

Polar Stratospheric Chemistry: Catalytic Reaction on Ice

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In this talk I will look at the chemical reactions that can occur on ice surfaces. These are particularly relevant to stratospheric ozone depletion.

I. THE COMPOSITION OF THE ATMOSPHERE

Although I will be focusing on only one part of the atmosphere during this talk, it would be good to get an overall view of the atmosphere as a whole.

The total mass of the atmosphere is about 5×10^{18} kg, with 50% of that below about 5.5 km, and 99% of that below 30 km. The two lowest regions are the *troposphere* and the *stratosphere*.

In the troposphere there is a lot of vertical mixing. Molecules can traverse the entire region in a few days in clean air, or in few minutes in the updraughts of large thunderstorms.

In the stratosphere there is very little vertical mixing, the time scale here being on the order of years. The troposphere and the stratosphere are separated by a region known as the tropopause, and the stratosphere is separated from the *mesosphere* above it by the stratopause:

Figure 1 shows data for the atmosphere at about 40° N.

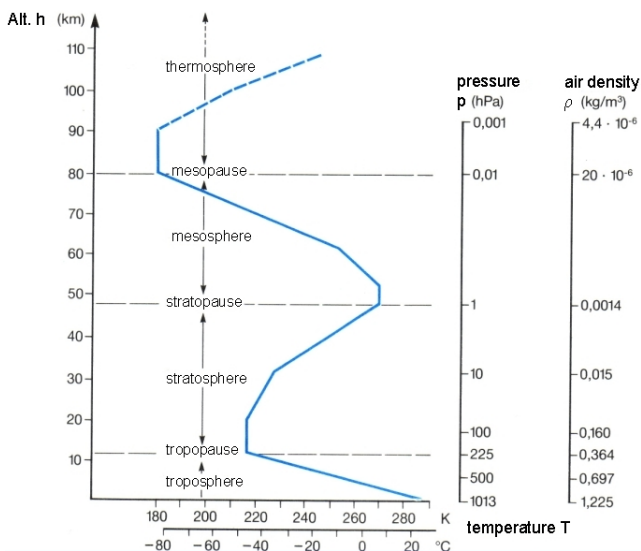


FIG. 1: Atmospheric Profile

Polar Ozone

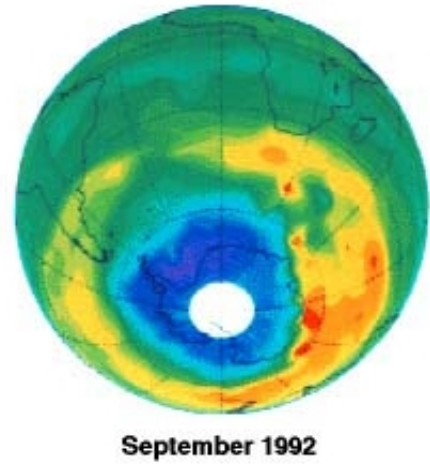


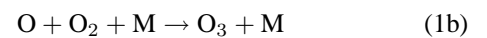
FIG. 2: Ozone Hole over Antarctica

II. THE OZONE LAYER

So - why all the interest in atmospheric chemistry? In 1985 Farman *et al* (*Nature* **315** 207) noticed that the ozone layer was depleting in the spring months over Antarctica (see fig. 3 on next page).

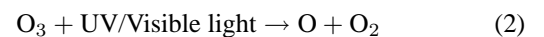
Figure 2 shows the hole over Antarctica (the big darker grey blob, as opposed to the smaller lighter grey blobs).

Ozone in the stratosphere is maintained through the *Ozone Cycle*, which is also used to reduce the amount of UV entering the atmosphere.

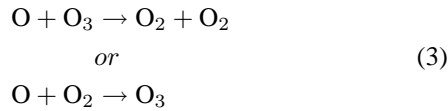


Where the M in (1b) is a third non-reacting molecule that is required for conservation of momentum. Here the UV wavelengths less than 240 nm.

