POLAR OZONE DEPLETION

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by
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> *In On the rigor of Science*
> *In that Empire, the Art of Cartography achieved such Perfection that the map of a single Province occupied an entire City, and the map of the Empire an entire Province. With time, those unwieldy maps did not satisfy and the Cartographers raised a Map of the Empire, with the size of the Empire and which coincided with it on every point . . .*
>
> Jorge Luis Borges

INTRODUCTION

The ozone layer acts as an atmospheric shield which protects life on Earth against harmful ultraviolet radiation coming from the sun. This shield is fragile: in the past two decades it has become very clear that it can be affected by human activities.

Roughly 90% of the Earth's ozone resides in the stratosphere, which is the atmospheric layer characterized by an inverted - that is, increasing - emperature profile that rises typically from -210 K at its base at 10-15 km altitude, to roughly 275 K at 50 km altitude. The maximum concentration of ozone is several parts per million; it is continuously being produced in the upper stratosphere by the action of solar radiation on molecular oxygen, and continuously being destroyed by chemical processes involving free radicals. Work by Paul Crutzen in the early 1970's [1] established that nitrogen oxides of natural origin, present at parts per billion levels in the stratosphere, are responsible for most of this chemical destruction, which occurs by means of catalytic cycles. Harold Johnston pointed out in 1972 [2] that the large fleets of supersonic aircraft which were being considered at that time could have seriously affected the ozone layer through their emissions of nitrogen oxides.

In early 1974 F. Sherwood (Sherry) Rowland and I proposed that chlorofluorocarbons (CFCs) would decompose in the stratosphere, releasing chlorine atoms which would catalytically destroy ozone [3]. The CFCs are industrial compounds which have been used as refrigerants, solvents, propellants for spray cans, blowing agents for the manufacture of plastic foams, etc. The

two important properties which make these compounds very useful are (1) they can be readily transformed from a liquid into a vapor under mild temperature and pressure conditions, as can be seen in Table 1, which displays vapor pressures and boiling points for some of the most common CFCs; and (2) they are chemically very inert, and hence are non-toxic, non-flammable, and do not decompose inside a spray can or a refrigerator.

Table 1. Physical Properties of Some Common CFCs

Compound	Formula	Vapor Pressure (atm)		Boiling Point
		260 K	300K	
CFC-11	$CFCl_3$	0.22	1.12	23.8°C
CFC-12	CF_2Cl_2	1.93	6.75	-29.8°C
CFC-113	$CFCl_2CClF_2$	0.08	0.47	47.7°C

Measurements reported by James Lovelock and coworkers [4] had indicated that the CFCs were accumulating throughout the Earth's atmosphere. In our 1974 paper we suggested that the CFCs will not be destroyed by the common cleansing mechanisms that remove most pollutants from the atmosphere, such as rain, or oxidation by hydroxyl radicals. Instead, the CFCs will be decomposed by short wavelength solar ultraviolet radiation, but only after drifting to the upper stratosphere - above much of the ozone layer - which is where they will first encounter such radiation. Upon absorption of solar radiation the CFC molecules will rapidly release their chlorine atoms, which will then participate in the following catalytic reactions [3,5]:

$$Cl + O_3 \rightarrow ClO + O_2 \quad (1)$$

$$ClO + O \rightarrow Cl + O_2 \quad (2)$$

$$\text{Net: } O + O_3 \rightarrow 2\,O_2 \quad (3)$$

These free radical chain reactions are terminated by reactions forming temporary reservoirs, the three most important ones being hydrogen chloride, chlorine nitrate, and hypochlorous acid:

$$Cl + CH_4 \rightarrow HCl + CH_3 \quad (4)$$

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \quad (5)$$

$$ClO + HO_2 \rightarrow HOCl + O_2 \quad (6)$$

The free radicals are regenerated by reactions such as the following:

$$HCl + OH \rightarrow Cl + H_2O \quad (7)$$

$$ClONO_2 + h\nu \rightarrow Cl + NO_3 \quad (8)$$

$$HOCl + h\nu \rightarrow Cl + OH \quad (9)$$

There are other reactions which affect the chlorine balance in the stratosphere; a schematic representation of the most important ones is shown in

Figure 1. The net effect of this chemistry is that the inorganic chlorine produced by the decomposition of the CFCs exists in free radical form - i.e., as "active chlorine" - only a few percent of the time. We have published more detailed reviews of stratospheric halogen chemistry; see, e.g., Abbatt and Molina [6] and Shen *et al.* [7]

In the decade following the publication of our Nature paper, field observations corroborated many of the predictions based on model calculations and on laboratory measurements of reaction rates. However, the effects on ozone were unclear, because the natural ozone levels have relatively large fluctuations.

