen, NO and NO<sub>2</sub>, collectively written as NO<sub>x</sub>.



3.

Crutzen postulated a vertical distribution of NO<sub>x</sub> in the stratosphere that gave agreement between calculated and observed vertical profile of ozone. As a logical and timely extension of Bates and Hayes' 1967 article on atmospheric nitrous oxide, Crutzen (1971) and Nicolet (1971) independently proposed the source of stratospheric nitrogen oxides to be reaction of nitrous oxide (NNO) with singlet atomic oxygen. Crutzen's 1970–1971 model of stratospheric nitrogen oxides is pictured on the left-hand panel of Figure 1 (which is also Figure 1 in my 1975 contribution to the *Annual Review of Physical Chemistry*). Nitrous oxide is stable in the troposphere with more than a one hundred-year atmospheric lifetime, is slowly transported into the stratosphere, is destroyed by far ultraviolet radiation there, and reacts in the middle stratosphere with electronically activated atomic oxygen to produce nitric oxide. Between 1972 and 1975, investigators measured the concentrations and vertical profiles of NO, NO<sub>2</sub>, and HNO<sub>3</sub> in the stratosphere, and Crutzen's 1970–1971 postulate was confirmed. A marvelous feature of Crutzen's mechanism is that it couples the biospheric nitrogen cycle with the global ozone balance; life on Earth controls the natural level of ozone in the stratosphere. This example deserves to be in college biology text books, but many biology teachers have never heard of it.

In 1972, with strong interdisciplinary, interagency, and international support, the US Department of Transportation's Climatic Impact Assessment Program began a crash program of stratospheric ozone research. This program closed in 1975. Since 1976, the Upper Atmosphere Research Program of the National Aeronautics and Space Administration (NASA)



**Figure 1** Parallels between the natural nitrogen oxides and the artificial chlorofluorocarbons with respect to stratospheric ozone. Both  $\text{N}_2\text{O}$  and compounds such as  $\text{CF}_2\text{Cl}_2$  are inert in the troposphere and are broken down to active radicals in the stratosphere; the active radicals engage in catalytic cycles that destroy ozone and in competing “do nothing” cycles; the active species are reversibly bound up as inactive gaseous acid species; the acids are rained out of the troposphere when they are transported into it.

has been the lead US agency for stratospheric research. Atmospheric scientists have identified other ozone-destroying catalytic cycles: five  $\text{HO}_x$ , two  $\text{NO}_x$ , one homogeneous  $\text{Cl}_x$ , and two heterogeneous  $\text{Cl}_x$ . Using the stratospheric distribution of nitrous oxide, as measured by NASA satellites, and with a one-step calculation of the steady-state concentration of singlet atomic oxygen, Crutzen and Schmailzl (1983) integrated the global rate of  $\text{NO}_x$  production from nitrous oxide:

$$\begin{aligned} \text{Global natural } \text{NO}_x \text{ rate} &= 24 \times 10^{33} \text{ molecules per year} \\ &= 1.2 \text{ megaton } (10^9 \text{ kg}) \text{ per year.} \end{aligned} \quad 4.$$

This nitric oxide production occurs primarily at  $30 \pm 5$  km. Between the upper stratospheric region of maximum ozone mole fraction and the lower stratospheric region of maximum ozone concentration, the nitrogen oxides are, by far, the most important agency for natural ozone destruction, accounting for more than 60% of the total.

The history of the global ozone balance gives an excellent example of the scientific method: observations, postulate, test of postulate, etc.

## SOME OF MY EDUCATION AND EARLY SCIENTIFIC EXPERIENCES

I was born in Woodstock, Georgia on October 11, 1920. I graduated from Emory University with a major in Chemistry and a minor in English Literature.

In the fall of 1941, I entered the California Institute of Technology as a graduate student, and Prof. Roscoe Dickinson agreed to be my director of research. After two quarters, I was admitted behind the locked doors into Dickinson's National Defense Research Council (NDRC) project, where John Otvos and Arthur Stosick were the senior graduate students. From unnamed laboratories, we received poisonous volatile chemicals. Flowing an air solution of each through a charcoal that was a candidate for use in gas masks, we measured the time it took for the compound to pass through the filter. We tested several charcoals against each chemical. After a few months, our charcoal testing ended. Our next project was to do research, in loose collaboration with Professor Don Yost's group (Cal Tech) and with Professor Wendell Latimer's group (University of California, Berkeley), toward understanding how gas clouds moved and dispersed over various terrains. At this point, I began my study of meteorology and micrometeorology.

In the atmosphere, air temperature usually decreases with altitude, and dry air is neutral with respect to vertical mixing when the temperature decrease is 1 K per 100 m, the dry adiabatic lapse rate. Air spontaneously mixes in the vertical direction, if the temperature decreases with altitude more rapidly than the dry adiabatic lapse rate. If air temperature decreases with altitude at a rate less than 1 K per 100 m, including temperature increases with altitude, there is a temperature inversion. With a temperature inversion, air moves freely in horizontal directions, but air is stable against vertical mixing. The Los Angeles basin regularly has large scale temperature inversions, as surface air chilled by contact with the Pacific Ocean moves onshore, thus displacing upward air that had been previously heated by sun-warmed surfaces. The entire stratosphere has a temperature inversion.

Our project developed a portable station that measured the vertical profiles of temperature, wind speed, and wind direction. We traced air motions with a turbulence meter, smoke candles, and meteorological balloons. Our first assignment was to assess coastal areas between the Mexican border and San Luis Obispo for air motions that would make a city especially vulnerable to gas attack.

Yost set up a field test station in the Mojave desert of California, and Latimer's group did field testing near Mt. Shasta. Kenneth Pitzer

persuaded the Army to let them test bomb-explosion dynamics and gas spread with butane instead of with phosgene; butane and phosgene have almost identical thermodynamic properties. To test for air motions during the night-time inversion, William Gwinn detonated a five-gallon can of mixed mercaptans and sent graduate students up and down the mountainside smelling the air, instead of using phosgene or mustard gas.

In 1943, the Chemical Warfare Service set up a test station in a forest in the Withlacoochee Land Use Area near Bushnell, Florida. Otvos and I developed a compact instrument that continuously measured the concentration in air of gases, such as phosgene, hydrogen cyanide, and cyanogen chloride. The Cal Tech shops built about 20 of these instruments, and, in a flat bed truck, we carried them and our meteorological instruments to Florida. Throughout the fall of 1943, our group and several other NDRC groups worked with the Dugway Proving Ground Mobile Field Unit of the US Chemical Warfare Service, who shot off poisonous gas bombs in the swamps of Florida. The NDRC groups, including ours, moved on to Panama for sites more nearly like jungles on the southwest Pacific islands. I remained as head of the meteorology department of the Dugway Proving Ground Mobile Field Unit. Through midsummer of 1945, we exploded bombs and prepared extensive tables of how the area covered by lethal amounts of gas depends on meteorological variables.

By the time I returned to graduate school at Cal Tech, Prof. Dickinson had died. Prof. Yost was my new research director, and for one year I worked jointly with Yost and Richard Dodson on a project involving radioactive isotopes of iodine and phosphorus. When Dodson left Cal Tech, I asked Yost for a new project. He said I should pick my own research project, but he provided some hints. At a war surplus store, he bought a DuMont oscilloscope for \$5, electron photomultiplier tubes, and miscellaneous electronic supplies. Yost set up the oscilloscope on a central table in the laboratory and announced to his group in general, "Chemists should use oscilloscopes, not test tubes." Clearly, this was a hint and a challenge. We graduate students discussed what Yost had in mind, and each of us played with the equipment.

I came up with the idea of the stopped-flow reactor for measuring the fast chemical reaction rates: The course of the reaction was measured photometrically and recorded as a time exposure photograph of a synchronized single sweep of the oscilloscope beam. From my literature reading in search of a research project, I listed, in order of preference, four fast reactions that might be studied in this way. The first was to react permanganate ion with other species in aqueous solutions, and the second was to react nitrogen dioxide with ozone to form nitrogen pentoxide; I have forgotten the third and fourth. I presented my proposed stopped-



flow method to Yost, who gave approval with minimum comment. I showed him my list of possible reactions and began to amplify why I preferred the permanganate system. With no word at all, he pointed to the reaction of nitrogen dioxide with ozone and then underlined it with pencil. Thus, I became a gas-phase photochemist and kineticist with strong ties to atmospheric science, instead of an inorganic chemist doing kinetics with transition metal complexes in solution. At this point, Yost freely made suggestions and introduced me to Dr. Oliver Wulf, a research scientist at Cal Tech. Wulf generously taught me how to prepare and handle ozone and introduced me to the tradition of Chapman and Dobson, the Umkehr method, and properties of the ionosphere. With the stopped-flow method, I obtained a time resolution of  $1/300$  second, which was two or three orders of magnitude faster than the fastest previous direct study of a gas-phase reaction. My PhD thesis (1947) and first publication (1948) was "The kinetics of the rapid reaction between ozone and nitrogen dioxide."

