

# MY LIFE WITH O<sub>3</sub>, NO, AND OTHER YZO<sub>x,s</sub>

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by

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*To the generation of Jamie Paul and our future grandchildren, who will know so much more and who will celebrate the disappearance of the ozone hole. I hope you will not be disappointed with us.*

I was born in Amsterdam on December, 3, 1933, the son of Anna Gurk and Jozef Crutzen. I have one sister who still lives in Amsterdam with her family. My mother's parents moved to the industrial Ruhr region in Germany from East Prussia towards the end of the last century. They were of mixed German and Polish origin. In 1929 at the age of 17, my mother moved to Amsterdam to work as a housekeeper. There she met my father. He came from Vaals, a little town in the southeastern corner of the Netherlands, bordering Belgium and Germany and very close to the historical German city of Aachen. He died in 1977. He had relatives in the Netherlands, Germany and Belgium. Thus, from both parents I inherited a cosmopolitan view of the world. My mother, now 84 years old, still lives in Amsterdam, mentally very alert, but since a few months ago, wheelchair-bound. Despite having worked in several countries outside The Netherlands since 1958, I have remained a Dutch citizen.

In May, 1940, The Netherlands were overrun by the German army. In September of the same year I entered elementary school, "de grote school" (the big school), as it was popularly called. My six years of elementary school largely overlapped with the 2nd World War. Our school class had to move between different premises in Amsterdam after the German army had confiscated our original school building. The last months of the war, between the fall of 1944 and Liberation Day on May, 5, 1945, were particularly horrible. During the cold "hongerwinter" (winter of famine) of 1944-1945, there was a severe lack of food and heating fuels. Also water for drinking, cooking and washing was available only in limited quantities for a few hours per day, causing poor hygienic conditions. Many died of hunger and disease, including several of my schoolmates. Some relief came at the beginning of 1945 when the Swedish Red Cross dropped food supplies on parachutes from airplanes. To welcome them we waved our red, white and blue Dutch flags in the streets. I had of course not the slightest idea how important Sweden would become later in my life. We only had a few hours of school

each week, but because of special help from one of the teachers, I was allowed together with two other schoolmates to continue to the next and final class of elementary school; unfortunately, all the others lost a year. More or less normal school education only became possible again with the start of the new school year in the fall of 1945.

In 1946, after a successful entrance exam, I entered the "Hogere Burgerschool" (HBS), "Higher Citizen School", a 5 year long middle school, which prepared for University entrance. I finished this school in June, 1951, with natural sciences as my focal subjects. However, we all also had to become proficient in 3 foreign languages: French, English and German. I got considerable help in learning languages from my parents: German from my mother, French from my father. During those years, chemistry definitely was not one of my favourite subjects. They were mathematics and physics, but I also did very well in the three foreign languages. During my school years I spent considerable time with a variety of sports: football, bicycling, and my greatest passion, long distance skating on the Dutch canals and lakes. I also played chess, which in the Netherlands is ranked as a "denksport" (thought sport). I read widely about travels in distant lands, about astronomy, as well as about bridges and tunnels. Unfortunately, because of a heavy fever, my grades in the final exam of the HBS were not good enough to qualify for a university study stipend, which was very hard to obtain at that time, only 6 years after the end of the 2nd world war and a few years after the end of colonial war in Indonesia, which had been a large drain on Dutch resources. As I did not want to be a further financial burden on my parents for another 4 years or more (my father, a waiter, was often unemployed; my mother worked in the kitchen of a hospital), I chose to attend the Middelbare Technische School (MTS), middle technical school, now called the higher technical school (HTS), to train as a civil engineer. Although the MTS took 3 years, the second year was a practical year during which I earned a modest salary, enough to live on for about 2 years. From the summer of 1954 until February, 1958, with a 21-month interruption for compulsory military service in The Netherlands, I worked at the Bridge Construction Bureau of the City of Amsterdam. In the meanwhile, on a vacation trip in Switzerland, I met a sweet girl, Terttu Soininen, a student of Finnish history and literature at the University of Helsinki. A few years later I was able to entice her to marry me. What a great choice I made! She has been the center of a happy family; without her support, I would never have been able to devote so much of my time to studies and science. After our marriage in February, 1958, we settled in Gävle, a little town about 200 km north of Stockholm, where I had found a job in a building construction bureau. In December of that same year our daughter Ilona was born. In March, 1964, she got a little sister, Sylvia. Ilona is a registered nurse, now living in Boulder, Colorado. Her son Jamie Paul is 12 years old. Sylvia is a 'marketing assistant in München, Germany. All were present in Stockholm, Upsala and Gävle during the Nobel week. We had a happy and unforgettable time.

All this time I had longed for an academic career. One day, at the beginning of 1958, I saw an advertisement in a Swedish newspaper from the Department of Meteorology of Stockholm Högskola (from 1961, Stockholm University) announcing an opening for a computer programmer. Although I had not the slightest experience in this subject, I applied for the job and had the great luck to be chosen from among many candidates. On July 1, 1959, we moved to Stockholm and I started with my second profession. At that time the Meteorology Institute of Stockholm University (MISU) and the associated International Meteorological Institute (IMI) were at the forefront of meteorological research and many top researchers worked in Stockholm for extended periods. Only about a year earlier the founder of the institutes, Prof. Gustav Rossby, one of the greatest meteorologists ever, had died suddenly and was succeeded by Dr. Bert Bolin, another famous meteorologist, now "retired" as director of the Intergovernmental Panel on Climate Change (IPCC). At that time Stockholm University housed the fastest computers in the world (BESK and its successor FACIT).

With the exception of participation in a field campaign in northern Sweden, led by Dr. Georg Witt to measure the properties of noctilucent clouds, which appear during summer at about 85 km altitude in the coldest parts of atmosphere, and some programming work related to this, I was until about 1966 mainly involved in various meteorological projects, especially helping to build and run some of the first numerical (barotropic) weather prediction models. I also programmed a model of a tropical cyclone for a good friend, Hilding Sundquist, now a professor at MISU. At that time programming was a special art. Advanced general computer languages, such as Algol or Fortran, had not been developed, so that all programmes had to be written in specific machine code. One also had to make sure that all operations yielded numbers in the range  $-1 \leq x < 1$ , which meant that one had to scale all equations to stay within these limits; otherwise the computations would yield wrong results.

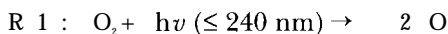
The great advantage of being at a university department was that I got the opportunity to follow some of the lecture courses that were offered at the university. By 1963 I could thus fulfill the requirement for the filosofie kandidat (corresponding to a Master of Science) degree, combining the subjects mathematics, mathematical statistics, and meteorology. Unfortunately; I could include neither physics nor chemistry in my formal education, because this would have required my participation in time consuming laboratory exercises. In this way I became a pure theoretician. I have, however, always felt close to experimental work, which I have strongly supported during my later years as director of research at the National Center of Atmospheric Research (NCAR) in Boulder, Colorado (1977-1980) and at the Max-Planck-Institute for Chemistry in Mainz, Germany (since 1980).

Being employed at the meteorological research institute, it was quite natural to take a meteorological topic for my filosofie licentiat thesis (comparable to a Ph.D. thesis). Building on my earlier experience further develop-

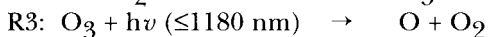
ment of a numerical model of a tropical cyclone had been proposed to me. However, around 1965 I was given the task of helping a scientist from the U.S. to develop a numerical model of the oxygen allotrope distribution in the stratosphere, mesosphere and lower thermosphere. This project got me highly interested in the photochemistry of atmospheric ozone and I started an intensive study of the scientific literature. This gave me an understanding of the status of scientific knowledge about stratospheric chemistry by the latter half of the 1960's, thus setting the "initial conditions" for my scientific career. Instead of the initially proposed research project, I preferred research on stratospheric chemistry, which was generously accepted. At that time the main topics of research at the Meteorological Institute at the University of Stockholm were dynamics, cloud physics, the carbon cycle, studies of the chemical composition of rainwater, and especially the "acid rain" problem which was largely "discovered" at MISU through the work of Svante Oden and Erik Eriksson. Several researchers at MISU, among them Prof. Bolin and my good friend and fellow student Henning Rodhe, now Professor in Chemical Meteorology at MISU, got heavily involved in the issue which drew considerable political interest at the first United Nation Conference on the Environment in Stockholm in 1972 (1). However, I wanted to do pure science related to natural processes and therefore I picked stratospheric ozone as my subject, without the slightest anticipation of what lay ahead. In this choice of research topic I was left totally free. I can not overstate how I value the generosity and confidence which were conveyed to me by my supervisors Prof. Georg Witt, an expert on the aeronomy of the upper atmosphere, and the head of MISU Prof. Bert Bolin. They were always extremely helpful and showed great interest in the progress of my research.