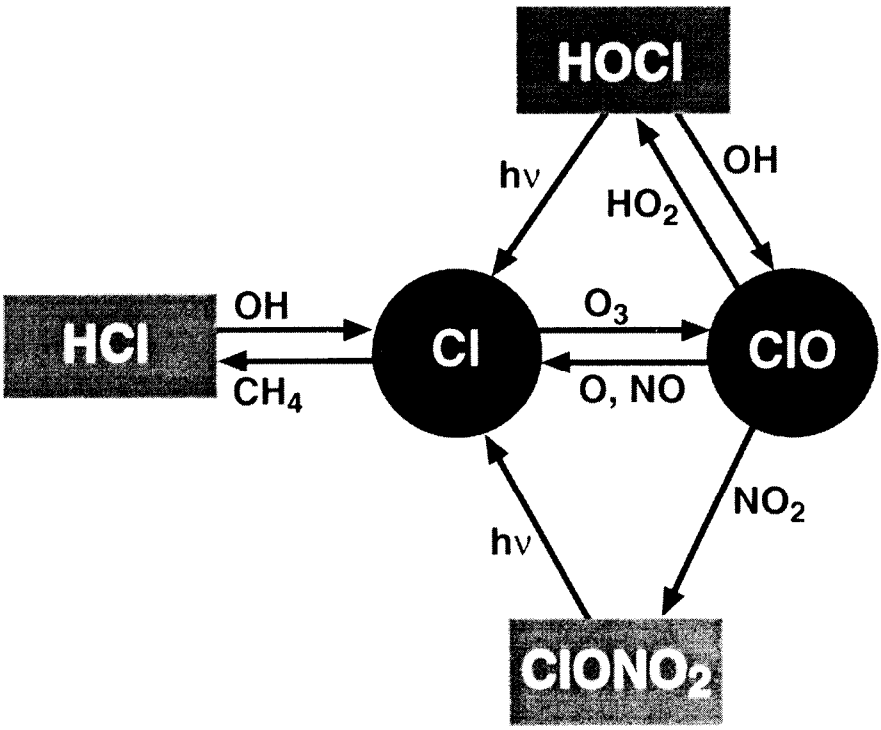

Fig I: Schematic representation of chlorine chemistry in the stratosphere at mid and low latitudes.

POLAR OZONE LOSS

The rapid seasonal decline of stratospheric ozone over the South Pole - the so called "Antarctic ozone hole" - is a startling phenomenon: a large fraction of the total column ozone - more than a third - disappears in the spring months over an area coinciding largely with the Antarctic continent (see Figure 2). In recent years it has become more severe: in October 1992 and 1993 more than 99% of the ozone disappeared at altitudes between about 14 and 19 km [8], where concentrations of this species are usually largest; and in 1995, in mid-September, the ozone hole was the largest ever recorded that early in the austral spring.

Significant ozone depletion over Antarctica started in the early 1980's, but

it was not until 1985 that Farman *et al.* [9] announced their discovery of the ozone hole, suggesting furthermore a possible link with the growth of active chlorine in the stratosphere released by the decomposition of CFCs. Satellite data subsequently confirmed Farman *et al's* findings. This discovery was surprising, not only because of the magnitude of the depletion, but also because of its location. We had originally predicted that chlorine-initiated ozone loss would occur in regions of efficient ozone production, that is, predominantly in the upper stratosphere at middle and low latitudes; it is only there that the concentration of free oxygen atoms is large enough for catalytic reactions such as (1) and (2) to occur efficiently. Furthermore, the expectation was that at high latitudes active chlorine would be relatively less abun-