Farrington Daniels and E. H. Johnston (1921) accurately measured the rate of the thermal decomposition of nitrogen pentoxide over a substantial range of pressure and temperature. I use "accurately" instead of "precisely," because at least 30 investigators, who used many different methods, studied the kinetics of this reaction during the period 1921–1934, and all careful investigators obtained results in agreement with Daniels. The overall reaction is  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ , and the kinetics is first order, rate =  $-k[\text{N}_2\text{O}_5]$ , over a wide range of conditions. During this same period, Lindemann, Kassel, Rice, Ramsperger, Tolman, and others developed a theory of unimolecular chemical reactions that was firmly grounded in fundamental molecular physics. Linhorst and Hodges, Schumacher and Sprenger, and Ramsperger and Tolman measured the rate of  $\text{N}_2\text{O}_5$  decomposition in large bulbs and down to one millitorr pressure to find the "fall-off" region predicted by theory. The theory and data were in utter disagreement. The story was told at Cal Tech that someone asked Richard Tolman why he had switched his area of research from chemistry to astrophysics. "Because," he said, "chemistry is hard." Wulf told me that Tolman's frustration with the unimolecular decomposition of nitrogen pentoxide was part of the reason.

In the fall of 1947, I became an instructor in chemistry at Stanford University. J. Harold Smith and Farrington Daniels (1947) observed the kinetics of the reaction between nitric oxide and nitrogen pentoxide and were perplexed by their results. About the same time, Richard A. Ogg, Jr. proposed a new, four-step mechanism for the first-order decomposition of nitrogen pentoxide, which showed the rate to be a complex process that happened to have first-order kinetics. The measured rate was not that of

an elementary reaction. From a slight modification of Ogg's mechanism, I showed that by adding nitric oxide, Smith and Daniels had observed the elementary unimolecular decomposition rate of nitrogen pentoxide ( $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$ , slow;  $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$ , fast).

Using our stopped-flow fast-reactor method, Robert Mills, my first graduate student, and I added nitric oxide and measured rates of the elementary unimolecular decomposition of nitrogen pentoxide from its high-pressure first-order limit to its low-pressure second-order limit, which spanned a range of  $10^5$  in total pressure. Mills' study was the first time a unimolecular reaction was followed across these two limits. These rate constants were the quantities that should have been put in Kassel, Rice, and Tolman's theory; when we did that, the theory agreed with our observations. Both measurements and theory had been right all the time; the problem was that previous workers measured one thing and thought it was something else.

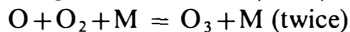
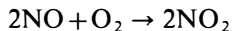
Other graduate students and I measured some fast reaction rates:  $\text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2$ ;  $\text{NO}_2 + \text{F}_2 = \text{FNO}_2 + \text{F}$ ;  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$  at high reactant pressures; and  $\text{N}_2\text{O}_5$  at high temperatures. For 15 minutes, figuratively speaking, we led the world in the fast-reaction race. I dropped out of this race, because of interest in unimolecular reactions, kinetic isotope effect, and reaction rate theory in general. For several years I worked on experiments and theory in these areas.

One of my freshman advisees, Dudley Herschbach, entered Stanford with a football scholarship. After making all As during his freshman year, he received an academic scholarship. When Dudley told his coach that he was leaving the team, his coach warned him that he was making a big mistake: "If you stay in football, I can get you a *job*." Herschbach did summer research with me, studying the fast reaction of nitric oxide with fluorine, among other things. Herschbach's article in the October 1956 *Journal of Chemical Physics*, "Theoretical pre-exponential factors for twelve bimolecular reactions," by D. R. Herschbach, H. S. Johnston, K. S. Pitzer, and R. E. Powell, was the origin of my book, *Gas Phase Reaction Rate Theory* (1966). Another one of my undergraduate advisees at Stanford, Professor Robert Charlson of the University of Washington, has made outstanding contributions to atmospheric science.

I recite here certain stages in my career, but discuss scientific matters according to topic in other sections. During 1956–1957, I was Associate Professor of Chemistry at Cal Tech. I came to Berkeley as Professor of Chemistry in 1957 and was Dean of the College of Chemistry in 1966–1970. In addition, I have been a Principal Investigator in the Lawrence Berkeley Laboratory since 1966.

## OZONE FROM PHOTOCHEMICAL SMOG

During World War II, Los Angeles citizens reported eye irritation from thin white fogs that spread out from the butadiene factories, according to the local newspapers. After the war, these complaints multiplied, and the affected areas included much of the Los Angeles basin. The eye-irritating fogs were identified as air pollutants and named "smog." Sulfur dioxide air pollution is a chemical reductant; smog is an oxidant. Many farmers who grew fresh vegetables and flowers found their crops spoiled from "new plant diseases." Arie J. Haagen-Smit, Professor of Biochemistry at Cal Tech, took an interest in the damage to plants, which he ascribed to smog. Haagen-Smit's mechanism was ozone production by ultraviolet photolysis of nitrogen dioxide; ozone reaction with olefins to produce ozonides, aldehydes, and aerosols; and nitrogen dioxide regeneration by Bodenstein's (1918) reaction of nitric oxide with oxygen:



I attended a seminar at which this mechanism was given and commented that one part per million of nitric oxide reacted with oxygen much too slowly to account for the observations. The Bodenstein reaction is too slow, but Harvey Crosby, in my laboratory, recently made the first measurement of the rate constant  $k$  of  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ . This fast reaction, not  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ , would rapidly follow Haagen-Smit's first two reactions, to set up a steady-state concentration of ozone

$$[\text{O}_3] = j[\text{NO}_2]/k[\text{NO}] \quad 7.$$

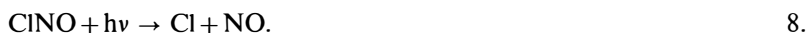
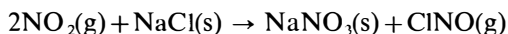
where  $j$  is the  $\text{NO}_2$  photolysis rate constant.

Stanford Research Institute (SRI) hired me as a part-time consultant and asked me to write a review of Haagen-Smit's "theory." The SRI managers and workers on the smog project were scornful of Haagen-Smit. They said that his work was irreproducible, his statements were illogical, and his motivation was publicity. My job was apparently to correct the mistakes of a sloppy, if not fraudulent, scientist, but I quickly concluded that Haagen-Smit's results were valid and that he was exceptionally creative. He invented and used the world's simplest quantitative ozone meter to discover the causes of smog. In his laboratory, he passed a known

stream of dilute ozone over cleaned pure rubber bands and, with good reproducibility, he measured the times that the rubber bands showed cracks and broke in two. With similar rubber bands, he measured ozone concentrations in the atmosphere. He found nitrogen dioxide, plus almost any volatile organic compound, plus sunlight produced ozone. Automobile exhaust and sunlight produced ozone. By flowing irradiated automobile exhaust across leaves, he duplicated plant damage of the sort observed during smog episodes.

I became interested in explaining Haagen-Smit's mechanism in terms of elementary chemical reactions. When I was a graduate student, *Atomic and Free Radical Reactions*, by E. W. R. Steacie, had been published, and I had read large sections of it. I postulated that free radicals were formed in the smog system and were an essential part of the mechanism. A free radical interpretation for photochemical smog seems tame in 1992; but after 1952, it took at least five years for the idea to begin to catch on. I constructed a free-radical mechanism to explain his results (R. Cadle and H. S. Johnston, "Chemical Reactions in Los Angeles Smog," pages 28–34, *Proceedings of the Second National Air Pollution Symposium*, Pasadena, California, published September 1952).