## STRATOSPHERIC OZONE CHEMISTRY

As early as 1930 the famous British scientist Sydney Chapman [2] had proposed that the formation of "odd oxygen",  $O_x = O + O_3$ , is due to photolysis of  $O_2$  by solar radiation at wavelengths shorter than 240 nm



Rapid reactions, R2 and R3, next lead to the establishment of a steady state relationship between the concentrations of O and  $O_3$



without affecting the concentration of odd oxygen. Destruction of odd oxygen, counteracting its production by reaction R1, occurs via the reaction



Until about the middle of the 1960's it was generally believed that reactions R1-R4 sufficed to explain the ozone concentration distribution in the stratosphere. However, by the mid 1960's, especially following a study by Benson and Axworthy (3), it became clear that reaction R4 is much too slow to balance the production of "odd oxygen" by reaction R1 (see Figure 1). In 1950 David Bates and Marcel Nicolet (4), together with Sydney Chapman the great pioneers of upper atmospheric photochemistry research, proposed

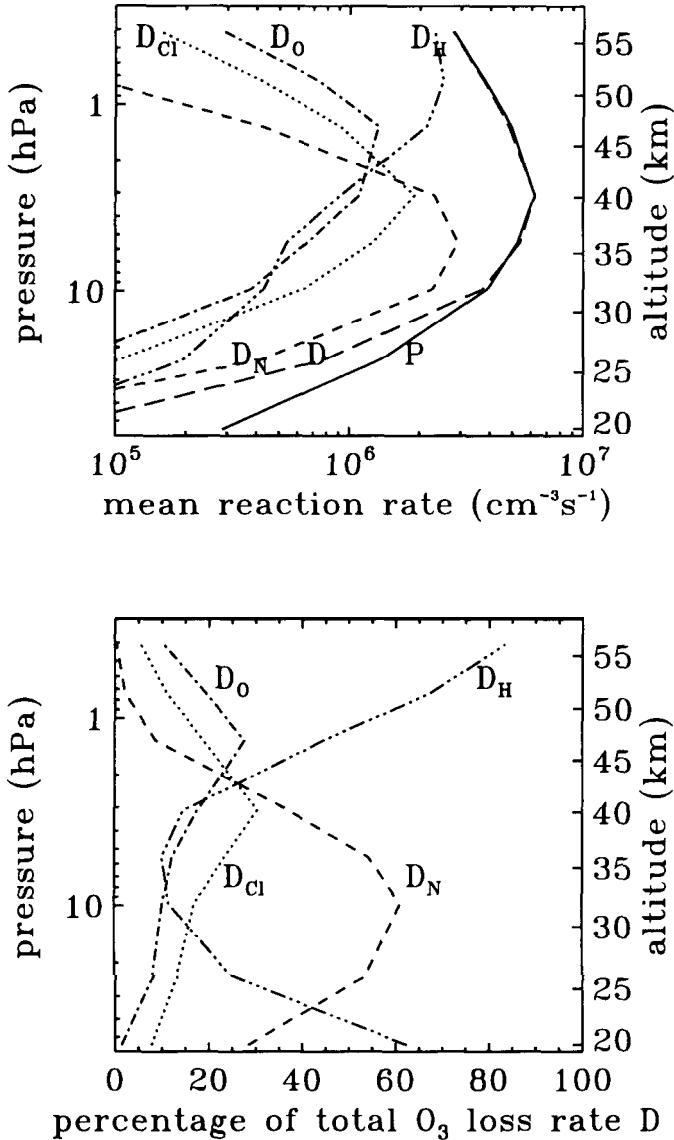
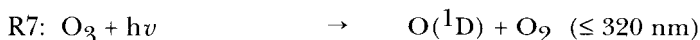


Figure 1: Ozone production and destruction rates, including absolute and relative contributions by the Chapman reaction R4 ( $D_{\text{O}}$ ),  $\text{NO}_x$  catalysis R11 + R12 ( $D_{\text{N}}$ ),  $\text{NO}_x$  catalysis R5 + R6 ( $D_{\text{H}}$ ) and  $\text{ClO}_x$  catalysis R21 + R22 ( $D_{\text{Cl}}$ ), (120). The calculations neglect the heterogeneous halogen activation which become very important below 25 km under cold conditions.

that catalytic reactions involving OH and HO<sub>2</sub> radicals could counterbalance the production of odd oxygen in the mesosphere and thermosphere. Building on their work and on laboratory studies conducted by one of the 1967 Nobel Prize Laureates in Chemistry, Prof. R. Norrish of Cambridge University and his coworkers (5, 6), the ozone destruction reaction pair (R5, R6) involving OH and HO<sub>2</sub> radicals as catalysts were postulated by Hampson (7) and incorporated in an atmospheric chemical model by Hunt (8):



The proposed primary source for the OH radicals was photolysis of O<sub>3</sub> by solar ultraviolet radiation of wavelengths shorter than about 320 nm, leading to electronically excited O(<sup>1</sup>D) atoms,



a small fraction of which reacts with water vapour



Most O(<sup>1</sup>D) reacts with O<sub>2</sub> and N<sub>2</sub> to rapidly reproduce O<sub>3</sub>, leading to a null cycle with no effect on ozone or odd oxygen



In the absence of laboratory measurements for the rate constants of reactions R5 and R6, and in order for these reactions to counterbalance the production of odd oxygen by reaction R1, Hunt adopted the rate constants

$$\begin{array}{l} k_5 = 5 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \\ k_6 = 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}. \end{array}$$

In my filosofie licentiat thesis of 1968 I analyzed the proposal by Hampson and Hunt and concluded that the rate constants for reactions R5 and R6 which they had chosen could not explain the vertical distribution of ozone in the photochemically dominated stratosphere above 25 km. Furthermore, I pointed out (9) that the above choice of rate constants would also lead to unrealistically rapid loss of ozone (on a timescale of only a few days) in the troposphere. Anticipating a possible role of OH in tropospheric chemistry, in the same study I also briefly mentioned the potential importance of a reaction between OH with CH<sub>4</sub>. We now know that reactions R5 and R6 proceed about 25 and 10 times slower, respectively, than postulated by Hunt and

Hampson and that the  $\text{CH}_4$  oxidation cycle plays a very large role in tropospheric chemistry, a topic to which we will return.

Regarding stratospheric ozone chemistry, I discarded the theory of Hampson and Hunt and concluded: "... at least part of the solution of the problem of the ozone distribution might be the introduction of photochemical processes other than those treated here. The influence of nitrogen compounds on the photochemistry of the ozone layer should be investigated".

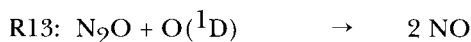
Unfortunately no measurements of stratospheric  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) were available to confirm my thoughts about their potential role in stratospheric chemistry. By the summer of 1969 I had joined the Department of Atmospheric Physics at the Clarendon Laboratory of Oxford University as a postdoctoral fellow of the European Space Research Organization and stayed there for a two year period. The head of the research group, Dr. (now Sir) John Houghton, hearing of my idea on the potential role of  $\text{NO}_x$ , handed me a solar spectrum, taken on board a balloon by Dr. David Murcray and coworkers of the University of Denver, and indicated to me that it might reveal the presence of  $\text{HNO}_3$  (10). After some analysis I could derive the approximate amounts of stratospheric  $\text{HNO}_3$ , including a rough idea of its vertical distributions. I did not get the opportunity to write up the result, because at about the same time, Rhine et al (11) published a paper, showing a vertical  $\text{HNO}_3$  column density of  $2.8 \times 10^{-4} \text{ atm.cm}$  ( $\approx 7.6 \times 10^{15} \text{ molecules cm}^{-2}$ ) above 18.8 km. With this information I knew that  $\text{NO}_x$  should also be present in the stratosphere as a result of the reactions,



This gave me enough confidence to submit my paper (12) on catalytic ozone destruction by  $\text{NO}$  and  $\text{NO}_2$ , based on the simple catalytic set of reactions:



The net result of reactions R11 and R12 is equivalent to the direct reaction R4. However, the rate of the net reaction can be greatly enhanced by relatively small quantities of  $\text{NO}_x$  on the order of a few nanomole/mole (or ppbv). I also included a calculation of the vertical distribution of stratospheric  $\text{HNO}_3$ . As the source of stratospheric  $\text{NO}_x$ , I initially accepted the proposal by Bates and Hays (13) that about 20% of the photolysis of  $\text{N}_2\text{O}$  would yield  $\text{N}$  and  $\text{NO}$ . Subsequent work showed that this reaction does not take place. However, it was soon shown that  $\text{NO}$  could also be formed to a lesser extent, but still in significant quantities, via the oxidation of nitrous oxide ( $\text{N}_2\text{O}$ )



(14-16). It was further shown by Davis et al. (17) that reaction R12 proceeds about 3.5 times faster than I had originally assumed based on earlier laboratory work. Later it was also shown that earlier estimates of  $\text{O}_3$  production by reactions R1 and R2 had been too large due to overestimations of both the absorption cross sections of molecular oxygen (18) and solar intensities in the ozone producing 200-240 nm wavelength region (19, 20). As a result of these developments it became clear that enough NO is produced via reaction R13 to make reactions R11 and R12 the most important ozone loss reactions in the stratosphere in the altitude region between about 25 and 45 km.

$\text{N}_2\text{O}$  is a natural product of microbiological processes in soils and waters. A number of anthropogenic activities, such as the application of nitrogen fertilizers in agriculture, also lead to significant  $\text{N}_2\text{O}$  emissions. The rate of increase in atmospheric  $\text{N}_2\text{O}$  concentrations for the past decades has been about 0.3% per year (21). That, however, was not known in 1971. The discovery of the indirect role of a primarily biospheric product on the chemistry of the ozone layer has greatly stimulated interest in bringing biologists and atmospheric scientists together. Other examples of such biosphere-stratosphere interactions are  $\text{CH}_4$  and OCS.

#### MAN'S IMPACT ON STRATOSPHERIC OZONE

In the fall of 1970, still in Oxford, I obtained a preprint of a MIT sponsored Study on Critical Environmental Problems (SCEP) which was held in July of that year (22). This report also considered the potential impact of the introduction of large stratospheric fleets of supersonic aircraft (U.S.: Boeing; Britain/France: Concorde; Soviet Union: Tupolev) and gave me the first quantitative information on the stratospheric inputs of  $\text{NO}_x$  which would result from these operations. By comparing these with the production of  $\text{NO}_x$  by reaction R13, I realized immediately that we could be faced with a severe global environmental problem. Although the paper in which I proposed the important catalytic role of  $\text{NO}_x$  on ozone destruction had already been published in April, 1970, clearly the participants in the study conference had not taken any note of it, since they concluded "The direct role of CO,  $\text{CO}_2$ , NO,  $\text{NO}_2$ ,  $\text{SO}_2$ , and hydrocarbons in altering the heat budget is small. It is also unlikely that their involvement in ozone photochemistry is as significant as water vapour". I was quite upset by that statement. Somewhere in the margin of this text I wrote "Idiots".