Because Ozone is more unstable than O_2 , it is destroyed by longer wavelengths.

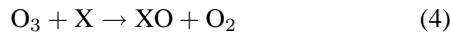


The free oxygen atom above can then



This whole group of reactions are known as *Chapman Reactions*.

However, most O_3 destruction takes place through catalytic processes, with free radical species such as nitrogen, chlorine, bromine etc.



Where X may be O, NO, OH, Br, Cl etc.

CFCs seep through the troposphere and then into the stratosphere where they break down through photo-dissociation. This releases Cl which then increases the destruction of O_3 by reaction 4 above.

III. SO - WHY THE OZONE DEPLETION OVER ANTARCTICA?

Before the hole was discovered, it was thought that polar stratospheric clouds could be made of ice, however, they are more commonly made of nitric acid hydrates (NAT or NAD for tri- and di-). These are known as type I polar stratospheric clouds (PSCs).

Ice crystals actually make up type II PSCs, which form in the springtime when the temperature falls below the frost point (around 185K). Moist air rises and cools adiabatically so that the water vapour becomes supersaturated and condenses, usually in the form of droplets, and these grow further to about $10 \mu\text{m}$. These droplets are extremely stable - they will not grow much bigger during the lifetime of the cloud, because of their aerodynamic properties they will not coalesce, and their terminal velocity is so low that they won't fall out of the cloud. These supercooled droplets do not become ice until the temperature becomes sufficiently low. Thus, the average ice crystal size in the polar stratosphere is about $10 \mu\text{m}$.

The graph (fig. 3) below shows the observed drop in ozone during the Antarctic spring. Mario Molina received the Nobel Prize in 1995 for his role in showing the causes of Ozone destruction, some of which involve reactions on ice surfaces.

So, why does the ozone count go down in the spring months over Antarctica? This is also the time when type II PSCs form, so it is sensible to ask; are there any reactions that involve ice that could account for the Ozone depletion? The answer is yes, being:

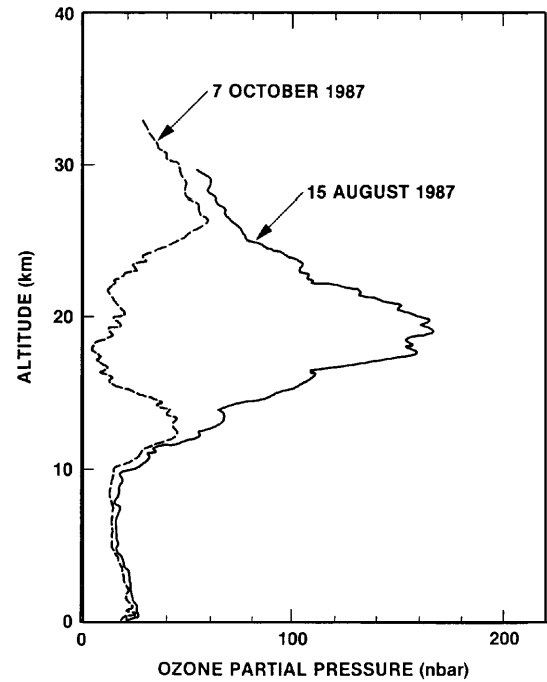
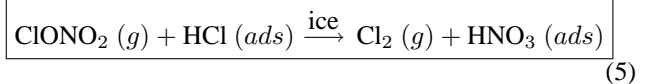


FIG. 3: Measurements taken over Halley Bay, Antarctica

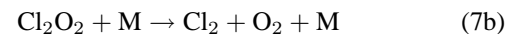


Where the HCl is adsorbed onto the ice surface.

The chlorine gas can then be dissociated by:



Which can then be used in equation 4. The upshot of this is to increase the amount of Cl in the atmosphere. The ClO from reaction 4 can then:



The Cl_2 is then recycled using reaction 6. While the reactions $7a \rightarrow 7b \rightarrow 6 \rightarrow 4$ form a cycle, reaction 5 introduces more chlorine into the atmosphere.