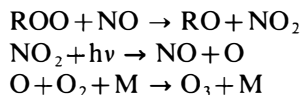
In this paper, we started with the photolysis of nitrogen dioxide and ten reactions of the oxides and oxyacids of nitrogen and made some half-life and steady-state calculations for ozone and other species. We demonstrated plausible mechanisms for forming HO, HOO, R, ROO, RO, HCO, and RCO free radicals. We pointed out that nitrogen dioxide reacts with solid sodium chloride to form nitrosyl chloride and atomic chlorine:



We proposed that ozone might be formed by reaction of organic peroxy radicals with molecular oxygen



There is currently no evidence that this reaction occurs as an elementary step. The accepted mechanism for ozone production in photochemical smog is



Thus, our primitive proposal in 1952 gave the correct net reaction, but not correct elementary reaction, for ozone production in photochemical smog.

I showed a version of this mechanism to Haagen-Smit in 1954. He said that it was interesting, but he hoped "photochemical smog could be explained in terms of normal reactions." Afterward, I came to know him fairly well and was distressed to see him misquoted and misrepresented by persons whose business interests were inconvenienced by his scientific discoveries.

Philip Leighton's book (3) critically summarizes the scientific progress in this field through 1960. This book identifies atomic, free radical, and molecular elementary reactions that occur in photochemical smog, but it labels more rate constants as unknown than it lists as measured. Another decade of progress was reported in a four-volume report by Project Clean Air 1970 of the Statewide University of California. I was co-chair of Task Force No. 7 on the subject of Atmospheric Chemistry and Physics. I was assisted by two postdoctoral fellows, two staff members, and 21 undergraduate students on this six-month project. We carried out a critical review of the rate constants and activation energies for 166 chemical reactions. In 1961, Leighton did not yet understand how smog reactions form ozone (Equation 10). By 1970, this process was thoroughly established.

In the Project Clean Air report, I emphasized "odd electron arithmetic." A free radical has one unpaired electron, and a molecule has zero unpaired electrons. Chemical reactions follow the rules of adding even and odd numbers. In addition to applying this arithmetic to radicals, I apply it inside reaction families: odd oxygen,  $O_x$ ,  $O$ , and  $O_3$ ; odd hydrogen,  $HO_x$ ,  $H$ ,  $HO$ , and  $HOO$ ; odd nitrogen,  $NO_x$ ,  $N$ ,  $NO$ ,  $NO_2$ , and  $NO_3$ ; odd chlorine,  $Cl_x$ ,  $Cl$ ,  $ClO$ ,  $ClOO$ ,  $OCIO$ , and  $ClO_3$ . Some examples of this arithmetic are illustrated here:

Arithmetic		Examples	
	Odd electrons	$O_x$	$HO_x$
$0 \rightarrow 1+1$	$H_2CO \rightarrow H+HCO$	$O_2 \rightarrow O+O$	$H_2O \rightarrow H+HO$
$1+0 \rightarrow 1+0$	$Cl+O_3 \rightarrow ClO+O_2$	$O(^1D)+M \rightarrow O(^3P)+M$	$HO+O_3 \rightarrow HOO+O_2$
$1+1 \rightarrow 0+0$	$2C_2H_5 \rightarrow C_2H_4+C_2H_6$	$O+O_3 \rightarrow O_2+O_2$	$HO+HOO \rightarrow H_2O+O_2$
$0+1 \rightarrow 0$	Impossible	$NO+O \rightarrow NO_2$	$HO+NO_2 \rightarrow HNO_3$
$1+1 \rightarrow 0$	$HO+NO_2 \rightarrow HNO_3$	$O+\bullet \rightarrow O_2$	$HO+HO \rightarrow H_2O_2$

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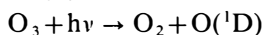
Some order can be found in extremely complicated systems, when one uses these arithmetics.

Methane is not important in urban air pollution, because it reacts slowly compared with the time it takes an air mass to move through a city. In the free troposphere and stratosphere, the abundance of methane is far greater

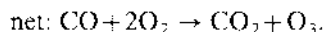
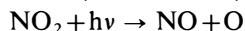
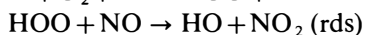
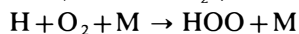
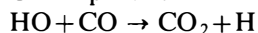
than that of other organic compounds, and the atmospheric residence time of methane is a matter of a few years. Crutzen (1972) and William Chameides and James C. G. Walker (1973) applied the smog mechanism to tropospheric methane, and Ed Quitevis and I (1974) modeled the methane- $\text{NO}_x$  smog reactions from the Earth's surface to the top of the stratosphere. We noted, in particular, the crossover altitude (13 km) where ozone destruction by Crutzen's  $\text{NO}_x$  mechanism falls to a value so low that it equals the rate of ozone production by the global methane- $\text{NO}_x$  smog reactions.

The essence of the smog reactions in producing and destroying ozone is most simply illustrated with carbon monoxide as the fuel:

Radical initiation



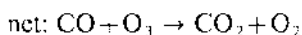
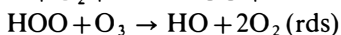
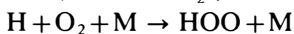
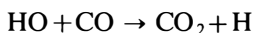
Ozone production



Radical termination



Ozone destruction



12.

Although not complete, this mechanism illustrates major features of photochemical smog: Smog formation is a free radical chain reaction, catalytic in nitrogen oxides,  $\text{NO}$  and  $\text{NO}_2$  ( $\text{NO}_x$ ), and catalytic in free radicals based on water,  $\text{H}$ ,  $\text{HO}$ ,  $\text{HOO}$  ( $\text{HO}_x$ ). The chain reaction is initiated by solar ultraviolet radiation and terminated by nitrogen dioxide, which combines with active free radicals. The chain reaction has a branching point at which one path leads to ozone formation and the other is ozone destruction, and the ratio of nitric oxide to ozone controls the branching. And, smog reactions are consumptive, not catalytic, in the fuel, which is carbon monoxide in this case.

## SUPERSONIC TRANSPORTS, TO 1975

Prof. Joe Hirschfelder, University of Wisconsin, invited me to a presentation by the Department of Commerce Advisory Board for Supersonic Transport (SST) Environmental Effects in Boulder, Colorado, on March 18 and 19, 1971. As a member of that board, Hirschfelder had persuaded

them to hold an open meeting to present the case for and against any adverse environmental effects by the planned fleet of American SSTs. Because I knew almost nothing about supersonic aircraft and the stratosphere, I studied some books concerning the stratosphere before going to Boulder.

Although I had read newspaper and magazine accounts of sonic booms and the SSTs before coming to Boulder, I was largely unaware of the following facts: During the late 1960s and into 1971, the United States government was financing the design and construction of two prototype SSTs, and the cost of these prototypes was to be repaid by the airframe manufacturers from profits from the sale of a planned fleet of 800 aircraft. In 1963, chemist and meteorologist Jerry Pressman first suggested that SSTs might have an effect on the global stratosphere, especially water vapor from the exhaust. By using Hunt's chemical model (Equation 2), Halsted Harrison (1970) calculated a 3% ozone reduction from the water vapor of the proposed fleet of SSTs. Negligible climatic effects were anticipated from these ozone reductions. During 1970 and early 1971, there was intense political debate whether the government should continue to finance the SST program. The debate primarily concerned economics, national priorities, and sonic boom. In the winter of 1971, congressional opponents of governmental support of the SST project were pushing a bill to cancel it altogether. The following newspapers headlines give a flavor of what was happening:

*San Francisco Chronicle*, March 1, 1971, p. 2, "SSTs strong comeback—new fight in Congress."

*New York Times*, March 3, 1971, p. 87, "Scientist calls SST skin cancer hazard."

*New York Times*, March 4, 1971, "Experts assure House SST would not be harmful."

*New York Times*, March 18, 1971, p. 1, "White House and Proxmire in dispute on SST hazard."

The House of Representatives scheduled March 18, 1971 as the date for the deciding vote on terminating the SST program.

From this paragraph on, I obtain the information from two filing cabinets full of information, including detailed notes I took at meetings, abstracts and proceedings of meetings, preprints and reprints of journal articles, technical monographs, correspondence, notes of telephone calls, newspapers, magazines, and a 600-page summary that I wrote of it all in 1976.