After it became quite clear to me that I had stumbled on a hot topic, I decided to extend my 1970 study by treating in much more detail the chemistry of the oxides of nitrogen ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$ ), hydrogen ( $\text{OH}$ ,  $\text{HO}_2$ ), and  $\text{HNO}_3$ , partially building on a literature review by Nicolet (23). I soon got into big difficulties. In the first place, adopting Nicolet's reaction scheme I calculated high concentrations of  $\text{N}_2\text{O}_4$ , a problem which



I could soon resolve when I realized that this compound is thermally unstable, a fact which was not considered by Nicolet. A greater headache was caused by the supposedly gas phase reactions



and



for which the only laboratory studies available at that time had yielded rather high rate coefficients:  $k_{14} = 1.7 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  and  $k_{15} = 1.7 \cdot 10^{-17} \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  at room temperatures. A combination of reactions R14 and R15 with these rate constants would provide a very large source of OH radicals, about a thousand times larger than supplied by reaction R8, leading to prohibitively rapid catalytic ozone loss. This was a terribly nervous period for me. At that time no critical reviews and recommendations of rate coefficients were available. With no formal background in chemistry, I basically had to compile and comprehend much of the needed chemistry by myself from the available publications, although I profited greatly from discussions with colleagues at the University of Oxford, especially Dr. Richard Wayne of the Physical Chemistry Laboratory, a former student of Prof. R. Norrish in Cambridge. I discussed all these difficulties and produced extensive model calculations on the vertical distributions of trace gases in the  $\text{O}_x\text{-NO}_x\text{-HO}_x\text{-HNO}_x$  system in a paper which was submitted by the end of 1970 to the *Journal of Geophysical Research* (received January 13, 1971) and which, after revision, was finally published in the October 20 issue of 1971 (15). The publication of this paper was much delayed because of an extended mail strike in Britain. Because of the major problems I had encountered, I did not make any calculations of ozone depletions, but instead drew attention to the potential seriousness of the problem by stating "An artificial increase of the mixing ratio of the oxides of nitrogen in the stratosphere by about  $1 \times 10^8$  may lead to observable changes in the atmospheric ozone level" and further in the text "It is estimated that global nitrogen oxide mixing ratios may increase by almost  $10^8$  from a fleet of 500 SSTs in the stratosphere. Larger increases, up to  $7 \times 10^8$ , are possible in regions of high traffic densities .... Clearly, serious decreases in the total atmospheric ozone level and changes in the vertical distributions of ozone, at least in certain regions, can result from such an activity..."

#### THE SUPERSONIC TRANSPORT CONTROVERSY IN THE U.S.

Unknown to me, a debate on the potential environmental impact of supersonic stratospheric transport (SST) had erupted in the U.S. Initially the concern was mainly enhanced catalytic ozone destruction by OH and  $\text{HO}_2$  radi-

cals resulting from the release of H<sub>2</sub>O in the engine exhausts (24). By mid-March, 1971, a workshop was organized in Boulder, Colorado, by an Advisory Board of the Department of Commerce, to which Prof. Harold Johnston of the University of California, Berkeley, was invited. As an expert in laboratory kinetics and reaction mechanisms of NO<sub>x</sub> compounds (e.g. 25-27), he immediately realized that the role of NO<sub>x</sub> in reducing stratospheric ozone had been grossly underestimated. Very quickly (submission 14 April, revision 14 June) on August 6, 1971, his paper appeared in *Science* (27) with the title "Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from Supersonic Transport Exhaust". In the abstract of this paper Johnston stated "... oxides of nitrogen from SST exhaust pose a much greater threat to the ozone layer than does the increase in water. The projected increase in stratospheric oxides of nitrogen could reduce the ozone shield by about a factor of 2, thus permitting the harsh radiation below 300 nanometers to permeate the lower atmosphere". During the summer of 1971, I received a preprint of Johnston's study via a representative of British Aerospace, one of the Concorde manufacturers. This was the first time I had heard of Harold Johnston, for whom I quickly developed a great respect both as a scientist and a human being. Although I had expressed myself rather modestly about the potential impact of stratospheric NO<sub>x</sub> emissions from SST's, for the reasons given above, I fully agreed with Prof. Johnston on the potential severe consequences for stratospheric ozone and I was really happy to have support for my own ideas from such an eminent scientist. For a thorough resume of the controversies between scientists and industry, and between meteorologists and chemists, recurring themes also in later years, I refer to Johnston's article "Atmospheric Ozone" (28). It should also be mentioned here that Prof. Johnston's publications in the early 1970's removed several of the major reaction kinetic problems which I had encountered in my 1971 study (15). It was shown, for instance, that neither reaction R14 nor R15 occur to a significant degree in the gas phase, and that the earlier laboratory studies had been strongly influenced by reactions on the walls of the reaction vessels (29), an advice which was earlier also given to me in a private communication by Prof. Sydney Benson of the University of Southern California.

In July, 1971, I returned to the University of Stockholm and devoted myself mainly to studies concerning the impact of NO<sub>x</sub> releases from SST's on stratospheric ozone. In May, 1973, I submitted my inaugural dissertation "On the Photochemistry of Ozone in the Stratosphere and Troposphere and Pollution of the Stratosphere by High-Flying Aircraft" to the Faculty of Natural Sciences and was awarded the degree of Doctor of Philosophy with the highest possible distinction, the third time this had ever happened during the history of Stockholm University (and earlier Stockholm "Högskola"). This was one of the last occasions in which the classical and rather solemn "Filosofie Doktor", similar to the Habilitation in Germany and France, was awarded. I had to dress up just like during the Nobel Ceremonies. First and second "opponents" were Dr. John Houghton and Dr.

Richard Wayne of the University of Oxford, who wore their college gowns for the occasion. Dr. Wayne also served as a most capable, not obligatory, third opponent, whose task it was to make a fool of the candidate. Unfortunately, the classical doctoral degree has been abolished (I was one of the last ones to go through the procedure). The modern Swedish Filosofie Doktor degree corresponds more closely to the former Filosofie Licentiat degree.

In large part as a result of the proposal by Johnston (27) that  $\text{NO}_x$  emissions from SST's could severely harm the ozone layer, major research programs were started, the Climate Impact Assessment Program (CLAP), organized by the U.S. Department of Transportation (30), and the COVOS/COMESA (31, 32) program, jointly sponsored by France and Great Britain (the producers of the Concorde Aircraft). The aim of these programs was to study the chemical and meteorological processes that determine the abundance and distribution of ozone in the stratosphere, about which so little was known that the stratosphere was sometimes dubbed the "ignorosphere". The outcome of the CIAP study was summarized in a publication by the U.S. National Academy of Sciences in 1975 (33). "We recommend that national and international regulatory authorities be alerted to the existence of potentially serious problems arising from growth of future fleets of stratospheric airlines, both subsonic and supersonic. The most clearly established problem is a potential reduction of ozone in the stratosphere, leading to an increase in biologically harmful ultraviolet light at ground level".

The proposed large fleets of SST's never materialized, largely for economic reasons; only a few Concorde's are currently in operation. The CLAP and COVOS/COMESA research program, however, greatly enhanced knowledge about stratospheric chemistry. They confirmed the catalytic role of  $\text{NO}_x$  in stratospheric ozone chemistry. A convincing example of this was provided by a major solar proton event which occurred in August, 1972 and during which, within a few hours, large quantities of NO, comparable to the normal  $\text{NO}_x$  content, were produced at high geomagnetic latitudes ( $> 65^\circ$ ), as shown in Figure 2. With such a large input of NO, a clear depletion of stratospheric ozone was expected (34), a hypothesis which was confirmed by

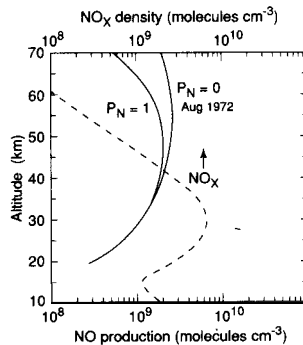


Figure 2: Production of NO at high geomagnetic latitudes during the solar proton event of 1972 for two assumptions about the electronic states of the N atoms formed ( $P_N = 0$ , or 1). Also shown are the average  $\text{NO}_x$  concentrations for these locations.

analysis of satellite observations (35). Figure 3 shows results of the calculated and observed ozone depletions, the former obtained with a model which also considered chlorine chemistry (36).

Although I had started my scientific career with the ambition to do basic research related to natural processes, the experiences of the early 1970's had made it utterly clear to me that human activities had grown so much that they could compete and interfere with natural processes. Since then this has been an important factor in my research efforts. Already by the end of 1971 I wrote in an article published in the "The Future of Science Year Book" of the USSR in 1972:

"... the upper atmosphere is an important part of our environment. Let us finish by expressing a sincere hope that in the future environmental dangers

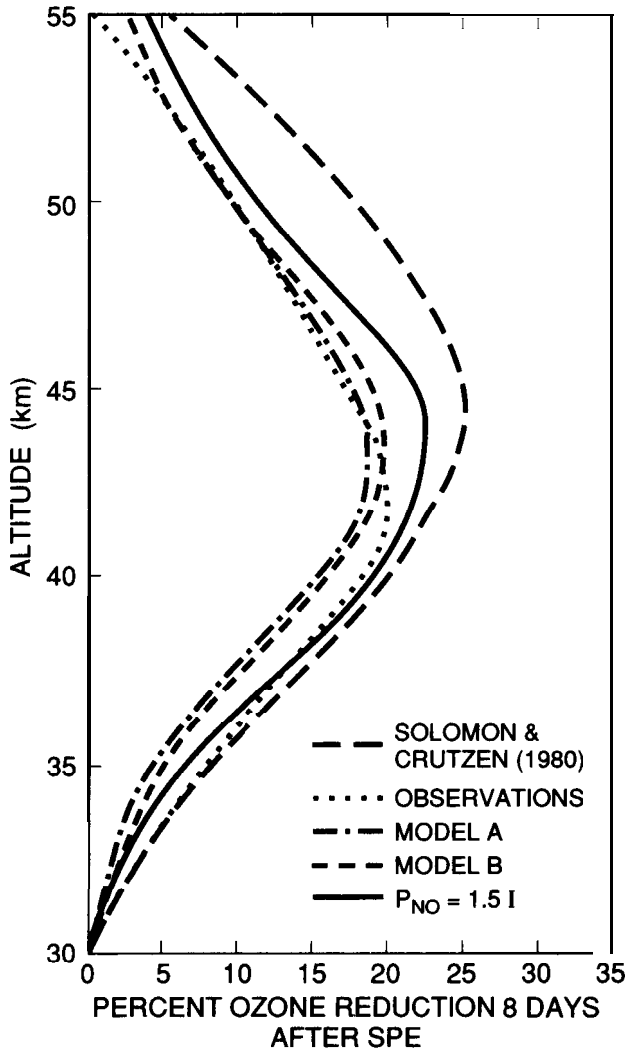


Figure 3: Observed and calculated percentage ozone depletions resulting from the 1972 solar proton event. The various calculated curves correspond to assumed values of parameters that were not well known.

of new technological development will be recognizable at an early stage. The proposed supersonic air transport is an example of a potential threat to the environment by future human activities. Other serious problems will certainly arise in the increasingly complicated world of tomorrow".