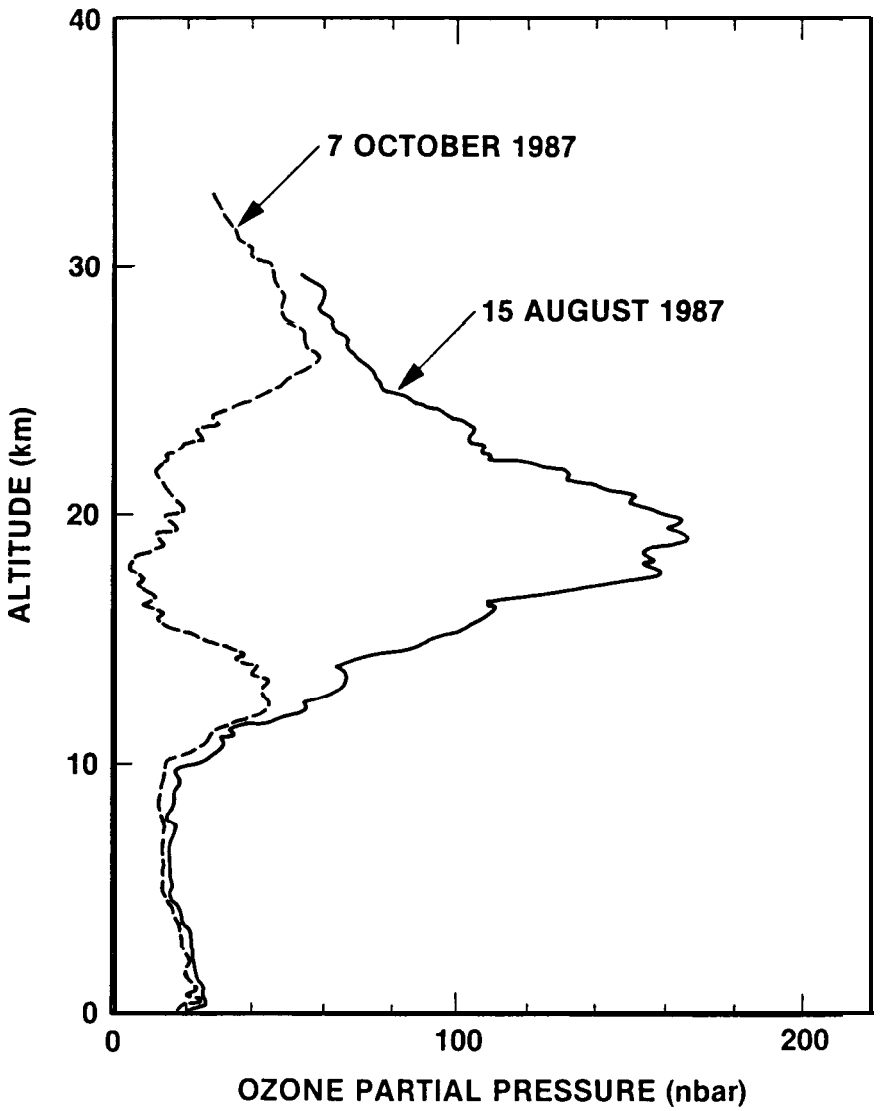

Fig. 2: Balloon measurements of ozone profiles over Halley Bay, Antarctica [30].

dant, because the reservoir species would be more stable - reactions such as (7) and (8) slow down as a consequence of the decrease in temperature as well as the decrease in solar radiation at the higher zenith angles, that is, the lower sun elevation.

The initial question was, thus, whether the observed polar ozone loss was of human origin, or else merely a periodic natural phenomenon, only never before noticed. A prominent early theory put forth to explain this phenomenon had as a principal cause atmospheric dynamics driven by extreme cold temperatures: the hypothesis was that upon first sunrise in the spring, warming of the Antarctic stratosphere would lead to a net upward lifting of ozone-poor air from the troposphere or lower stratosphere. If so, no ozone destruction would be taking place; it would merely be redistributed periodically. Another theory suggested that the 11 year solar cycle was responsible for the effect: chemical destruction of ozone involving catalytic NO_X cycles would occur, with the catalysts being generated in the upper stratosphere by high energy particles or by ultraviolet radiation following enhanced solar activity. A third theory suggested that chlorine and bromine free radicals were the catalysts for the chemical destruction of ozone, the source of these radicals being compounds of industrial origin-CFCs and halons (these are compounds containing bromine which are used as fire extinguishers). This third theory is discussed next in more detail. It is based on our original CFC-ozone depletion hypothesis, but it is modified and extended to take into account the peculiar conditions prevailing over Antarctica: Figure 3 displays schematically the most important reactions of the modified theory (compare to Figure 1, the original chemistry).