On March 18, William Kellogg of the National Center for Atmospheric Research presided over the morning meeting. He gave a review of the

history behind the concerns of the SST Environmental Research Panel and this meeting. In July 1970, the Massachusetts Institute of Technology conducted a "Study of Critical Environmental Problems (SCEP)." (Hirschfelder handed out proofs of pages 65–74 and 106–107 of the SCEP report.) This summary study considered the effects of SST water on ozone. Kellogg continued: "Julius London and Jae Park made careful calculations for the first time, and their calculations will be presented here later by Prof. London. . . . Park and London calculated about 10% increase of global stratospheric water and 1–2% reduction of global ozone. The summer study concluded that the changes would be small compared with natural variations, but nevertheless came away with a feeling of genuine concern. . . . In updating the National Academy of Sciences work on climate modification, James McDonald, a physicist, brought in a new thought." Kellogg confided to the group, "I wish I had thought of it myself."

Ed Danielson presented an especially informative tutorial about the stratosphere, including the following: (a) Tropical tropospheric air slowly moves up into the stratosphere, and stratospheric air returns to the troposphere in polar regions, the Brewer model (1949). (b) There is a temperature inversion throughout the stratosphere. Carbon-14 and other products of the 1961–1962 nuclear bomb tests moved rapidly (fortnight or so) with longitude around the globe and moved much slower with latitude (many months from equatorial zone to polar region). The vertical spread in the stratosphere by turbulent diffusion-like processes was about 1000-fold less than north-south spread ( $K_{yy}/K_{zz} \approx 10^6$ ,  $K_{zz} \approx 2 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$ ,  $d^2 = 2K_{zz}\tau$ ). (c) The stratospheric lifetime ( $1/e$ ) of an inert tracer gas injected at 20 km altitude was about two years. (d) Ozone is primarily formed in the middle stratosphere (30–45 km) and is slowly mixed downward into the lower stratosphere. (e) The rate of photochemical ozone formation is slow in the region of maximum ozone concentration, which is at an altitude of about 20–25 km.

Largely based on the SCEP report, we were presented technical information about the proposed supersonic aircraft: (a) The planned size of the American fleet was 500 SSTs. (b) The cruise altitude would be 20 km. (c) The amount of fuel consumed by a fleet of 500 SSTs would be  $7.7 \times 10^{10} \text{ kg}$  per year. (d) General Electric engineers estimated the engine exhaust to contain 1250 g  $\text{H}_2\text{O}$  and 42 g  $\text{NO}$  per kg of fuel burned. (e) Because the stratospheric aircraft were expected to fly primarily at midlatitudes in the Northern Hemisphere, it was regarded as reasonable and prudent to assume that, near the main flight corridor, local vertical columns of engine exhaust would exceed the global average value by a factor of 10, the "corridor effect."



Before giving his talk, Prof. London, University of Colorado, distributed an eight-page extended abstract: "The photochemical relation between water vapor and ozone in the stratosphere" by Park and London. The abstract contained discussion, four figures, a table of 40 rate constants involving  $O_x$  and  $HO_x$  reactions with references, and three  $NO_x$  reactions in the text but not in the table (see Equation 3). The figures gave prescribed profiles of water vapor and nitrogen oxide, before and after operation of SSTs. The calculational method was "photochemical equilibrium," that is, no atmospheric motions were included. London argued for the significance of photochemical equilibrium studies that use prescribed  $H_2O$  and  $NO_x$  profiles. After a long, interesting talk, London gave their results: 1.2% ozone reduction calculated from SST water and 1.8% ozone reduction calculated from SST nitrogen oxides. I had been following his presentation closely enough to doubt his final conclusion concerning nitrogen oxides. During the discussion period after the formal talk, I said that I thought the assumed amount of  $NO_x$  would cause a much larger ozone reduction than 1.8%. London conceded that they had found a larger ozone reduction at higher altitudes, but that ozone reformed at lower altitudes, which reduced the net effect to his reported value. I recognized that inclusion of  $NO_x$ -methane smog reactions in his mechanism could have such an effect and dropped the question until I could study his extended abstract in detail.

In the afternoon, McDonald presented the "new thought" alluded to by Kellogg: "Effects of changes of ozone." He presented the epidemiology of skin cancer as a function of latitude. In any homogeneous population, the fraction of persons who get skin cancer increases from north to south in the Northern Hemisphere and from south to north in the Southern Hemisphere. Annual average overhead ozone changes in the opposite sense. McDonald related skin cancer to overhead ozone via latitudinal epidemiology and then predicted how much additional skin cancer would be caused by long-term 1% ozone reduction by SSTs. Although McDonald presented his material in a scholarly, dignified manner, Arnold Goldberg, the Boeing Company representative, heckled him relentlessly and scornfully throughout his talk.

Toward the end of the afternoon session on March 18, a piece of paper was handed to the chairman, who read it to the group, "The House of Representatives has just voted 215 to 204 to cut off Federal funds for the SST as of March 30, 1971." The chairman said the meeting would continue the next day, as planned, and noted that the Senate would vote on the matter in one week, perhaps reversing this vote.

That night, I read Park and London's long abstract. Mostly, it concerned the effect of water vapor on ozone. In addition, London constructed two

profiles of  $\text{NO}_x$  mixing ratios, by extrapolating the observed nitric oxide in the ionosphere (80 km, 50 ppb) through the mesosphere, stratosphere, and troposphere to the surface, where it was assigned the value of 1 ppb for the  $\text{NO}_x$  background and 20 ppb for SST operation. The increase of  $\text{NO}_x$  at 20 km was 30 ppb. One of his figures showed the calculated ozone profiles before and after adding  $\text{NO}_x$  from SSTs. There was a large ozone reduction between 25 and 35 km, zero ozone reduction at 20 km, and an ozone increase, up to  $3 \times 10^{12}$  molecules  $\text{cm}^{-3}$ , below 18 km. This additional low-altitude ozone could not be from smog reactions, because the mechanism included neither the reaction  $\text{HOO} + \text{NO} \rightarrow \text{HO} + \text{NO}_2$  nor any fuel gas, such as methane or carbon monoxide. I submitted all 43 reactions in London's mechanism to odd electron, odd oxygen, odd  $\text{HO}_x$ , and odd  $\text{NO}_x$  arithmetic and proved that there was no way London's mechanism could generate this ozone at low altitudes. I concluded that there must be some mistake in his calculation.

I next read the pages of the MIT summer study that were handed out that day, and soon found the following paragraph on page 69:

Both carbon monoxide and nitrogen in its various forms can also play a role, but despite greater uncertainties in the reaction rates of CO and  $\text{NO}_x$  than for water vapor, these contaminants would be much less significant than the added vapor and may be neglected.

From my experience, I knew that everything in this sentence after the word "but" was wrong. I then took it as my job to correct the error declared in that sentence. I read all my notes, studied all the handouts, and considered several relaxation times given by this chart:

$\text{O}_3$ photochemical replacement time	$[\text{O}_3]/2j[\text{O}_2]$	"Very long"
Stratospheric dynamical residence time		"2 years"
Vertical transport from ozone formation region		" $\approx 2$ years?"
$\text{O}_3$ destruction time from $\text{O}_x$	$[\text{O}_3]/2k_1[\text{O}][\text{O}_3]$	8 years
$\text{O}_3$ destruction time from $\text{NO}_x$		
From natural $\text{NO}_x$	$[\text{O}_3]/2k_2[\text{O}][\text{NO}_2]_B$	$x$ months
From SST added $\text{NO}_x$	$[\text{O}_3]/2k_2[\text{O}][\text{NO}_2]_S$	
global average		7 months
local corridor		3 weeks
From total $\text{NO}_x$	$[\text{O}_3]/2k_2[\text{O}][\text{NO}_2]_T$	$7/(1+7/x)$ months.

13.

The entries in quotation marks were the values given to us during the

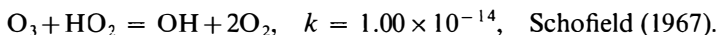
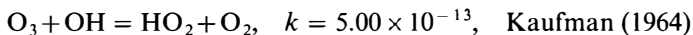
tutorials that day. I calculated the other times that night. I spread the two-year inventory of SST of added nitrogen oxides uniformly around the globe in a 5 km shell at a 20 km altitude. I obtained the 5 km spread from the vertical diffusion coefficient given to us that day ( $d^2 = 2K_{zz}\tau$ ). To obtain the number molecules of SST-added  $\text{NO}_x$ , I took the SCEP values, but I reduced them by a factor of three for a reason that seemed valid at the time. From books I brought with me to Boulder, I found the ozone concentration at 20 km to be  $2 \times 10^{12}$  and atomic oxygen to be  $1 \times 10^6$  molecules  $\text{cm}^{-3}$ .