The relationship between ClO and ozone depletion can be seen clearly from fig. 4 (dark colours mean a greater concentration).

It should be noted that other reactions involving pollutants occur on the ice surface, but most of these involve ice taking part in the reaction directly, rather than acting as catalyst.

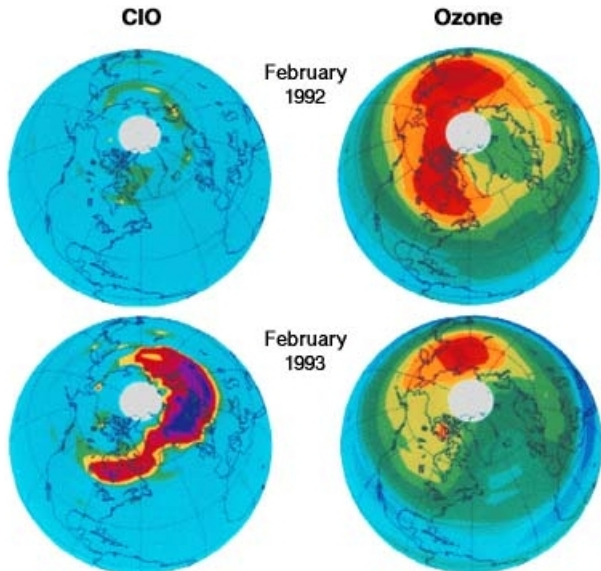


FIG. 4: CIO and Ozone levels over the North Pole

IV. THE PROCESS OF THE REACTION ON ICE

HCl will melt ice surfaces under low-temp, high partial-pressure conditions, however, with low partial-pressures, mono-layer amounts of HCl exist on the surfaces, and are sufficient to promote efficient reactions. The rate of reaction is also independent of HCl partial pressure in the range of 10^{-5} to 10^{-7} Torr. The kinetics on the crystals are not changed by different methods of forming the crystals.

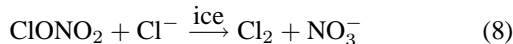
Two mechanisms have been suggested for reaction 5, both involving an adsorbed ionic chloride species. The timescale of this reaction, in total, has been observed at 180-200K to be of the order of tens of milliseconds or less.

A. Mechanism 1: Direct Reaction

In this mechanism, the HCl dissociates, forming a contact ion pair, $\text{Cl}^- \text{H}_3\text{O}^+$, which then reacts with the ClONO_2 . This has an estimated barrier height of 6.4 kcal/mol.

However, if the proton is far removed from the chlorine ion,

this reaction can take place:

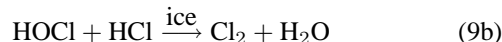


Roberto Bianco and James T. Hynes have performed some Hartree-Fock calculations (*J. Phys. Chem A* **103** 5253), giving the estimated barrier height of this reaction to be 5.7 kcal/mol.

An interesting study could be to compare the two reactions, only using DCl on D_2O .

B. Mechanism 2: Two Step Reaction

In this mechanism, the following two step reaction occurs:



The estimated experimental barrier height for this mechanism is 6.6 kcal/mol. Although the barrier height for reaction 9a has been estimated to be ≈ 3 kcal/mol, this is not an appropriate comparison due to the acidic environment of the whole system. Any H/D isotope effects are probably not observable because the HOCl desorption energy (13 kcal/mol) exceeds the reaction barrier (3 kcal/mol).

There is growing support for the one step mechanism dominating, especially under acidic conditions.

V. CONCLUSIONS

This particular area of chemistry is only twenty years old, and there is still a lot that requires investigation. The acidity can affect the reaction mechanisms, and experimental data is still a little thin on the ground for some of these reactions.

There are a number of avenues for study that seem promising, and there are a large number of other pollutants that can be adsorbed onto ice that react with the water directly that could also be studied.