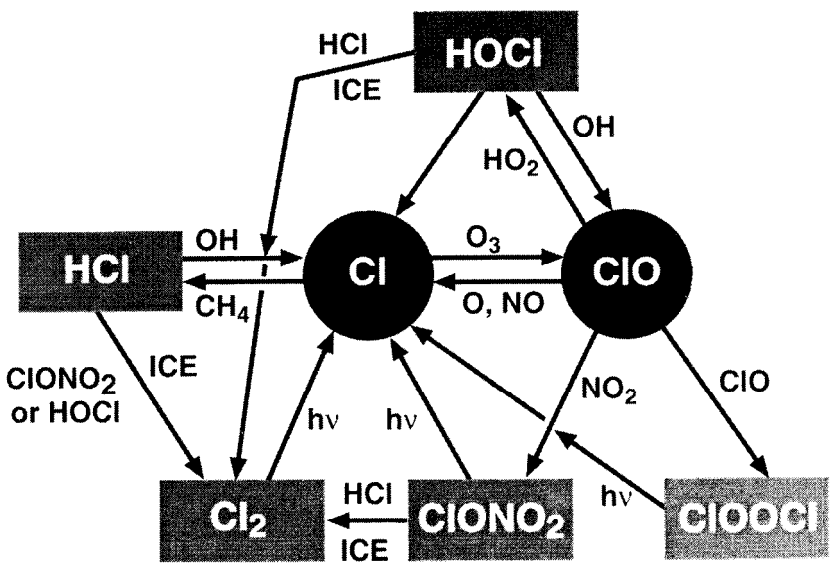

Fig. 3: Schematic representation of chlorine chemistry in the polar stratosphere.

GAS PHASE CHEMISTRY OF THE POLAR STRATOSPHERE

The large solar zenith angle characteristic of the polar stratosphere results in little, if any photodissociation of oxygen, and hence in practically no new ozone production. Similarly, ozone itself photolyzes only rather slowly in those regions, so that the concentration of free oxygen atoms remains very small–particularly in the lower stratosphere, where the ozone loss is largest. Consequently, catalytic cycles which require the presence of atomic oxygen are ineffective for ozone destruction, as mentioned above. Several cycles not involving oxygen atoms were proposed after the discovery of the ozone hole, such as the following one, based on the coupling of HO_x and ClO_x radicals [10]:

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (9)$$
$$Cl + O_3 \rightarrow ClO + O_2 \quad (1)$$
$$ClO + HO_2 \rightarrow HOCl + O_2 \quad (10)$$
$$HOCl + h\nu \rightarrow OH + Cl \quad (11)$$
$$\text{Net: } 2\,O_3 + h\nu \rightarrow 3\,O_2 \quad (12)$$

Measurements of the abundance of HOCl in the Antarctic stratosphere indicate, however, that this cycle does not make a major contribution to ozone depletion. McElroy *et al.* [11] proposed another cycle involving bromine:

$$Cl + O_3 \rightarrow ClO + O_2 \quad (1)$$
$$Br + O_3 \rightarrow BrO + O_2 \quad (13)$$
$$ClO + BrO \rightarrow Cl + Br + O_2 \quad (14)$$
$$\text{Net: } 2\,O_3 \rightarrow 3\,O_2 \quad (12)$$

The reaction between ClO and BrO regenerates the free atoms in this cycle, but the reaction has actually three channels:

$$ClO + BrO \rightarrow Cl + Br + O_2 \quad (15)$$
$$ClO + BrO \rightarrow BrCl + O_2 \quad (16)$$
$$ClO + BrO \rightarrow Br + OClO \quad (17)$$

Laboratory investigations have shown that the first and third channels are approximately equally fast, whereas production of BrCl is relatively slow.

In 1987 we proposed a mechanism involving the self reaction of ClO to form chlorine peroxide [12], a compound which had not been previously characterized:

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \quad (18)$$
$$Cl_2O_2 + h\nu \rightarrow 2\,Cl + O_2 \quad (19)$$
$$2\,(Cl + O_3 \rightarrow ClO + O_2) \quad (1)$$
$$\text{Net: } 2\,O_3 + h\nu \rightarrow 3O_2 \quad (12)$$

The reaction of ClO with itself has three bimolecular channels, as is the case for the ClO + BrO reaction:

$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (20)$$
$$ClO + ClO \rightarrow Cl + ClOO \quad (21)$$
$$ClO + ClO \rightarrow Cl + OClO \quad (22)$$

These bimolecular reactions are too slow to be of importance in the atmosphere. However, the termolecular reaction that leads to the formation of chlorine peroxide can occur efficiently in the lower stratosphere at high latitudes, as it is facilitated by the lower temperatures and higher pressures prevailing in those regions.