In a kinetics situation, characteristic times are not additive, but reciprocal times (first-order rate constants) are. It is more intuitive to work with times, but analyses are based on rate constants or rates. The global average SST increment of  $\text{NO}_x$  gave a calculated ozone destruction time shorter than local photochemical replacement time or the replacement time by air transport from the middle stratosphere. Therefore, SST added  $\text{NO}_x$  is an important variable in this problem. If the background  $\text{NO}_x$  is added to the SST added  $\text{NO}_x$ , the ozone destruction time would be even shorter, and the argument that  $\text{NO}_x$  is an important variable is strengthened.

I wrote a 16-page report, which discussed catalytic cycles, odd oxygen arithmetic, and various characteristic times for ozone at 20 km altitude, and I handed it out the next morning. The conference was divided into two groups: photochemical modeling and atmospheric dynamics. I presented my report to the photochemical group and emphasized  $\text{NO}_x$  catalytic cycles and the thesis that stratospheric  $\text{NO}_x$  should not be neglected and that we should advocate learning all we can about it. Comments from the audience emphasized technical features that I had not explained: I had not considered atmospheric motions. Could I explain why ozone had increased over the past ten years? The  $\text{NO}_x$  engine emissions that SCEP used were too high.

The chairman recognized Arthur Westenberg as the next speaker. Before coming to the meeting, Westenberg had used a computer to make some steady-state photochemical calculations that corresponded to conditions at 20 km altitude and  $45^\circ$  north latitude. He used only the Chapman reactions and the three  $\text{NO}_x$  reactions that London considered. He calculated the ozone concentration for the following concentrations of  $\text{NO}_x$ : 0,  $10^{-16}$ ,  $10^{-15}$ , and  $10^{-14}$  moles per cubic centimeter (a chemist's familiar unit, but units rarely encountered by atmospheric scientists). The calculated relative ozone concentrations were, in order: 100, 95, 40, and 15, the last case being an 85% reduction of ozone. Westenberg had not mentioned SSTs. A member of the audience declared, "There is so much  $\text{NO}_x$  already in the stratosphere that SST-added  $\text{NO}_x$  would have no effect." When Westenberg later submitted this material for publication, I, as one referee, said it should be published, but it was rejected.

During the rest of the morning, we considered London's list of 40 reactions, commented on them one by one, and offered London useful suggestions. In due time, we came to London's Reactions 15 and 16 (Hunt's  $k_1$  and  $k_2$ ), presented as follows:



Fred Kaufman spoke up: "I appreciate what you guys are trying to do. People want you to make these calculations, and I sympathize with what you are up against. But, this is not what I said in 1964. I did not say  $k_{15}$  is equal to  $5 \times 10^{-13}$ ; I said it was less than  $5 \times 10^{-13}$ . If it had been  $5 \times 10^{-13}$  or faster, we could have measured it in our apparatus. We couldn't measure a thing. If you want to assume it is  $5 \times 10^{-13}$ , go ahead and assume it, but don't put my name down as justifying it. Also, your rate constant for Reaction 16 is a pure guess. Nobody has ever measured anything about this reaction."

After lunch, the entire group met for a "summing up." After several people had commented, I proposed and defended the following motion: "We recommend that the oxides of nitrogen be regarded as potentially an important variable in problems concerning stratosphere photochemistry." In the discussion of this motion, someone stated that  $\text{NO}_x$  emission from the SST engine would be less than the SCEP report said. Another pointed out the importance of air motions in the stratosphere, and he was reinforced by someone who said, "This problem is so dominated by air motions that chemistry is unimportant." Finally, someone else said, "I don't think we are in a position to make firm conclusions at this time. I recommend that we table this motion." The motion was tabled by an overwhelming vote. This meeting of the Panel of the Department of Commerce Technical Advisory Board formally endorsed the conclusion that in stratospheric photochemistry,  $\text{NO}_x$  may be neglected.

During the next few months, I was kept busy with fast moving developments in the stratospheric ozone problem. In both published books and hearsay, there are some incorrect statements about what I said and did and what happened during these months. I list important dates and briefly discuss some events.

March 25. Senate voted 51 to 46 to terminate Federal funding for the development of two SST prototypes.

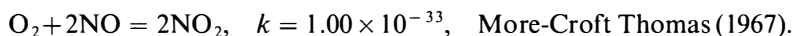
March 25. I telephoned the President's Science Advisory Committee and told Russell Drew about my calculations concerning SSTs and  $\text{NO}_x$ . He appeared to be uninterested and unconcerned.

March 29. I received the first of many telephone calls from a young man,

David Elliott, member of the National Aeronautics and Space Council in the Executive Office Building. He said that he was my contact with the White House staff. During the next few months, I kept him informed about my SST calculations, and he told me about many things that happened in Washington.

April 2. I completed the first draft of what I intended to be an article to *Science*. This article was an expanded version of my March 18 paper. I had read about the effect of ultraviolet radiation on snowblindness, and I included a foolish statement about that in my draft article. A few days later, I removed the foolish statement, but it was already too late. I sent copies of the April 2 report to Hirschfelder, London, Elliott, and three senior Berkeley professors for their review.

April 9. I discovered London's error. On the second copy of his extended abstract that I had brought home, I found a list of four  $\text{NO}_x$  reactions at the end. Three were those listed in the text of the other version of the extended abstract, and the fourth was Bodenstein's reaction:



The correct value for this rate constant is  $7.6 \times 10^{-38}$ , which is 13,000 times smaller than the value London used. With this reaction, there is indeed an  $\text{NO}_x$  catalytic cycle that forms ozone, as Haagen-Smit said in 1952 (Equation 5). By using the correct rate constant, I found that it would take 300 years to produce London's excess ozone formed at 15 km. On April 14, I described this in a letter to only London, Hirschfelder, and Elliott. On April 30, London acknowledged his error. (Later, he told me that he had copied the erroneous value from a set of rate constants prepared by Harold Schiff.) London said he would redo his calculations, and I thought that he intended to submit his work for publication. In mid-May, I calculated the ozone reduction based on London's natural and SST-perturbed  $\text{NO}_x$  profiles and found a 40% ozone reduction.

April 14. I sent the first draft of my  $\text{NO}_x$  article to *Science*. At the same time, I sent a copy to George Kistiakowsky and requested his review of it. This version had very little in common with the April 2 draft article; it consisted of modeling calculations. It did not include ozone photochemical self-healing, but later versions did.

May 10. Elliott told me that he had sent my material out for review. His referees agreed in general, but not in all detail, with my work.

May 12. From *Science*, I received two reviews of my paper, a copy of Crutzen's 1970 paper, and an invitation to send back a revised version. One reviewer pointed out that Crutzen had published a paper on nitrogen oxides in 1970 (see Equation 3), which was the first time that I had heard

of Crutzen. Upon reading his article, I found it to be a brilliant original contribution, and he had already done what I thought I had discovered during the past few weeks. Crutzen's 1970 article had no mention of aircraft. However, it quantitatively showed the sensitivity of stratospheric ozone to nitrogen oxides and should have caught the attention of readers interested in the effect of SSTs on ozone. Crutzen's name was not included in the list of references in the published SCEP report, the account of the MIT 1970 summer study. Upon carefully rereading Park and London's extended abstract, I found the statement that their report "... constitutes a continuation of studies of Hunt, Hesstvedt, Crutzen, and others," which was the only place his name appeared on any of the written material handed out at Boulder. In the verbal presentations at the meeting in Boulder, I never heard Crutzen's name.

As I heard later, Crutzen had a paper accepted for publication in the *Journal of Geophysical Research* (his great 1971 article, published in October). In that paper, he explicitly identified the amount of SST nitrogen oxides that would seriously perturb ozone. Early in 1972, he published an article with much better atmospheric dynamics than mine, in which he calculated large ozone reductions by a large fleet of SSTs cruising at 20 km altitude. I have always regarded him as codiscoverer of the SST/NO<sub>x</sub>/O<sub>3</sub> problem.

May 11. *New York Times*, p. 22, "SST backers, with Nixon support, seek to revive project in House today."

May 13. *San Francisco Chronicle*, p. 1, "201-197 vote, House revives the SST—fight goes to Senate."