### *Tropospheric Ozone*

My first thoughts on tropospheric ozone photochemistry go back to 1968, as discussed briefly above (9). However, in the following 3 years, my research was largely devoted to stratospheric ozone chemistry. Then in 1971 a very important paper with the title "Normal Atmosphere: Large Radical and Formaldehyde Concentrations Predicted" was published by Hiram Levy III, then of the Smithsonian Astrophysical Observatory in Cambridge, Massachusetts (37). Levy proposed that OH radicals could also be produced in the troposphere by the action of solar ultraviolet radiation on ozone (Reaction R8), and that they are responsible for the oxidation of CH<sub>4</sub> and CO, an idea which was also quickly adopted by Jack McConnell, Michael McElroy and Steve Wofsy (38) of Harvard University. The recognition of the important role of OH was a major step forward in our understanding of atmospheric chemistry. Despite very low atmospheric concentrations, currently estimated at 10<sup>6</sup> molecules/cm<sup>3</sup>, corresponding to a mean tropospheric volume mixing ratio of 4 x 10<sup>-14</sup> (39), it is this ultramajor constituent - and not the 10<sup>13</sup> times more abundant O<sub>3</sub> - which is responsible for the oxidation of almost all compounds that are emitted into the atmosphere by natural processes and anthropogenic activities. The lifetimes of most atmospheric gases are, therefore, largely determined by the concentrations of OH and the corresponding reaction coefficients (40) (see Table 1). Those gases

**Table 1:** Schematic representation of importance of OH radicals in atmospheric chemistry.

#### PRIMARY PRODUCTION OF OH RADICALS



GLOBAL, 24 HOUR, AVERAGE (OH) = 10<sup>6</sup> MOLECULES/CM<sup>3</sup>

MOLAR MIXING RATIO IN TROPOSPHERE ≈ 4 x 10<sup>-14</sup>

#### REACTION WITH OH DETERMINES THE LIFETIME OF MOST GASES IN ATMOSPHERE

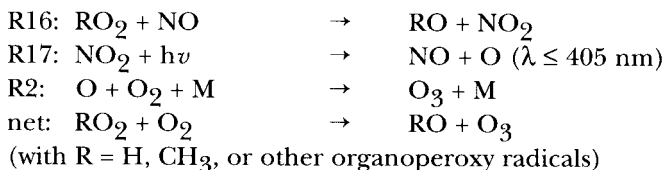
##### EXAMPLES:

|                                    |           |
|------------------------------------|-----------|
| CH <sub>4</sub> :                  | 8 YEARS   |
| C <sub>2</sub> H <sub>6</sub> :    | 2 MONTHS  |
| C <sub>3</sub> H <sub>8</sub> :    | 10 DAYS   |
| C <sub>5</sub> H <sub>8</sub> :    | HOURS     |
| (CH <sub>3</sub> ) <sub>2</sub> S: | 2-3 DAYS  |
| CH <sub>3</sub> Cl:                | ≈ 1 YEAR  |
| CH <sub>3</sub> CCl <sub>3</sub> : | ≈ 5 YEARS |
| NO <sub>2</sub> :                  | ≈ 1 DAY   |

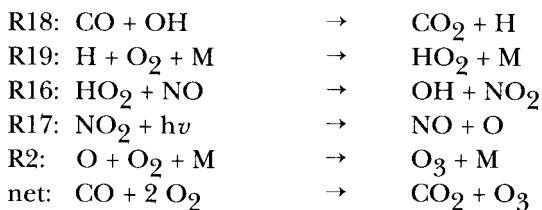
CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>, N<sub>2</sub>O do not react with OH. They are broken down in the stratosphere and have a large influence on ozone chemistry.

that do not react with OH have very long atmospheric residence times and are largely destroyed in the stratosphere. Examples of the latter class of compounds are  $N_2O$ , and several fully halogenated, industrial organic compounds, such as  $CFCl_3$ ,  $CF_2Cl_2$ , and  $CCl_4$ . These play a major role in stratospheric ozone chemistry, an issue to which we will return.

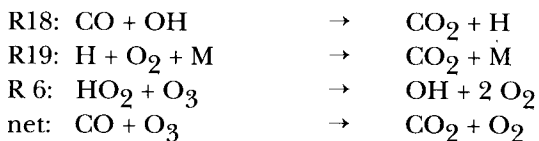
Following Levy's paper my attention returned strongly to tropospheric chemistry. Starting with a presentation at the 1972 International Ozone Symposium in Davos, Switzerland, I proposed that *in situ* chemical processes could produce or destroy ozone in quantities larger than the estimated downward flux of ozone from the stratosphere to the troposphere (41, 42). Destruction of ozone occurs via reactions R7 + R8 and R5 + R6. Ozone production takes place in environments containing sufficient  $NO_x$ , via



The catalytic role of NO in atmospheric chemistry is, therefore, twofold. At altitudes above about 25 km, where O atom concentrations are high, ozone destruction by reactions R11 + R12 dominates over ozone production by reactions R16 + R17 + R2. The latter chain of reactions is at the base of all photochemical ozone formation in the troposphere, including that taking place during photochemical smog episodes, originally discovered in southern California, as discussed by Johnston (28). Such reactions can, however, also take place in background air with ubiquitous CO and  $CH_4$ , serving as fuels: in the case of CO oxidation



This reaction chain requires the presence of sufficient concentrations of NO. At low NO volume mixing ratios, below about 10 pmole/mole ( $p = \text{pico} = 10^{-15}$ ), oxidation of CO may lead to ozone destruction since the  $HO_2$  radical then reacts mostly with  $O_3$ :



In a similar way, the oxidation of  $\text{CH}_4$  in the presence of sufficient  $\text{NO}_x$  will lead to tropospheric ozone production.

Besides reacting with  $\text{NO}$  or  $\text{O}_3$ ,  $\text{HO}_2$  can also react with itself



to produce  $\text{H}_2\text{O}_2$  which serves as a strong oxidizer of S (IV) compounds in cloud and rain water.

My talk at the International Ozone Symposium was not well received by some members of the scientific establishment of that time. However, in the following years, the idea gradually received increased support. In particular, Bill Chameides and Jim Walker (43), then of Yale University, took it up and went as far as proposing that even the diurnal variation of lower tropospheric ozone could be explained largely by *in situ* photochemical processes. Although I did not agree with their hypothesis ( $\text{CH}_4$  and  $\text{CO}$  oxidation rates are just not rapid enough), it was good to note that my idea was being taken seriously. (I should immediately add that especially Bill Chameides in subsequent years added much to our knowledge of tropospheric ozone). A couple of years later, together with two of my finest students, Jack Fishman and Susan Solomon, we presented observational evidence for a strong *in situ* tropospheric ozone chemistry (44, 45). Laboratory measurements by Howard and Evenson (46) next showed that reaction R16 proceeded about 40 times faster than determined earlier, strongly promoting ozone production and increased OH concentrations with major consequences for tropospheric and stratospheric chemistry (47). A consequence of faster rate of this reaction is a reduction in the estimated ozone depletions by stratospheric aircraft as the ozone production reactions  $\text{R16} + \text{R17} + \text{R2}$  are favoured over the destruction reaction R6. Furthermore, a faster reaction R16 leads to enhanced OH concentrations and thus a faster conversion of reactive  $\text{NO}_x$  to far less reactive  $\text{HNO}_3$ . Table 2 summarizes a recent ozone budget calculated with a

**Table 2:** Tropospheric ozone budgets, globally and for the northern (NH) and southern (SH) hemisphere in  $10^{13}$  mole/year. Only  $\text{CH}_4$  and  $\text{CO}$  oxidation cycles were considered. Calculations were made with the latest version of the global, three-dimensional MOGUNTIA model (48).

|   | Global | NH  | SH  |
|---|--------|-----|-----|
| Sources   |        |     |     |
| $\text{HO}_2 + \text{NO}$                               | 6.5    | 4.1 | 2.4 |
| $\text{CH}_3\text{O}_2 + \text{NO}$                     | 1.7    | 1.0 | 0.7 |
| Transport from stratosphere                             | 1.0    | 0.7 | 0.3 |
| Sinks   |        |     |     |
| $\text{O}(^1\text{D}) + \text{H}_2\text{O}$             | 3.8    | 2.2 | 1.6 |
| $\text{HO}_2 + \text{O}_3$ and $\text{OH} + \text{O}_3$ | 2.8    | 1.8 | 1.0 |
| Deposition on surface                                   | 2.7    | 1.8 | 0.9 |
| Net chemical source                                     | 1.6    | 1.1 | 0.5 |

three-dimensional chemistry transport model of the troposphere. The results clearly show the dominance of *in situ* tropospheric ozone production and destruction. With the same model, estimates were also made of the present and pre-industrial ozone concentration distributions. The calculations, shown in Figures 4 and 5, indicate a clear increase in tropospheric ozone