The structure of the product formed in the termolecular ClO self reaction has been shown by both theory [13] and experiment [14] to be indeed ClOOCl, rather than ClOClO (see Figure 4). Furthermore, photodissociation of ClOOCl yields predominantly Cl atoms, rather than ClO radicals, as we and others have shown in laboratory experiments [15, 16]. Formation of ClOO is also possible; however, even under polar stratospheric conditions ClOO rapidly decomposes to yield free chlorine atoms, since the Cl-OO bond strength is only about 5 kcal/mole.

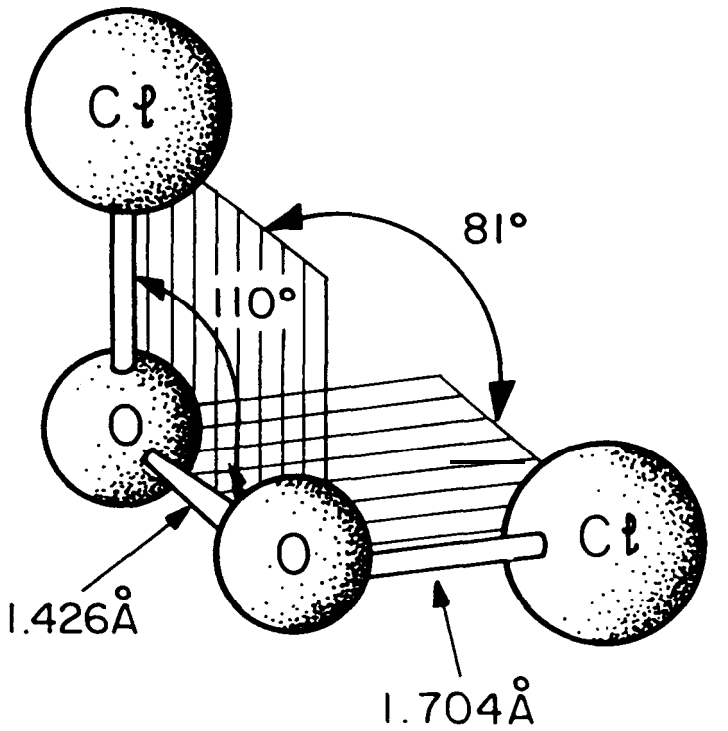

Fig. 4: Structure of chlorine peroxide [14].

POLAR STRATOSPHERIC CLOUDS

In contrast to the troposphere, the stratosphere is extremely dry and practically cloudless - the concentration of water vapor is measured in parts per million, and is, in fact, comparable to that of ozone. Normally, there is a thin layer of aerosol throughout the lower stratosphere - a haze - first described in 1961 by Junge and co-workers [17]. The aerosols droplets are mostly liquid and consist of supercooled aqueous sulfuric acid solutions - about 75% H_2SO_4 by weight at mid and low latitudes, with radius roughly 0.1 μm. The "background" number density falls typically in the 1-10 cm^{-3} range, but it may increase between one and two orders of magnitude following the injection of SO_2 directly into the stratosphere by major volcanic eruptions, such as El Chichon in 1982 and Mount Pinatubo in 1991. The SO_2 is oxidized in the stratosphere to form H_2SO_4 on a time scale of months, and the excess particles decay over a period of a few years. SO_2 emitted at the earth's surface by processes such as the combustion of coal is mostly oxidized and removed from the atmosphere (as acid rain) before reaching the stratosphere. The background aerosols arise mainly from COS, which is also emitted at the earth's surface but is sufficiently stable to reach the stratosphere, where it photooxidizes to yield SO_2 and subsequently H_2SO_4.

Polar stratospheric clouds (PSCs) form seasonally over the polar regions. Satellite-based instruments have been monitoring these clouds long before the discovery of the ozone hole by observing the attenuation of sun light, which is scattered at wavelengths characteristic of the size of the cloud particles. In the winter and spring months, sharp increases in the attenuation resulting from the presence of PSCs are evident, followed by a decrease in the summer after the cloud particles evaporate or sediment out.