May 14. *New York Times*, pp. 1, 67, "Washington, May 13—The board chairman of the Boeing Company, William M. Allen, said today that revival of the supersonic transport program would require at least half a billion dollars more in government financing than was needed before the project was cancelled."

May 17. Someone had leaked my April 2 draft paper to a small southern California newspaper, the *Newhall Signal*, which gave it a spectacular presentation, especially on "blindness." The University of California Public Relations Office, released the April 2 paper with a covering statement. I declined all requests for radio and television interviews. For months and years to come, my technical statement that at 20 km, the ozone halftime with respect to destruction by NO<sub>x</sub> catalysis is six months ( $t_{1/2} = 0.693[\text{O}_3]/2k[\text{O}][\text{NO}_2] = 6 \text{ months}$ ) was misunderstood by the press and stated as "stratospheric ozone will be cut in half in six months."

May 17. Hearsay was volunteered from two sources. Apparently unaware that Elliott was in contact with me, two members of the White

House staff went to a high officer in the National Bureau of Standards to find out “if that guy Johnston knows anything about ozone.”

May 18. *New York Times*, p. 66. “Senate SST hopes fade, ozone peril called grave. Washington, May 17.—Senate backers of the supersonic transport acknowledge today that chances for a revival of the SST were dwindling rapidly under the weight of its projected cost.”

May 19. The Senate turns down funds for the SST by a vote of 58 to 37.

May 30. Walter Sullivan, Science Editor of *New York Times*, gave a clear exposition of my April 2 paper. He clearly stated the nature of the catalytic cycles and how a relatively small amount of nitrogen oxides could have a significant impact on ozone.

June 14. I submitted the second revised version of my article to *Science*, and it was accepted for publication. These were steady-state calculations with prescribed  $\text{NO}_x$  background profiles. The steady state was found by the mathematical method that we teach freshmen chemistry students in solving complex chemical equilibria; this method is especially fast and accurate for this problem. The model had 1 km vertical grid spacing, extended from 0 to 50 km, and was nominally for spring equinox at  $45^\circ$  north latitude. Photolysis rate constants were evaluated for each hour of the day and averaged. The solar radiation field was self-consistent with the calculated ozone distribution, that is the “ozone self-healing effect” was included. The magnitude of  $\text{NO}_x$  injection was one third the SCEP quantity for two years operation of 500 SSTs. I constructed 11 nonuniform distributions of background  $\text{NO}_x$  and selected the one that gave the best agreement with a standard ozone profile.

A major problem was the vertical spread of the exhaust gases. The tutorial at Boulder on the grand stratospheric circulation—rising air entering at equatorial latitudes and exiting at the poles after numerous trips around the world—suggested a simple analogy for the spread of exhaust gases from stratospheric aircraft. Consider continuous introduction of a dye into a broad river flowing a distance down its channel and then going over a waterfall. How wide is the plume of dye when the river reaches the waterfall? How wide is the plume of aircraft exhaust gas as it exits the stratosphere in polar regions? For some problems in physical chemistry, a difficult dynamical problem is rigorously replaced by a static ensemble that contains all possible configurations of the system. I used this logic as an operational approach to the problem of vertical spread, but, of course, my ensemble failed to contain all possible configurations. In lieu of the impossible task of our calculating the vertical spread of the exhaust gases, I assigned an “ensemble” of vertical spreads: 20–21, 19–23, 18–25, 17–27, 16–29, and 15–31 km, designed to span any realistic distribution. I assumed the two-year accumulation of  $\text{NO}_x$  from the SSTs

to be uniformly spread over these vertical shells and added these  $\text{NO}_x$  increments to the background amounts. The calculated global average ozone reductions for these successive vertical spreads were 3, 12, 20, 22, 23, 22, and 20%. The SST  $\text{NO}_x$  increment was multiplied by ten to represent the corridor effect. The calculated ozone reductions for the flight corridor for these successive vertical spreads were 3, 14, 28, 42, 48, and 50%. The calculated 50% ozone reduction was the worst-case local effect, not a world wide 50% ozone reduction, as many detractors later asserted. The greatest flaw of this paper was that it underestimated the amount of nitric acid that would be formed. Otherwise, for proving  $\text{NO}_x$  to be an important variable, its logic and method were appropriate for the state of knowledge of the stratosphere at that time. (In subsequent years, some modelers found that a nitric acid-free scenario gave about twice the calculated ozone reduction than a scenario that includes nitric acid. If my 1971 ozone maximum reductions, 23% and 50%, are reduced by a factor of two, they are in agreement with the 1975 MIT model results, 12% and 25%, respectively; the MIT model was three-dimensional in atmospheric motions and two-dimensional in photochemistry.)

Since May 1971, I responded as helpfully as possible to all who requested information. With equal consideration, I sent out packages of information to the White House, the Citizen's League Against the Sonic Boom, the Cabinet Office of London, the Anti-Concorde League, universities, and industries.

August 4. Elliott told me that a panel set up by the National Academy of Sciences (NAS) under the chairmanship of Dr. Herbert Friedman, had met on July 29 and reviewed my work on ozone at the request of the head of the National Oceanographic and Atmospheric Administration. When their report was published, it began as follows:

There was general agreement with the conclusions of Johnston and of Crutzen that the introduction of nitrogen oxides from SST exhausts in the stratosphere can have important effects on the ozone concentration. However, with respect to the details of the Johnston analysis, both Johnston and the reviewers have expressed reservations of three types, which introduce uncertainties into the calculations.

August 6. My article is published by *Science*: "Reduction of stratospheric ozone by nitrogen oxide catalysts from supersonic transport exhaust," 173: 517-22.

Early August. The participants of the MIT summer study of 1971, which was a follow-up of the MIT summer study of 1970 and its SCEP report, released a summary report, "Study of man's impact on climate (SMIC)." In an article in the *Washington Post*, Claire Sterling reviewed the SMIC report and related matters. This article was reprinted in the Congressional Record S14627, from which I excerpt the following:



Now that *Science* magazine (in its August issue) has finally decided to publish one expert's chilling view of the matter . . . it might help to know what others think. . . . He was challenged sharply at an international Study of Man's Impact on Climate (SMIC) in Stockholm this summer by 30 of the world's most distinguished scientists. . . . To a man, scientists at last July's elite Stockholm conference refused to accept this. Most of them had attended . . . SCEP the previous summer. . . . In the intervening year, they concluded at Stockholm with a pointed snub . . . "no new information has been developed appreciably to alter the SCEP judgment." . . . The trouble with his [Johnston's] findings, according to SMIC scientists, was that all his work was done in the laboratory. Neither he nor anybody else has done any sampling in the stratosphere. . . .

After Sterling recounted, in much more length than given here, what SMIC said, she gave her own opinion of the situation:

To anybody standing above this particular fray, what leaps to mind is not as much one scientist's capacity for error as a kind of neoncandertal ignorance on the subject in general. Who would have thought it possible, in this age of research and development, with billions of dollars already invested in supersonic transport and both the Concorde and Tupolev very nearly operational, that not a single American, British, French, or Russian scientist has yet gotten off his laboratory stool and gone out and done some relevant sampling of the stratosphere? . . . Though any scientist will tell you how urgent such research is . . . none of the aircraft industries involved, or their sponsoring governments, has yet made a move or put up money. Before we find ourselves groping sightlessly around a lifeless planet, it would be nice to think that at least one of them might.

September 21. Senators Bayh and Church introduced bill S 2555, "The Stratosphere Protection Act of 1971," which mandated a stratospheric research program. Senator Bayh made a long statement on the bill, which he published, along with a letter from me and Sterling's article, in the Congressional Record. I received a call from Elliott late in September that a bill to place the stratospheric research program in the Department of Transportation was passed and that Al Grobecker from the Institute of Defense Analysis would be in charge of the program. The program would open with a symposium.

On March 18, 1971, in Boulder, Verner Suomi mentioned a possible stratospheric research program. Elliott kept me informed of these proposals throughout the spring and summer. Robert Cannon, Department of Transportation, had proposed to rebudget some of its funds appropriated for SST work to a program of stratospheric research, but Elliott said that this plan was disapproved at higher levels of government.