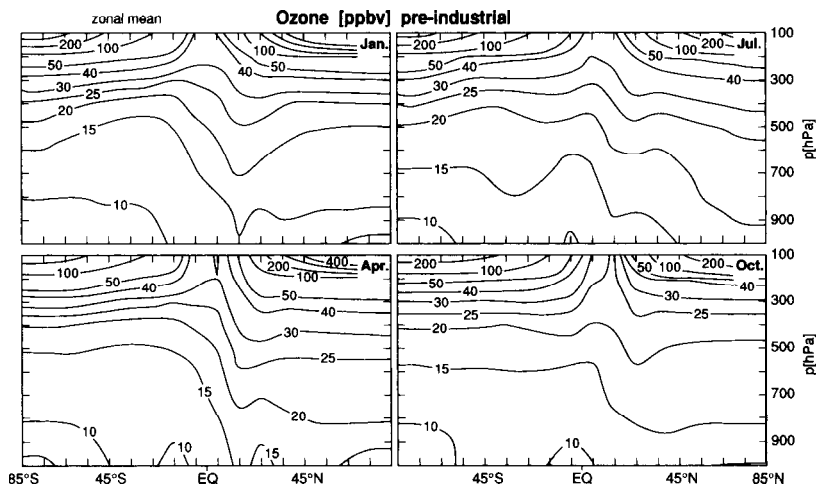


Figure 4: Calculated zonal average ozone volume mixing ratios in units of nanomole/mole (or ppbv) for the pre-industrial era (nano =  $10^{-9}$ ) for different months.

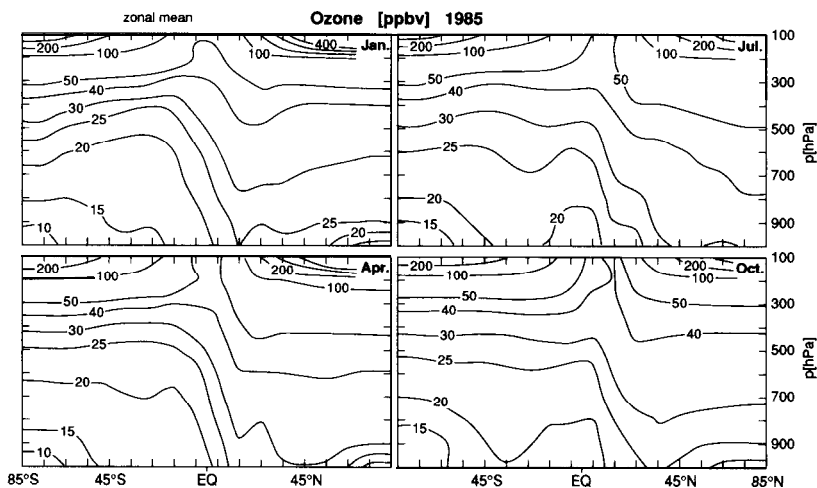


Figure 5: Same as figure 4, but for mid-1980's.

concentrations over the past centuries (48). In Figure 6 we also show the meridional cross sections of zonal average ozone, as compiled by Jack Fishman (unpublished data).

With the same model we have also calculated the OH concentration distributions for pre-industrial and present conditions. Since pre-industrial times,  $\text{CH}_4$  volume mixing ratios in the atmosphere has increased (49) from



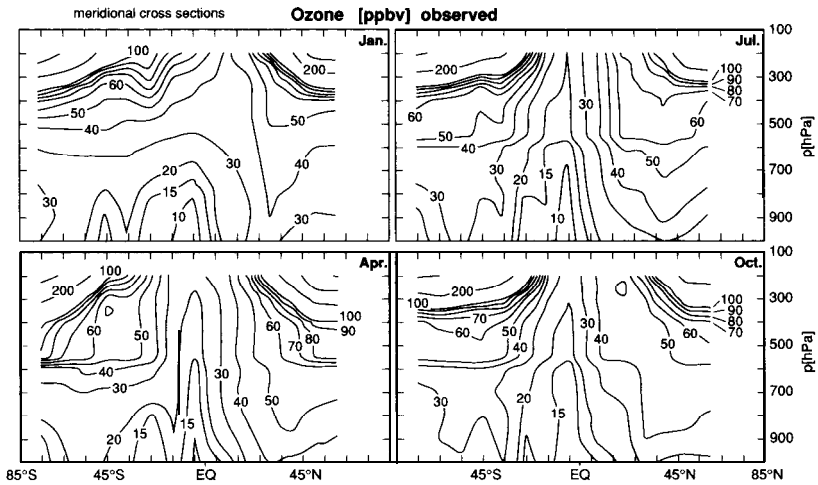


Figure 6: Compilation of observed ozone distributions prior to 1989, compiled by Jack Fishman of NASA Langley Research Center. It should be mentioned that the data base is very limited and has not much improved for the tropics and subtropics.

about 0.7 to 1.7 ppmv ( $1 \text{ ppmv} = 10^{-6} \text{ volume/volume}$ ). Because reaction with  $\text{CH}_4$  is one of the main sinks for OH, an increase in  $\text{CH}_4$  should have led to a decrease in OH concentrations. On the other hand, increased ozone concentrations, leading to enhanced OH production by reactions R7 + R8, and the effect of the reactions,



and



both stimulated by strongly enhanced anthropogenic NO production, should have worked in the opposite direction. Figures 7 and 8 show calculated zonally and diurnally averaged, meridional distributions of the OH con-

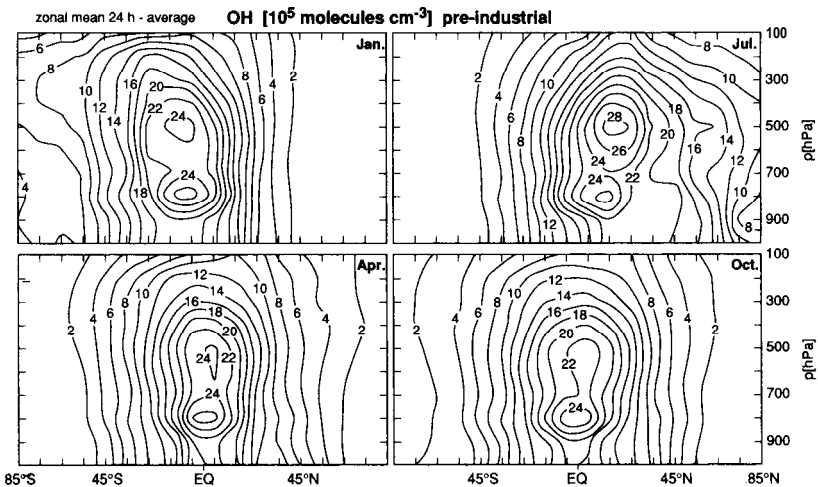


Figure 7: Calculated zonal and 24-hour average OH concentrations in units of  $10^5 \text{ molecules/cm}^3$  for the pre-industrial period for January, April, July and October.

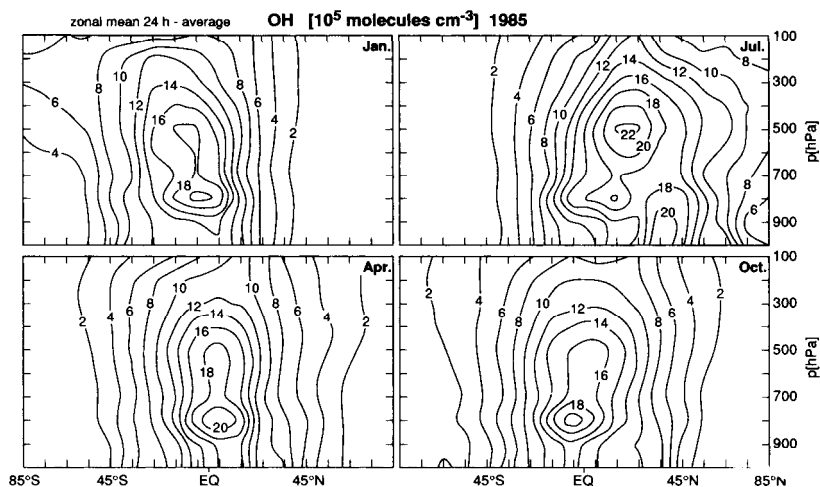


Figure 8: Same as figure 7 for 1985.

centrations, both for the pre-industrial and industrial periods. They indicate:

- a) strong maxima of OH concentrations in the tropics, largely due to high intensities of ultraviolet radiation as a consequence of a minimum vertical ozone column. Consequently the atmospheric oxidation efficiency is strongly determined by tropical processes. For instance, most  $\text{CH}_4$  and CO is removed from the atmosphere by reaction with OH in the tropics.
- b) the possibility of a significant decline in OH concentrations from pre-industrial to industrial conditions.

The results presented in Figure 8 are of great importance, as they allow estimations of the sink of atmospheric  $\text{CH}_4$  by reaction with OH. Prior to the discovery of the fundamental role of the OH radical (37), estimates of the sources and sinks of trace gases were largely based on guess work without a sound scientific basis. As shown in Table 3, this recognition has led to very large changes in the budget estimates of  $\text{CH}_4$  and CO. "Authoritative" estimates of the  $\text{CH}_4$  budget of 1968 (no reference will be given) gave much higher values for  $\text{CH}_4$  releases from natural wetlands. With such a dominance of natural sources, it would have been impossible to explain the annual increase in atmospheric  $\text{CH}_4$  concentrations by almost 1% per year. Early estimates of CO sources, on the other hand, were much too low.

The dominance of OH concentrations and the high biological productivity in the tropics clearly points at the great importance of the tropics and subtropics in atmospheric chemistry. Despite this fact, research on low latitude chemistry is much neglected, such that we do not even have satisfactory statistics on the ozone distribution in this part of the world. Tropical chemistry is a topic which has played and will continue to play a large role in my research. Contrary to what was commonly believed prior to the early 1980's, the chemical composition of the tropical and subtropical atmosphere is substan-

Table 3: Estimated budgets of important atmospheric trace gases made in 1968 and at present.