The PSC particles form by condensation of vapors on the pre-existing sulfuric acid aerosols. Observations have also indicated the existence of different types of clouds, the two most common ones being often referred to as Type I and Type II PSCs. The later ones are present only when the temperatures fall below the frost point of water, which is typically about 185-187 K the particles are roughly 10 micrometer in diameter and are composed principally of water-ice crystals. These Type II clouds are more prevalent over Antarctica, because of its lower temperatures compared to the Arctic. Type I PSCs are observed more frequently, forming at temperatures above the frost point of water but below 190-195 K, with particle diameters of roughly one micrometer. Thermodynamic considerations coupled with laboratory experiments indicate that Type I PSC particles consist most likely of nitric acid trihydrate (NAT), which is the most stable condensed phase under the conditions which lead to the formation of these clouds. However, more recent laboratory experiments indicate that the aerosol particles are not likely to freeze at temperatures above the water frost point [18]. Furthermore, investigations performed in the field [19] and in the laboratory [20, 21] indicate that the liquid sulfuric acid droplets should absorb significant amounts of nitric acid and of water vapors under polar stratospheric conditions, with a

very rapid change in composition - and hence size - occurring over a narrow temperature range [22, 23], thus explaining the formation of Type I clouds below a certain temperature threshold. Hence, it appears that Type I PSCs are sometimes liquid - particularly over the Arctic - and sometimes solid.

CHEMISTRY ON CLOUD PARTICLES

Laboratory experiments, field observations and atmospheric modeling calculations have now established that chemical reactions occurring on PSC particles play a central role in polar ozone depletion. These reactions have two separate effects, referred to as chlorine activation and nitrogen deactivation: first, chlorine is transferred from the relatively inert reservoir compounds HCl and $ClONO_2$ into forms that can be readily photolyzed (mostly Cl_2); and second, nitrogen oxides are removed from the gas phase, through incorporation of nitric acid into the PSCs, thus preventing the formation of $ClONO_2$, a species that interferes with the catalytic chlorine cycles which destroy ozone. In fact, some PSC particles grow large enough to precipitate, permanently removing nitric acid from the stratosphere; this is the process labeled denitrification.

The following are the key chlorine activation reactions:

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \quad (23)$$

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \quad (24)$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O \quad (25)$$

The most important reaction is (23), the first one among these three. Our early laboratory experiments indicated that this reaction does not occur in the gas phase at significant rates [24a]. However, we noticed in those experiments that this and other reactions involving chlorine nitrate are very sensitive to surface effects; similar observations had been reported by Sherry Rowland's group [24b]. In 1986 Solomon *et al.* [10] suggested that reactions (23) and (24) would be promoted by PSCs, setting the stage for efficient ozone depletion over Antarctica. In 1987 we carried out a series of laboratory measurements showing that indeed reaction (23) is remarkably efficient, requiring only a few collisions of the reactant $ClONO_2$ with ice exposed to HCl vapor [25]. This peculiar chemical reactivity of ice was surprising; in contrast to liquid water - and the well-established chemistry of aqueous ions - reactions promoted by ice at temperatures down to 180 K were unprecedented. Our results were subsequently corroborated by several other groups (for a review, see Kolb *et al.* [26]).

MECHANISM FOR CHLORINE ACTIVATION REACTIONS

The net effect of reactions (24) and (25) occurring sequentially is reaction (23), suggesting that the mechanism for this last reaction involves two

steps-reactions (24) and (25). Also, while the high efficiency of reaction (24) on ice is understandable - the reactant H_2O is already in condensed phase-both reactants for reaction (23) are originally in the gas phase; hence, it proceeds most likely through sequential, rather than simultaneous collisions of the reactants with the surface. This implies that at least one of the reactants - most likely HCl - has a high affinity for the condensed phase. Previous measurements had shown, though, that HCl is only sparingly soluble in ice; more recent investigations have indicated, however, that monolayer amounts of HCl are taken up by the ice surface under temperature and HCl partial pressure conditions similar to those prevailing in the polar stratosphere [26, 27].

Physical adsorption of HCl is expected to incorporate only negligible amounts of HCl on the ice surface [28], even allowing for a very strong hydrogen bond. These expectations led early on to the suggestion that reaction (23) should not occur on ice under stratospheric conditions of temperature and HCl partial pressure, and the results of laboratory measurements were considered to be artifacts resulting from grain boundary effects.