This project was named the Climatic Impact Assessment Program (CIAP). Its administrative organization started in the fall of 1971, and its public activities started with the Survey Conference of February 15–16, 1972. At the end of 1975, CIAP was terminated. There was much to learn about the stratosphere, and 1972–1975 was the first golden age of stratospheric research. (The second golden age of stratospheric research followed the discovery of the Antarctic ozone hole in 1985.) Among other

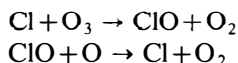
things, CIAP concluded that  $\text{NO}_x$  from stratospheric aircraft would reduce ozone, recommended that aircraft engines be redesigned for a 100-fold reduction in amount of  $\text{NO}_x$  from their exhaust, and published six monographs detailing its massive findings during 1975 (4).

To advise CIAP and issue an independent report, the NAS appointed its Climatic Impact Committee in 1972. Its final, one-volume report (5) was in agreement with CIAP's six technical monographs (4).

## CHLORINE AND OZONE

### *Space Shuttle*

In December 1972, I was approached by a government employee and, in effect, asked to "blow the whistle" on the space shuttle: He said that chlorine from the space shuttle would reduce ozone by reactions similar to Crutzen's nitrogen oxides cycle:



The space shuttle has a solid-propellant booster rocket with ammonium perchlorate as oxidizer and powdered aluminum and asphalt as fuel. It burns the booster rocket through the stratosphere, thus releasing aluminum oxide and hydrogen chloride and other gaseous products. Hydroxyl radicals would react with hydrogen chloride to release atomic chlorine. The government employee asked me to write an article for *Science* on the subject. I declined, saying that I had no independent knowledge of the space shuttle and not enough time to master the problem.

One of my jobs with CIAP was to work with David Garvin and others at the National Bureau of Standards to prepare tables of reaction-rate constants for use by atmospheric modelers. I alerted our group to include chlorine chemistry as a class of reactions to tabulate and began to read up on chlorine reactions, waiting for the telephone to ring.

On August 22, 1973, Larry Anderson from Lockheed Research Laboratory in Palo Alto called me. He said that Hiro Hoshizaki and coworkers at Lockheed had discovered that chlorine would reduce stratospheric ozone, and a summary of their work was included in their quarterly report to Grobecker and CIAP. He sent me a copy of Section 4 of his report, "Potential destruction of ozone by HCl in rocket exhaust." I encouraged Anderson to submit his material to a scientific journal. Anderson said that NASA had invited Hoshizaki and him to Washington to present their case to NASA scientists. From two sources, I heard the following story: Some

“space shuttle people objected” to Hoshizaki and Anderson’s findings, and NASA Headquarters contacted high level managers at Lockheed Palo Alto and persuaded them to keep Hoshizaki and Anderson at home. The Lockheed theory of ozone destruction was published only in laboratory reports and has largely been forgotten.

I was told by CIAP officers that Sidney Benson telephoned them early in 1973 and advised CIAP to investigate the role of chlorine in the stratosphere.

Somewhat later, I came across an 80-page report by R. J. Cicerone, D. H. Stedman, R. S. Stolarski, A. N. Dingle, and R. A. Cellarius, University of Michigan, dated June 3, 1973 and entitled: “Assessment of possible environmental effects of space shuttle operations,” NASA Contractor Report-129003. It appeared to be prepared in response to a general request from NASA. One chapter, “Stratospheric effects of space shuttle effluents,” included a discussion of catalytic cycles involving chlorine. In the summer of 1973, Stolarski and Cicerone submitted a paper to *Science* on the possible role of chlorine in stratospheric photochemistry, but it was criticized by one referee and rejected.

Supported in part by CIAP, there was a large international meeting in Kyoto, Japan, in September 1973. At this meeting, Stolarski and Cicerone presented a paper on “Stratospheric chlorine: A possible sink for ozone,” and Crutzen included chlorine chemistry in his paper, “A review of upper atmospheric photochemistry.” The space shuttle, as such, was not mentioned.

For years, Mike McElroy had considered the role of chlorine in the atmosphere of Venus. He produced a complete theory of stratospheric chlorine reactions.

Once the idea was “in the air,” several groups independently discovered the role of stratospheric chlorine. It is possible that the NASA officer who failed to get me to “pull his hot chestnut out of the fire” in December 1962 went about it more subtly, by placing the idea in the air in several locations.

In December 1973, Robert Hudson, a NASA scientist, who had made an important contribution to CIAP Monograph 1, told me that NASA was concerned about the chlorine problem and would conduct a meeting in Coco Beach, Florida, on January 21–23, 1974. At this meeting, we agreed that the chlorine from 50 space shuttles a year was 300-fold less than the natural source of stratospheric nitrogen oxides, and its effect on ozone probably would be exceedingly small.

### *Chlorofluorocarbons*

After my 1971 articles on stratospheric ozone appeared, I was invited to many places to give a seminar on the subject. I varied the talks as CIAP

produced new data, but I always discussed the global ozone balance, the dominance of  $\text{NO}_x$  in the natural destruction of stratospheric ozone, nitrous oxide source of stratospheric  $\text{NO}_x$ , and the fact that a large fleet of SSTs would release nitrogen oxides into the stratosphere at about the same rate as the natural  $\text{NO}_x$  production, which was about one megaton per year. Sherwood Rowland heard my seminar on the global ozone balance and SSTs at Irvine, California, early in 1972, at Lake Arrowhead, California, in the spring of 1973, and at Irvine again in the fall of 1973. I apologized to Rowland for his having to sit through my talk for three times, and he accepted this imposition in good spirits.

When I gave my seminar at the University of California at Riverside in November 1973, Norman Hester called my attention to his recent measurements in the atmosphere of chlorinated hydrocarbons and of chlorofluorinated methanes. He gave me several reprints of articles that he and others had published in 1973, which I read with interest, especially J. E. Lovelock's article in the January 19 *Nature*, from which I give a brief quotation:

During the past few decades the production of the chlorofluorocarbons, the propellant solvents for aerosol dispensers, has grown exponentially. R. L. McCarthy (unpublished) estimates that the integrated production of  $\text{CCl}_2\text{F}_2$  and of  $\text{CFCl}_3$  . . . was about one megaton each in mid-1971; they are unusually stable chemically and only slightly soluble in water and might therefore persist and accumulate in the atmosphere. . . . The presence of these compounds constitutes no conceivable hazard. . . .

In late December 1973, Rowland telephoned to say that he and Mario Molina seemed to find that chlorofluoromethanes building up in the atmosphere might reduce stratospheric ozone by 20–40%. He asked if I had heard of anyone proposing this idea. I had not. He and Molina came to Berkeley a day or two later to see if I could find any flaws in their logic or facts. I found that their set of chlorine reactions and rate constants was incomplete and gave them a photocopy of the first-draft, hand-written review of chlorine reactions, just completed by Robert Watson, then a postdoctoral fellow working with me on the CIAP project. We discussed the parallels between the CFC/ $\text{Cl}_x$  system and the nitrous oxide/ $\text{NO}_x$  system, with which they were quite familiar. I found no flaws in their logic, as they had built a tight case with the following components:

1. Lovelock's and others' measurements of CFCs in the atmosphere.
2. The production rate of CFCs from the chemical industry.
3. Spectroscopic and chemical data measured in laboratories and critically compiled in tables.
4. Their computer calculation, which used a one-dimensional eddy

diffusion model to find the altitude at which CFCs would be broken down by far ultraviolet radiation.

5. Comparison of the CFC/chlorine system with the strikingly similar  $\text{N}_2\text{O}/\text{NO}_x$  system, for which CIAP had provided recent experimental verification.

They wrote their paper during the first week of January, sent me a pre-print, and sent the article to *Nature*, which published the article in June 1974.

The hand-in-glove analogies between the  $\text{NO}_x$  and the  $\text{Cl}_x$  systems are shown in Figure 1. Throughout 1973, I showed the left-hand panel in the seminars I gave. In 1974, I added the right-hand panel. There is one outstanding difference between the two systems: Hydroxyl radicals react with active nitrogen dioxide to form inert nitric acid; hydroxyl radicals react with inert hydrogen chloride to release active atomic chlorine. The two systems are strongly and oppositely affected by processes that determine the atmospheric concentrations of hydroxyl radicals.

The article in *Nature* made little impression on the press, the general public, the scientific public, or government officials. At a meeting of the American Chemical Society in Atlantic City on September 11, 1974, Molina and Rowland presented their findings in person, were explicit about the damage that might be done, and held a hard-hitting press conference in support of their work.