DMS denotes dimethylsulfide

|  | 1968                       | 1995                    |
|--|----------------------------|-------------------------|
| <b>CH<sub>4</sub> BUDGET (Tg/year)</b>   |                            |                         |
| Natural wetlands                         | 1180                       | 275                     |
| Anthropogenic                            | <u>270</u>                 | <u>265</u>              |
|  | 1450                       | 540                     |
| <b>CO BUDGET (Tg/year)</b>               |                            |                         |
| Natural                                  | 75                         | 860                     |
| Anthropogenic                            | <u>274</u>                 | <u>1640</u>             |
|  | 350                        | 2500                    |
| <b>S BUDGET (Tg S/year)</b>              |                            |                         |
| Pollutants                               | 76                         | 78                      |
| Oceanic emissions                        | 30 (H <sub>2</sub> S)      | 25 (DMS)                |
| Land emissions                           | <u>70 (H<sub>2</sub>S)</u> | few (various compounds) |
|  | 176                        | 105                     |
| <b>NO<sub>x</sub> BUDGET (Tg N/year)</b> |                            |                         |
| Biological                               | 150                        | 10                      |
| Pollution                                | 15                         | 24                      |
| Lightning                                | <u>-</u>                   | <u>2-10</u>             |
|  | 165                        | 36-44                   |
| <b>N<sub>2</sub>O BUDGET (Tg N/year)</b> |                            |                         |
| Biological                               | 340                        | 15                      |
| Anthropogenic                            | <u>-</u>                   | <u>3.5</u>              |
|  | 340                        | 18.5                    |

tially affected by human activities, in particular biomass burning which takes place during the dry season. The high temporal and spatial variability of ozone in the tropics is shown in figure 9. Highest ozone concentrations are

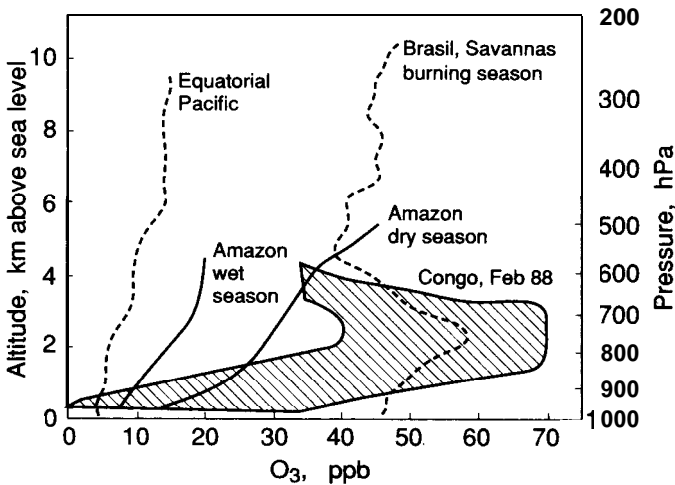


Figure 9: Variability of ozone profiles in the tropics, including contrast between dry and wet season, and continents versus marine soundings.

observed over the polluted regions of the continents during the dry season, lowest values in the clean air over the Pacific. I will return to the topic of tropical tropospheric ozone, but will first review the stormy developments in stratospheric ozone depletion by halogen compounds that started in 1974.

#### POLLUTION OF THE STRATOSPHERE BY ClO<sub>x</sub>

Towards the end of the CIAP programme some researchers had turned their interest to the potential input of reactive chlorine radicals on stratospheric ozone. In the most thorough of these studies, Stolarski and Cicerone (50) calculated significant ozone depletions if inorganic chlorine were to be present in the stratosphere at a volume mixing ratio of 10<sup>-9</sup> mole/mole of air (1 nanomole/mole). Odd oxygen destruction would take place via the catalytic reaction cycle



This reaction sequence is very similar to the catalytic NO<sub>x</sub> cycle R11 + R12 introduced before. The study by Stolarski and Cicerone, first presented at a conference in Kyoto, Japan, in the fall of 1973, mainly considered volcanic injections as a potential source of Cl<sub>x</sub> (their initial interest in chlorine chemistry was, however, concerned with the impact of the exhaust of solid rocket fuels of the space shuttle). Two other conference papers (51, 52), also dealt with ClO<sub>x</sub> chemistry. All three papers struggled, however, with the problem of a missing chlorine source in the stratosphere (research over the past 20 years has shown that the volcanic source is rather insignificant).

In the fall of 1973 and early 1974 I spent some time looking for potential anthropogenic sources of chlorine in the stratosphere. Initially my main interest was with DDT and other pesticides. Then by the beginning of 1974 I read a paper by James Lovelock and coworkers (53) who reported atmospheric measurements of CFC<sub>1</sub><sub>3</sub> (50 picomole/mole) and CFC<sub>1</sub><sub>2</sub> (71 pmole/mole) over the Atlantic. (Such measurements had been made possible by Lovelock's invention of the electron capture detector for gas chromatographic analysis, a major advance in the environmental sciences). Lovelock's paper gave me the first estimates of the industrial production rates of CFC<sub>1</sub><sub>2</sub> and CFC<sub>1</sub><sub>3</sub>. It also stated that these compounds "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". This statement had just aroused my curiosity about the fate of these compounds in the atmosphere when a preprint of a paper by M.J. Molina, and F.S. Rowland with the title "Stratospheric Sink for Chlorofluoromethanes - Chlorine Atom Catalyzed Destruction of Ozone" was sent to me by the authors. I knew immediately that this was a very important paper and decided to mention it briefly during

a presentation on stratospheric ozone to which I had been invited by the Royal Swedish Academy of Sciences in Stockholm. What I did not know was that the press was likewise invited to the lecture. To my great surprise, within a few days, an article appeared in the Swedish newspaper "Svenska Dagbladet". This article quickly attracted wide international attention and soon I was visited by representatives of the German chemical company Hoechst and also by Professor Rowland, who at that time was spending a sabbatical year at the Atomic Energy Agency in Vienna. This was the first time I had heard of Molina or Rowland, which is not surprising as they had not been active in studies on the chemistry of the atmosphere. Needless to say, I remained highly interested in the topic and by September, 1974, about 2 months after the publication of Molina's and Rowland's paper (54) I presented a model analysis of the potential ozone depletion resulting from continued use of the chlorofluorocarbons (CFC's) (55) which indicated the possibility of up to about 40% ozone depletion near 40 km altitude as a result of continued use of these compounds at 1974 rates. Almost simultaneously, Cicerone et al. (56) published a paper in which they predicted that by 1985-1990, continued use of CFCs at early 1970's levels could lead to  $\text{ClO}_x$  catalyzed ozone destruction of a similar magnitude as the natural sinks of ozone. Following Molina's and Rowland's proposal, research on stratospheric chemistry further intensified, now with the emphasis on chlorine compounds.

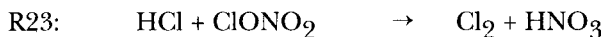
By the summer of 1974, together with my family, I moved to Boulder, Colorado, where I assumed two halftime positions, one as a consultant at the Aeronomy Laboratory of the National Oceanic and Atmospheric Administration (NOAA), the other at the Upper Atmosphere Project of the National Center for Atmospheric Research (NCAR). The NOAA group, which under the able direction of Dr. Eldon Ferguson had become the world leading group in the area of laboratory studies of ion-molecule reactions, had just decided to direct their considerable experimental skills to studies of stratospheric chemistry. My task was to guide them in that direction. I still feel proud to have been part of a most remarkable transformation. Together with Eldon Ferguson, scientists like Dan Albritton, Art Schmeltekopf, Fred Fehsenfeld, Paul Goldan, Carl Howard, George Reid, John Noxon, and Dieter Kley rapidly made major contributions to stratospheric research, including such activities as air sampling with balloon borne evacuated cans, so-called "salad bowls" for later gas-chromatographic analysis, optical measurements of the vertical abundances and distributions of  $\text{NO}_2$  and  $\text{NO}_3$  (later expanded by Susan Solomon to  $\text{BrO}$  and  $\text{OCIO}$ ), the design and operation of an instrument to measure extremely low water vapour mixing ratios, and laboratory simulations of important, but previously poorly known rate coefficients of important reactions. In later years the NOAA group also devoted itself to studies of tropospheric chemistry, reaching a prominent position in this research area as well. At NCAR the emphasis was more on infrared spectrographic measurements by John Gille and Bill Mankin, work

which also developed into satellite-borne experiments. Another prominent activity was the analysis of the vertical distributions of less reactive gases, such as  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ , and the CFC's, employing the cryogenic sampling technique which had been pioneered by Ed Martell and Dieter Ehhalt.

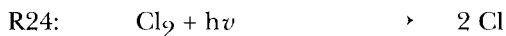
In 1977, I took up the directorship of the Air Quality Division of NCAR, my first partially administrative position. I continued, however, my scientific work, something which many thought would be impossible. Fortunately, in Nelder Medrud I had a highly competent administrative officer. In my position as director I promoted work on both stratospheric and tropospheric chemistry. My own research was mostly devoted to the development of photochemical models, conducted mostly with my students Jack Fishman, Susan Solomon and Bob Chatfield. Together with Pat Zimmerman we started studies on atmosphere-biosphere interactions, especially the release of hydrocarbons from vegetation and pollutant emissions due to biomass burning in the tropics. I also tried to strengthen interactions between atmospheric chemists and meteorologists to improve the interpretation of the chemical measurements obtained during various field campaigns. To get this interdisciplinary research going was a challenge, particularly in those days.

During this period, as part of various US and international activities, much of my research remained centered on the issue of anthropogenic, chlorine-catalyzed ozone destruction. However, because I am sure that this topic will be covered extensively by my two fellow recipients of this year's Nobel Prize, I would like to make a jump to the year 1985, when Joe Farman and his colleagues (57) of the British Antarctic Survey published their remarkable set of October total ozone column measurements from the Halley Bay station, showing a rapid depletion on the average by more than 3% per year, starting from the latter half of the 1970's. Although their explanation ( $\text{ClO}_x/\text{NO}_x$  interactions) was wrong, Farman et al. (57) correctly suspected a connection with the continued increase in stratospheric chlorine (nowadays more than 5 times higher than natural levels). Their display of the downward trend of ozone, matching the upward trend of the chlorofluorocarbons (with the appropriate scaling) was indeed highly suggestive.