The high affinity of HCl for the ice surface can be explained, however, by assuming that the HCl solvates, forming hydrochloric acid, as is the case with liquid water. This process is exothermic by -18 kcal/mole; in contrast, a hydrogen bond of HCl with ice is estimated to be only 5 kcal/mole. Solvation can occur because the surface layers of ice are disordered, with the water molecules there having much larger mobility than in the bulk crystal. This behavior leads to the formation of a quasi-liquid layer on the ice surface which can be experimentally observed at temperatures down to about 240 K. The presence of HCl strongly depresses the freezing point (a 9-molal HCl solution freezes at ~190 K), so that formation of a quasi-liquid HCl solution layer appears plausible under polar stratospheric conditions [28]. Furthermore, the large reaction probabilities for reactions (23) and (25) can be understood with the quasi-liquid layer model: the mechanism for these reactions most likely involves aqueous-like ions. In contrast, adsorbed molecular HCl is expected to behave rather similarly to gaseous HCl, and hence should react only very slowly with $ClONO_2$, as noted above.

Laboratory measurements of the uptake of HCl by NAT have also been conducted. For NAT, however, an additional parameter that needs to be taken into account is its H_2O vapor pressure: at any given temperature it can have a range of values, whereas for water-ice it has, of course, only one value. Observations show that when the H_2O vapor pressure of NAT approaches that of ice its surface takes up as much HCl as ice, whereas the amount decreases by more than two orders of magnitude as the H_2O vapor pressure drops. The reaction probabilities for reactions (23) and (25) behave accordingly: they have large values when the H_2O vapor pressure of NAT is within a factor of ~3 of that of ice [26, 29]. It appears that the uptake as well as the reaction probabilities are controlled by the availability of water at the surface.

The chlorine activation reactions (23-25) occur rather slowly on sulfuric

acid aerosols at mid-latitudes, because HCl is only very sparingly soluble in relatively concentrated H_2SO_4 solutions, and because the water in those solutions is not available for reaction with $ClONO_2$. However, as the temperature drops towards high latitudes and the sulfuric acid solution becomes more dilute, the HCl becomes more soluble, and the efficiency of these reactions increases dramatically over a relatively narrow temperature range: under conditions of thermodynamic stability for type I PSCs, chlorine activation occurs rapidly on both liquid and solid particles [20].

MEASUREMENTS OF KEY SPECIES OVER ANTARCTICA

Beginning in 1986, a series of field experiments were designed to test the various hypothesis which had been put forth to explain the Antarctic ozone hole. For example, observations of upward flow in the polar stratosphere would have verified the "dynamics only" theory. The solar cycle theory would have been supported by observations of high NOx levels in regions where ozone was being depleted; furthermore, according to this theory in years of low solar activity the polar stratosphere would recover to normal pre-ozone hole conditions. In contrast, expectations from the halogen theory were low levels of nitrogen oxides, and high levels of active chlorine.

The first observational campaign designed to test these theories - the National Ozone Experiment (NOZE) - was mounted in the winter of 1986. The NOZE scientists, based on McMurdo, Antarctica, and led by Susan Solomon, performed remote sensing measurements of key stratospheric species such as NO_2, O_3, and chlorine free radicals. Their findings provided the first evidence that the chemistry of the Antarctic stratosphere was highly perturbed, with the halogen chemistry mechanism appearing most likely. A second NOZE campaign, as well as the Airborne Antarctic Ozone Experiment (AAOE) were conducted in 1987. This expedition was based on Punta Arenas, Chile: the results from flights conducted over a six week period largely confirmed and extended the results from the NOZE experiment. The observations provided very clear evidence of a strong downward flow within the Antarctic polar vortex, which is the region of the stratosphere where the ozone hole develops: contrary to predictions based on the dynamics only theory, the levels of tracers such as the CFCs, CH_4 and N_2O were typical of air coming from higher altitudes - "aged" air which had been exposed to short-wavelength ultraviolet radiation. Furthermore, the concentration of NOx was remarkably low, in contrast with expectations from the solar cycle theory.