Some members of the Congress asked the NAS for a statement on this question. I was one of five members of a NAS panel that met on October 26, 1974, to comment on this development. Another panel member and I developed and pushed the following argument: "This problem was unanticipated by everyone. The chemical industry has manufactured and marketed a nontoxic, nonflammable, useful substance. The chemical industry is entitled to a couple of years, first to learn about the stratospheric problem and recent CIAP progress in this field, and second to see if they can find a serious flaw in the theory, such as now unknown stratospheric reservoirs for  $\text{Cl}_x$  or unknown tropospheric sinks for CFCs." By mid-afternoon we had reached a consensus and composed a one-page report, including the following recommendation:

The National Academy of Sciences and National Research Council, without now accepting or rejecting Rowland and Molina's overall case, should inform the general public that the concern is a legitimate one, should advise scientists to try to confirm or disprove the case as soon as possible, and should advise the Congress to begin now to understand the problem and its implications.

Two things happened to prevent our report and recommendations from ever being released: First, one member of the panel unwisely talked to

newspaper reporters, from which came the headline, "Halt urged in buying spray cans that might hurt ozone," and representatives of the chemical industry sent powerful objections to NAS. Second, the November issue of *Aerosol Age* did not address the scientific issues that had been raised, but slandered the scientists who raised them: "... sensationalized and premature announcements by some members of the scientific community ... some computer jockeys take their giant machines and feed into them material designed to prove a preconceived idea ... was designed more to get newspaper space than to solve a potential problem."

For the next few years, the industry took the initiative in polarizing the situation and, typically, misrepresented the contents of a scientific article and ridiculed the misrepresented portion. In its official *Letter to Members*, Volume 7, Number 1, November 1976, the NAS repudiated DuPont's response to a NAS report of September 13, 1976: "The action was unworthy of a great institution that has long been a major contributor to chemical research and to sound technological progress."

In Congressional hearings on December 12, 1974, Raymond L. McCarthy, technical manager and laboratory director for the Freon Products Division of E. I. DuPont de Nemours & Co. repeatedly stated, "In fact, there is no experimental evidence supporting the chlorine-ozone theory." I heard him make essentially the same statement on May 15, 1975. In response to these categorical assertions of "no experimental evidence," I, somewhat later, posed for the photograph at the beginning of this review, where I stacked documents produced since 1971 concerning stratospheric ozone and its vulnerability to human perturbation.

## CURRENTLY PROPOSED SUPERSONIC AIRCRAFT

At present, there is new interest in building large fleets of supersonic passenger aircraft. The Upper Atmosphere Research Program of NASA is the leading agency in this country for stratospheric research. NASA has a High-Speed Research Program (HSRP), which is concerned with many aspects of commercial supersonic aircraft, now called High Speed Civil Transports (HSCT). The High-Speed Research Program supervises a program on the Atmospheric Effects of Stratospheric Aircraft, which is establishing a base of scientific information about the impact of aircraft emissions on the atmosphere. In 1990, HSRP became a funding agency for a six-year research program. "Recent NASA-sponsored studies show that, with sufficient technology development, future high-speed civil transports can be economically competitive with long-haul subsonic aircraft" (6).

Starting in 1987, my graduate student, Doug Kinnison, and I joined forces with Don Wuebbles at Lawrence Livermore National Laboratory

(LLNL) to make the first broad modeling study since 1979 of the atmospheric effects of a large fleet of supersonic aircraft. Our article was published in November 1989 (7). We carried out 260 calculations by using the LLNL one-dimensional model and 16 calculations by using the LLNL two-dimensional model. We covered large variations of  $\text{NO}_x$  injection rate, flight altitude, stratospheric chlorine, water vapor, and methane. Where the SST-added  $\text{NO}_x$  is  $24 \times 10^{33}$  molecules  $\text{NO}_x$  per year, except as noted, we found the following results with the two-dimensional model:

Flight at 37–49°N Altitude/km	Calculated percent ozone change		
	Global	N.H.	S.H.
15–18	–0.7	–0.9	–0.4
18–21	–7.6	–10.4	–5.9
21–24	–8.6	–13.1	–3.9
24–27	–9.6	–15.6	–3.5
27–30	–10.1	–16.4	–3.5
30–33	–9.8	–16.0	–3.4
33–36	–9.2	–14.9	–3.2
21–24 one third $\text{NO}_x$	–2.8	–4.3	–1.2
21–24 threefold $\text{NO}_x$	–19	–28	–6.7

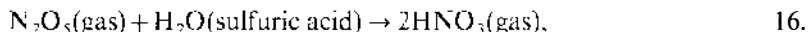
15.

If 500 supersonic aircraft were equipped with jet engines that used 1990 technology, the  $\text{NO}_x$  emissions would correspond with the last entry in the chart above, with a calculated 19% global ozone reduction. If the engines are redesigned to achieve a factor of nine less  $\text{NO}_x$  than that expected from 1990 technology, the next-to-last entry in the chart applies, and 2.8% global ozone reduction is calculated. If engine technology achieves a threefold reduction of  $\text{NO}_x$ , the first seven entries apply. The calculated ozone reduction depends strongly on the flight altitude, and the maximum ozone reduction occurs at 27–30 km flight altitude. There is a factor of ten difference in calculated ozone reduction, depending on whether flight occurs at 15–18 km or 18–21 km. Commercial subsonic aircraft cruise up to about 12 km, and the LLNL one-dimensional model predicts a 0.4% global ozone increase from the standard  $\text{NO}_x$  injection at 12 km; this increase is caused by the methane- $\text{NO}_x$  smog reactions. For supersonic flight, the Mach number and flight altitude are closely coupled:  $M = 1.6$ ,  $z = 14$ –17 km;  $M = 2.4$ ,  $z = 17$ –20 km;  $M = 3.2$ ,  $z = 21$ –24 km. Two options for HSCT planners are to accept lower Mach numbers, which goes with lower cruise altitudes and lower calculated ozone reductions, and to redesign jet engines so that they emit less  $\text{NO}_x$ .

We presented this material to NASA in Washington on December 1988, almost a year before it was published. NASA made constructive use

of this material, as they formulated their program and considered their options.

The most dramatic event in the history of ozone is the appearance of the seasonal Antarctic ozone hole, which was first reported in 1985. It has been conclusively shown to be caused by active chlorine species, Cl and ClO, but not by the Cl/O<sub>3</sub>/ClO/O catalytic cycle (Figure 1 and Equation 14) proposed in connection with the space shuttle and by Molina and Rowland. The new feature is heterogeneous chemistry, which occurs on ice crystals and on nitric acid-trihydrate crystals. One important reaction is the conversion of inactive chlorine nitrate and inactive HCl on ice to active Cl<sub>2</sub>(gas) plus HNO<sub>3</sub>(adsorbed). It has been proposed that additional NO<sub>x</sub> from aircraft might increase this conversion, and the released chlorine radical might then additionally reduce ozone. On the other hand, model results (8) published in 1991 have shown that another heterogeneous reaction



which occurs on the worldwide stratospheric sulfuric acid aerosols, results in a calculated ozone increase by a large fleet of HSCT operating at altitudes between 17 and 20 km. Other heterogeneous reactions on the sulfuric acid aerosols have been proposed, but the sign of their effects is not known. Heterogeneous chemistry in the stratosphere will be an active and interesting subject during the next few years. (See Refs. 9 and 10 for general information on recent activities in this field.)

## CONCLUSIONS

When new scientific developments impinge on society, business, and politics, mechanisms other than the scientific method come into play. Sometimes it works this way: Scientist A publishes an article. Interest group B, with or without distorting the article, uses it to advance its cause and makes demands that conflict with the interests of group C. Group C hastily attacks A's person and motives. Both C and A feel outraged. Typically, neither B nor C understands the science of the original article. On the other hand, when X files a lawsuit against Y and newspaper reporters ask Y for comment, the usual answer is, "No comment until I have studied their suit." Surely this is a better model for C to follow when A's science is used as a weapon by B. However, if one person assumes the role of both A and B, that person is in politics already. In the long run, application of the scientific method found that space shuttles do not harm ozone and that chlorofluorocarbons caused the Antarctic ozone hole, regardless of politics on both sides of both issues. As far as stratospheric ozone and



aircraft are concerned, the scientific method may or may not find conditions under which it is safe to fly a large fleet of SSTs.

#### ACKNOWLEDGMENT

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