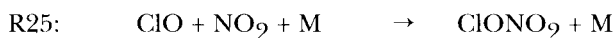
The discovery of the ozone hole came during a period in which I was heavily involved in various international studies on the potential environmental impacts of a major nuclear war between the NATO and Warsaw Pact nations, an issue to which I will briefly return in one of the following chapters. Because so many researchers became quickly involved in the "ozone hole" research, initially I stayed out of it. Then, in early 1986 I attended a scientific workshop in Boulder, Colorado, which brought me up-to-date with the various theories which had been proposed to explain the ozone hole phenomenon. Although it turned out that some of the hypotheses had elements of the truth, in particular the idea put forward by Solomon et al. (58) of chlorine activation on the surface of stratospheric ice particles, via the reaction,



followed by rapid photolysis of Cl<sub>2</sub> and production of highly reactive Cl atoms



I felt dissatisfied with the treatment of the heterogeneous chemistry. On my flight back to Germany (I hardly sleep on trans-Atlantic flights), I had good time to think it over and suddenly realized that if HNO<sub>3</sub> and NO<sub>x</sub> were removed from the gas phase into the particulate phase, then an important defense against the attack of ClO<sub>x</sub> on O<sub>3</sub> would be removed. The thought goes as follows. Under normal stratospheric conditions, there are strong interactions between the NO<sub>x</sub> and ClO<sub>x</sub> radicals which lead to protection of ozone from otherwise much more severe destruction. Important examples of these are the reactions,



and the pair of reactions,



producing HCl and ClONO<sub>2</sub>, which do not react with O or O<sub>3</sub>. Due to these reactions, under normal stratospheric conditions most of the inorganic chlorine is present as HCl and ClONO<sub>2</sub>. Like two mafia families, the ClO<sub>x</sub> and NO<sub>x</sub> thus fight each other, to the advantage of ozone. As shown in Figure 10, there are plenty of complex interactions between the OX, HX,

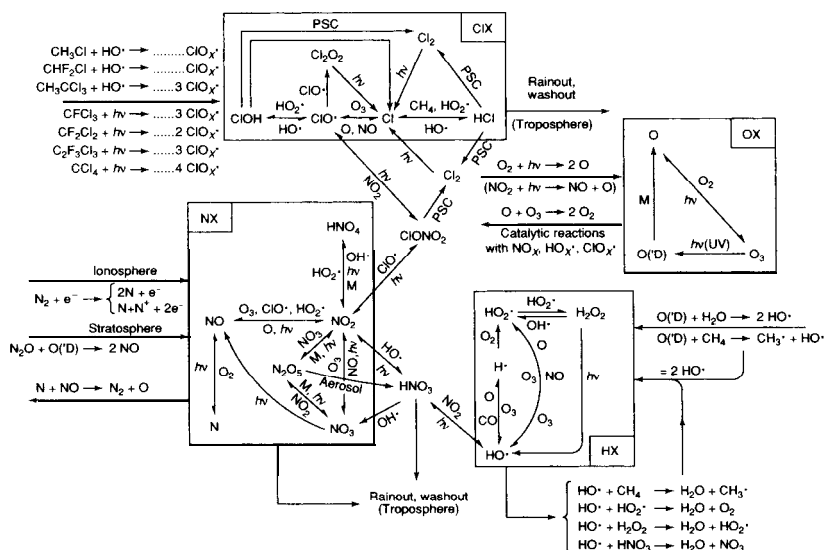
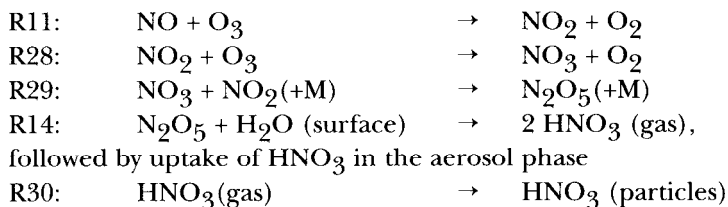
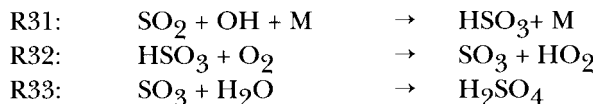


Figure 10: Schematic presentation of the chemical interactions in the stratosphere. At the start of my scientific career only the OX and some of the HX reactions had been taken into account. Note that OX stands for the odd oxygen compounds, HX for H, OH, HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>; NX for N, NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub> and HNO<sub>4</sub>; and CIX for all inorganic chlorine compounds, Cl, ClO, Cl<sub>2</sub>O<sub>2</sub>, ClONO<sub>2</sub>, HCl, ClOCl and Cl<sub>2</sub>. Not included are the bromine compounds which likewise play a significant role in stratospheric ozone depletion.

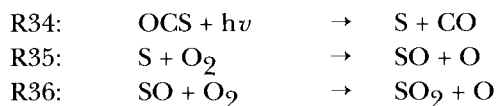
NX and ClX families. (We should even have included BrX). Now, if the NX compounds were removed from the gas phase, then reactions R25-R27 would not occur and most inorganic chlorine would be available in the activated, ozone destroying forms. A possible scenario would involve conversion of  $\text{NO}_x + \text{HNO}_3$ , via the nighttime reactions



As noted before, reaction R14 does not occur in the gas phase, but it readily occurs on wetted particulate surfaces. These are always present in the lower stratosphere in the form of sulfate particles, a fact which was first discovered by Christian Junge, a pioneer in atmospheric chemistry and my predecessor as director at the Max-Planck-Institute of Chemistry in Mainz (59). The sulfate particles are formed by nucleation of gas phase  $\text{H}_2\text{SO}_4$ , which is formed from  $\text{SO}_2$ , following attack by OH (60, 61)



The sources of stratospheric  $\text{SO}_2$  are either direct injections by volcanic explosions (59) or oxidation of OCS, produced at the earth's surface (62) via

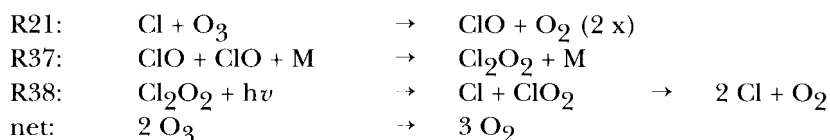


The possibility of  $\text{HNO}_3$  formation via heterogeneous reactions on sulfate particles was already considered in a 1975 paper which I co-authored with Richard Cadle and Dieter Ehhalt (63). Based on laboratory experiments, this reaction was, however, for a long while thought to be unimportant, until it was discovered that the original laboratory measurements were grossly incorrect and that reaction R14 readily occurs on  $\text{H}_2\text{O}$  containing surfaces (64-66). (Earlier tropospheric measurements had already indicated this (67)). The introduction of reaction R14 leads to a significant conversion of reactive  $\text{NO}_x$  to much less reactive  $\text{HNO}_3$  thus diminishing the role of  $\text{NO}_x$  in ozone chemistry, especially in the lower stratosphere. By including reaction R14, better agreement is obtained between theory and observations



(68). The experience with reaction R14 and earlier discussed reactions R6, R14 and R15, emphasizes the importance of high quality measurements.

As soon as I had returned to Mainz, I contacted Dr. Frank Arnold of the Max-Planck-Institute for Nuclear Physics in Heidelberg to explain to him my idea about NO<sub>x</sub> removal from the gas phase. After about a week he had shown that under stratospheric conditions, solid nitric acid trihydrate (NAT) particles could be formed at temperatures below about 200K, that is a temperature about 10 K higher than that needed for water ice particle formation. The paper about our findings was published in Nature at the end of 1986 (69). Independently, the idea had also been developed by Brian Toon, Rich Turco and coworkers (70). Subsequent laboratory investigations, notably by David Hanson and Konrad Mauersberger (71) then of the University of Minnesota, provided accurate information on the thermodynamic properties of NAT. It was next also shown that the NAT particles could provide excellent surfaces to catalyze the production of ClO<sub>x</sub> by reactions R23 and R24 (72, 73). Finally, Molina and Molina (74) proposed a powerful catalytic reaction cycle, involving ClO-dimer formation,



completing the chain of events causing rapid ozone depletion under cold, sunlit stratospheric conditions. Note that reaction R37 implies an ozone depletion response which is proportional to the square of the ClO concentrations. Furthermore, as chlorine activation by reaction R23 is also non-linearly dependent on the stratospheric chlorine content, a powerful non-linear, positive feedback system is created, which is responsible for the accelerating loss of ozone under "ozone hole" conditions. The "ozone hole" is a drastic example of a man-made chemical instability, which developed at a location most remote from the industrial releases of the chemicals responsible for the effect.

The general validity of the chain of events leading to chlorine activation has been confirmed by both ground based (75,76) and airborne in-situ (77) radical observations. Especially the latter, performed by James Anderson and his students of Harvard University, have been very illuminating, showing large enhancements in ClO concentrations in the cold, polar region of the lower stratosphere, coincident with a rapid decline in ozone concentrations. Together with other observations this confirms the correctness of the ozone depletion theory as outlined above. In the meanwhile the seriousness of this global problem has been recognized by all nations of the world and international agreements have been signed to halt the production of CFC's and halons from this year on. Although the cause-effect relationship is very clear, for the layperson as well, it is depressing to see that it is, nevertheless, not accepted by a small group of very vocal critics without any record of achieve-

ments in this area of research. Some of these have recently even succeeded in becoming members of the U.S. Congress.