The chemical CFC-halogen hypothesis received strong support from the results of the field experiments. The measurements conducted by James Anderson and co-workers [31] showed that the ClO concentrations in the polar vortex were greatly enhanced (see Figure 5), showing that more than half of the chlorine was present there as a free radical-chlorine that had been released in the stratosphere at lower latitudes by the decomposition of

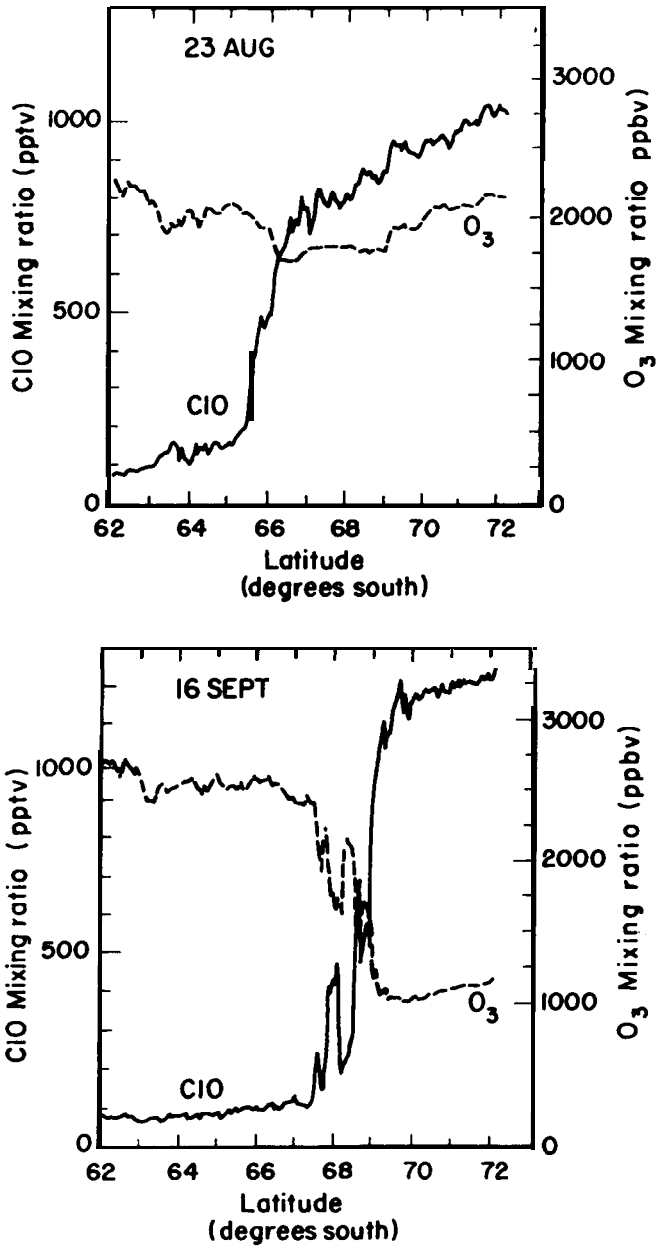

Fig. 5: Mixing ratios of ClO and ozone measured in 1987 during the AAOE expedition; adapted from [31].

the CFCs. These measurements, coupled with the observations of the rate of disappearance of ozone, indicated that the chlorine peroxide cycle that we had suggested (reactions 1, 18, and 19) was responsible for more than two thirds of the ozone loss, with most of the rest of the loss resulting from bromine chemistry.

The unique instruments required for all these experiments - as well as the

halogen hypothesis itself - were developed in a relatively short amount of time': the community was well prepared for these new developments, since it had vigorously continued for over a decade the pursuit of scientific research on the stratospheric ozone issue.

CONCLUSIONS

Much remains to be learned about stratospheric chemistry - and, in more general terms, about the physics and chemistry of the global atmosphere. On the other hand, the cause-effect relationship between human-produced chemicals and ozone depletion is rather well established now: the signals connected with the Antarctic ozone hole are very large indeed. The stratospheric ozone issue has shown us that mankind is quite capable of significantly affecting the atmosphere on a global scale: the most striking effects of CFCs, which are emitted mostly in the north, are seen as far away as possible from the sources, namely over the South Pole. This global problem has also shown us that different sectors of society can work together - the scientific community, industry, environmental organizations, government representatives and policy makers - to reach international agreements: the Montreal Protocol on Substances that Deplete the Ozone Layer has established a very important precedent for the solution of global environmental problems.

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