Chemistry 471/671

Atmospheric Chemistry IV: Human Impact on the Stratosphere
The Ozone Hole

But where do the X-O species come from?
NO$_2$ comes from the photolysis of N$_2$O, a naturally occurring species
HO$_2$ comes from water, but the stratosphere is very cold, and very dry
BrO comes largely from CH$_3$Br, which is both a pesticide and a naturally occurring compound
ClO comes from a class of compounds called chlorofluorocarbons, or CFCs
The Role of CFCs

What are CFCs?
Compounds which contain only C, F, Cl
Widely used examples: CFCl$_3$ ("F-11"), CF$_2$Cl$_2$ ("F-12")
Nontoxic, nonflammable, nonreactive
Replaced NH$_3$ and SO$_2$ as refrigerants
Used to create bubbles in plastic foams
Used as propellants in aerosol spray cans
Used as residue cleaners in electronic fabrication

So… what’s the problem?
Is gas water soluble or fully oxidized? Yes → Gas eventually returns to Earth’s surface

No → Does gas photodecompose in sunlight?

Yes → Free radicals are produced (see Fig. 3-1b)

No → Do gas molecules have multiple bonds that OH\(^-\) can add to?

Yes → OH\(^-\) addition occurs

No → Do gas molecules have an H that OH\(^-\) can abstract in an exothermic reaction?

Yes → OH\(^-\) abstraction occurs

No → Gas is inert in troposphere; will rise to stratosphere
The Role of CFCs

The problem: CFCs are so nonreactive that they are completely inert in the troposphere.

They diffuse upward to the stratosphere, where they are exposed to shorter wavelength UV light.

Photolysis occurs, and F and Cl are released into the stratosphere, in the heart of the ozone layer.
Other problematic compounds:

CCl$_4$ – widely used as solvent, dry-cleaning
CH$_3$Br - pesticide
CH$_3$CCl$_3$ - metal cleaning agent
Halons - contain Br in addition to C, F, Cl
   Used as fire extinguisher
HCFCs – have largely replaced CFCs in developed nations
   H abstraction pathways destroy most in the troposphere (and then...?)
BUT – the C-Cl bond is weaker than in CFCs, and its *short term* impact on O$_3$ is large
Other problematic compounds:

HCFCs – a temporary solution, and regulated as such

The long-term solution appears to be HFCs Why? HFCs which reach the stratosphere will still release F atoms

But F reacts rapidly with methane to form HF, which is remarkably stable

F atoms form extremely stable reservoir species which are not re-activated by photolysis or on PSC surfaces
Regulation of CFCs

The U.S. banned CFCs in spray aerosols in 1978, but international regulation was required. 1985 saw the Vienna Convention on the Protection of the Ozone Layer, which led to scientific discussion, but the science wasn’t well understood. The Montreal Protocol was signed in 1987, and made sweeping changes. Kofi Annan: “[It is] perhaps the single most successful international agreement to date...”
Regulation of CFCs – The Montreal Protocol

Developed countries ceased CFC production by 1995, along with CCl$_4$ and CH$_3$CCl$_3$, and agreed to cease HCFC production by 2030.

Developing nations pledged to stop CFC production by 2010 and HCFCs by 2040.

Halon production banned in developed countries in 1994.

Developing countries have until 2010.

China, Korea have been problematic.

CH$_3$Br banned in developed countries in 2005.

Developing countries have until 2015.
Regulation of CFCs – The Montreal Protocol

Bound nations to reduce their CFC output to one half of 1986 levels by 1998

Required future meetings to revise standards

In 1990, 100+ nations agreed to halt CFC production altogether by 2000, and this phase-out was accelerated further at later meetings

The Beijing Amendment of 1999 added bromine-containing “halons” …

… AND required the regulation of the short-term replacement HCFCs

Important provisions were made for developing nations whose economies couldn’t sustain the mandated changes
Global Production of CFCs

Stratospheric concentrations of chlorine
Figure 1-21
Environmental Chemistry, Third Edition
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Ozone Depletion

In addition to the isolated and seasonal depletion of ozone over the poles, there has been a steady ~4% per decade decline in stratospheric ozone throughout the world.

Halogens? Sulfate aerosols? Meteorology? Some combination?
Most reports indicate that a given % reduction in O$_3$ concentration will produce about twice that % increase in skin cancer.
Mid-latitude ozone depletion

There has been recent evidence of sporadic, isolated events where ozone levels at mid-latitudes are dramatically reduced. This cannot be explained by the polar vortex or by the presence of PSC particles. There is a lively debate about how this occurs... Which we don’t have time to cover.

A fine presentation topic?
Unforeseen consequences:

The long-term solution appears to be HFCs

BUT...

1) OH + HFC $\rightarrow$ $\rightarrow$ $\rightarrow$ CF$_3$COOH
   Trifluoroacetic acid (TFA)
   Water soluble – rains out
   What happens then?

2) HFCs have atmospheric lifetimes of decades
   HFCs have strong IR absorptions
   HFCs are almost certainly Greenhouse Gases