#### AND THINGS COULD HAVE BEEN MUCH WORSE

Gradually, over a period of a century or so, stratospheric ozone should recover. However, it was a close call. Had Joe Farman and his colleagues from the British Antarctic Survey not persevered in making their measurements in the harsh Antarctic environment for all those years since the International Geophysical Year 1958/1959, the discovery of the ozone hole may have been substantially delayed and there may have been far less urgency to reach international agreement on the phasing out of CFC production. There might thus have been a substantial risk that an ozone hole could also have developed in the higher latitudes of the northern hemisphere.

Furthermore, while the establishment of an instability in the  $O_3$ - $ClO_x$  system requires chlorine activation by heterogeneous reactions on solid or supercooled liquid particles, this is not required for inorganic bromine, which is normally largely present in its activated forms due to gas phase photochemical reactions. This makes bromine on an atom to atom basis almost a hundred times more dangerous for ozone than chlorine (78, 52). This brings up the nightmarish thought that if the chemical industry had developed organobromine compounds instead of the CFCs - or alternatively, if chlorine chemistry would have run more like that of bromine - then without any preparedness, we would have been faced with a catastrophic ozone hole everywhere and at all seasons during the 1970s, probably before the atmospheric chemists had developed the necessary knowledge to identify the problem and the appropriate techniques for the necessary critical measurements. Noting that nobody had given any thought to the atmospheric consequences of the release of Cl or Br before 1974, I can only conclude that mankind has been extremely lucky, that Cl activation can only occur under very special circumstances. This shows that we should always be on our guard for the potential consequences of the release of new products into the environment. Continued surveillance of the composition of the stratosphere, therefore, remains a matter of high priority for many years ahead.

In the meanwhile, we know that freezing of  $H_2SO_4$ - $HNO_3$ - $H_2O$  mixtures to give NAT particle formation does not always occur and that supercooled liquid droplets can exist in the stratosphere substantially below NAT nucleation temperatures, down to the ice freezing temperatures (79). This can have great significance for chlorine activation (80, 81). This issue, and its implications for heterogeneous processes, have been under intensive investigation at a number of laboratories, especially in the U.S., notably by the groups headed by A.R. Ravishankara at the Aeronomy Laboratory of NOAA, Margaret Tolbert at the University of Colorado, Mario Molina at MIT, Doug Worsnop and Chuck Kolb at Aerodyne, Boston, and Dave Golden at Stanford Research Institute in Palo Alto. I am very happy that a team of young collea-











prising behaviour are not known. They may consist of a combination of: (i) variable annual emissions from biomass burning, (ii) higher concentrations of OH radicals, maybe due to loss of stratospheric ozone, triggered by an increase in reactive aerosol surfaces in the stratosphere following the Pinatubo volcanic eruption in June, 1991, (iii) a dynamically forced global redistribution of CO, introducing a bias due to the location of the limited number of measuring sites, (iv) reduced CO formation from the oxidation of natural hydrocarbons emitted by tropical forests due to globally altered precipitation and temperature patterns, or, most likely, a combination of these plus other, yet unknown factors. At this stage we can only conclude that the causes for the surprisingly rapid CO trend changes are not known, the main reason being incomplete global coverage of the CO measurement network. The same applies for CH<sub>4</sub>.

*Intensive measurement campaigns:* Comprehensive field programmes that have been conducted in the past with detailed observations of all factors that influence the photochemistry of the troposphere will also be much needed in the future, especially in various regions of the marine and continental tropics and subtropics, in order to find out whether we understand the major processes that determine the chemistry of ozone and related photochemically active compounds. Applications of comprehensive chemical-transport models should be an important part of these activities. Topics in which greatly improved knowledge is necessary, are especially: improved quantification of the stratospheric influx of ozone; distributions, sources and sinks of CH<sub>4</sub>, reactive hydrocarbons, CO, NO<sub>x</sub> and NX; quantification of natural NO emissions from lightning and soils.

*Cloud transport:* The role of clouds as transporters of boundary layer chemical constituents, such as CO, NO<sub>x</sub>, reactive hydrocarbons and their oxidation products to the middle and upper troposphere (and possibly into the lower stratosphere) should be better understood and quantified, so that they can be parameterized for inclusion in large scale photochemical models of the atmosphere. Similarly the production of NO by lightning and its vertical redistribution by convective storms should also be much better quantified, both for marine and continental conditions. Current uncertainties of NO production by lightning are at least a factor of four.

*Chemical interactions with hydrometeors:* The interactions of chemical constituents emanating from the boundary layer with liquid and solid hydrometeors in the clouds will be of special importance. There is for instance the question of why strong ozone formation has not been noticed around the most convective regions in the continental tropics in which large amounts of forest-derived reactive hydrocarbons, such as isoprene (C<sub>5</sub>H<sub>8</sub>), and their oxidation products are rapidly lifted to the middle and upper troposphere and mixed with lightning-produced NO to provide favourable conditions for photochemical ozone formation. Could it be that the expected ozone formation is prevented by chemical interactions of the hydrocarbon reaction products and NO, with the hydrometeors? Could significant ozone destruc-

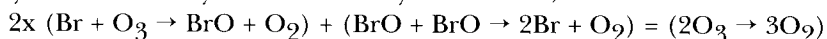


tion take place in cloud water and/or on the surface of ice particles which may be partially covered by water (114, 115)? Such questions regarding potential loss of ozone by reactions with hydrometeors may be especially relevant in connection with observations of record low O<sub>3</sub> volume mixing ratios often of less than 10 ppbv in the upper kilometers of the troposphere in March 1993 in an extended, heavily convective region between Fiji and Christmas Island over the Pacific Ocean (116). Although such low ozone volume mixing ratios had been noted on several occasions in the tropical marine boundary layer and can be explained by the ozone-destroying reactions R6-R8 in the lower troposphere, it should be ascertained whether these reactions alone suffice to explain the extremely low ozone concentrations in such a large volume of air.

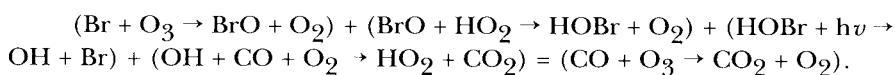
*Photolysis rates in cloudy atmosphere:* Regarding the photochemistry taking place in cloudy atmospheric conditions, recent observations of unexpectedly high absorption of solar radiation in cloudy atmospheres (117) point to the possibility that multiple scattering in broken cloud systems may lead to strongly enhanced photolysis rates and photochemical activity, leading e.g. to much higher O<sub>3</sub> destruction and OH production rates by reactions R7 and R8, or ozone production by reactions R16 + R17 + R2, than thought so far. The influence of clouds on the photochemically active UV radiation field is a potentially very important research topic which should be pursued by measurements and the development of appropriate radiative transfer models.

*Biogenic sources of hydrocarbons, CO and NO:* The continental biosphere is a large source of hydrocarbons. Quantification of these sources in terms of geophysical (e.g. temperature, humidity, light levels) and biogeochemical (soil physical and chemical properties, land use) parameters are urgently needed for inclusion in atmospheric models. The hydrocarbon oxidation mechanisms in the atmosphere should also be better understood, so that formation of ozone, carbon monoxide, partially oxidized gaseous hydrocarbons, and organic aerosol can be better quantified. The formation of organic aerosol from hydrocarbon precursors and their capability to serve as cloud condensation nuclei are related, potentially important, subjects which have not been studied in any depth so far.

*Potential role of halogen radicals in ozone destruction:* There are strong observational indications that tropospheric ozone can be destroyed by reactions in addition to those discussed so far. Surface ozone observations during polar sunrise in the Arctic have frequently shown the occurrence of unmeasurably low ozone concentrations, coinciding with high "filterable Br" (106). Further measurements (118) identified BrO as one of the active Br compounds, which, as is well known from stratospheric measurements, may rapidly attack ozone by a series of catalytic reactions, such as



or



It should be explored whether halogen activation reactions may also occur under different circumstances than indicated above (106-108).

*Heterogeneous reactions on aerosol particles* The issue of interactions between gases and atmospheric aerosol is largely unexplored and very little considered in tropospheric chemistry models. Examples are interactions of dimethyl sulfide-derived sulphur compounds with seasalt in the marine boundary layer and reactions of  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NO}_x$ ,  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$  on soil dust particles which remove these compounds from the gas phase. In the case of industrial  $\text{SO}_2$ , the neglect of such heterogeneous reactions may well have led to overestimations of the climatic cooling effects of anthropogenic aerosol, as any incorporation of sulphur in soil dust or sea salt will prevent the nucleation of new sunlight backscattering sulfate particles.

*Ozone/climate feedbacks in the stratosphere:* Ozone is a significant greenhouse gas with an infrared absorption band in the atmospheric window region, centered at 9.6  $\mu\text{m}$ . Although the tropospheric ozone amount is only about 10% of that of the stratosphere, the effective longwave optical depth of tropospheric ozone is larger. Of greatest importance would be any changes that might take place in the ozone concentrations in the tropopause regions as a result of human activities, such as  $\text{H}_2\text{O}$ ,  $\text{NO}$ ,  $\text{SO}_2$  and particulate emissions from expanding fleets of civil aircraft flying in the stratosphere and upper troposphere. On the one hand this may lead to increasing temperatures in the lower stratosphere. However, increased  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  concentrations in the lower stratosphere may increase the likelihood of polar stratospheric particle formation and ozone destruction. Such a course of events is also promoted by cooling of the stratosphere by increasing concentrations of  $\text{CO}_2$ . (This cooling effect increases with height in the stratosphere and mesosphere. The implications of this for the future dynamics of the stratosphere, mesosphere and lower thermosphere is likewise a topic, deserving attention). Changes in chemical and radiative conditions in the lower stratosphere may, therefore, create feedbacks which we need to understand well, including understanding their potential impact on tropopause heights and temperatures, stratospheric water vapor, lower stratospheric cloud characteristics and the tropospheric hydrological cycle. Recent observations of increasing trends of water vapour concentrations in the lower stratosphere over Boulder emphasize this point (119). All these factors should be taken into account before decisions are taken on vast expansions of aircraft operations in the stratosphere.

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