

# Organic Halides

A Global Concern  
1.4

## Chlorofluorocarbons (CFC) and fluorocarbons

...Carbon compounds containing fluorine and chlorine are called CFCs.

CFCs have been used as dispersing gases in aerosol cans for making foamed plastics and as refrigerants

Three common CFCs:

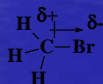
$\text{CFCl}_3$ , named as CFC 11, 1F and 3Cl replacing 4H in a  $\text{CH}_4$

$\text{CF}_2\text{Cl}_2$ , named as CFC 12, 2F and 2Cl replacing 4H in a  $\text{CH}_4$

$\text{CF}_2\text{ClCF}_2\text{Cl}$ , named as CFC 114, 4F and 2Cl replacing 6H in a  $\text{CH}_3\text{CH}_3$ ,

## Polarity and Reactivity

- Halogens are more electronegative than C.
- Carbon-halogen bond is polar, so carbon has partial positive charge.
- Carbon can be attacked by a nucleophile.
- Halogen can leave with the electron pair.



## Chlorinated hydrocarbons

Examples of hydrocarbons:

alkanes: Replacing H with Cl in a  $\text{CH}_4$   
 $\text{CH}_3\text{Cl}$ , methyl chloride, or chloromethane

$\text{CH}_2\text{Cl}_2$ , dimethyl chloride, or dichloromethane or methylene chloride

$\text{CHCl}_3$ , trimethyl chloride, or trichloromethane, or chloroform

$\text{CCl}_4$ , tetramethyl chloride, tetrachloromethane, or carbon tetrachloride

## Chlorinated hydrocarbons

...Chlorinated hydrocarbons can cause severe liver damage

...DDT (*d*ichloro*a*phenyl*t*richloroethane), highly toxic insecticides, banned now, PCBs, polychlorinated biphenyls

...All chlorinated hydrocarbons have similar properties, and mostly toxic

## Chlorofluorocarbons (CFC) and fluorocarbons

...CFCs are ideal as propellants widely used in aerosol cans for deodorants, hair spray, and food products

...CFCs are very inert, so highly persistent in the environment

...CFCs are bad for the "good ozone" in the atmosphere (discussed in more details later)

## Development of CFCs

1928; DuPont scientists develop CFCs "ideal compounds" for refrigerants and propellants



WHY??



## CFCs as Refrigerants

### Traditional Refrigerants vs. CFCs

(ammonia, sulfur dioxide, methyl chloride)

- |   |                                |
|---|--------------------------------|
| - Highly volatile   | - Non-flammable                |
| - Caustic and toxic   | - Non-toxic (relatively)       |
| - Remove heat through vaporization of liquefied gas (only adequate as refrigerants) | - Trap heat (good insulators!) |
| - Expensive   | - Inexpensive                  |
| - Heavy (transport, storage)  | - Light                        |
|   | -Extremely stable, inert       |

## CFCs as Propellants

- Light weight
- Extremely stable or "inert"

What are the consequences of these two physical characteristics?

- CFCs likely to migrate upwards
- Too light to precipitate out with rainfall
- 5-15 years to migrate to stratosphere

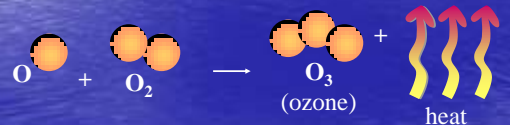
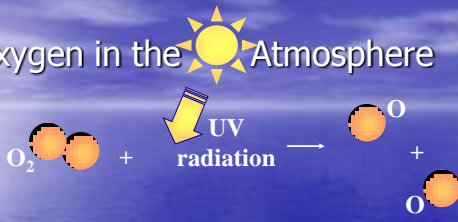
## Marketing of CFCs

1958: DuPont releases CFCs on the market commercially

1971: James Lovelock speculates that CFCs put into the atmosphere may still be present

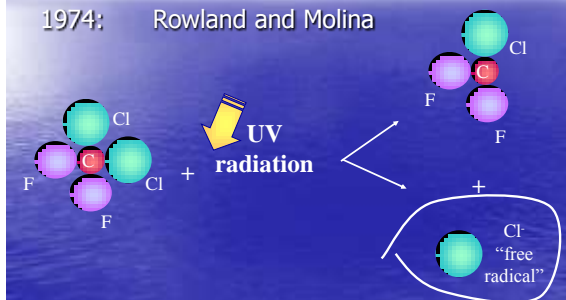
1973: Mario Molina and F. Sherry Roland start to investigate

## Oxygen in the Atmosphere

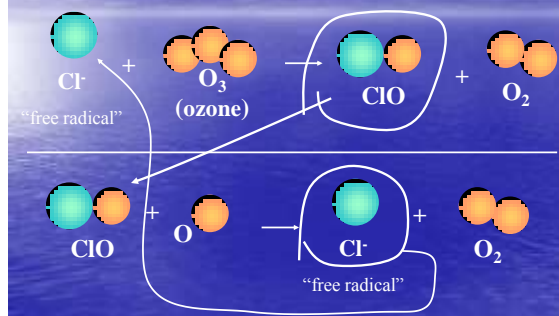


## Original Research

1974: Rowland and Molina



## Cl "Free Radicals"...



## In the news...

1974: Molina and Rowland publish their hypothesis in Nature.

New York Times runs front page

DuPont responds with study showing that CFCs in *troposphere* are benign

## High Risk and Political Savvy

1975: 200% increase in CFC use from 1968, only eight years

1979: The FDA, EPA ban non-essential uses of CFCs !

First time substance EVER banned without direct proof of harm

1982: 20 other countries join US in ban of CFCs

## Scientific Controversies

1982: British science teams in Antarctica observe 20% decline in O<sub>3</sub> layer

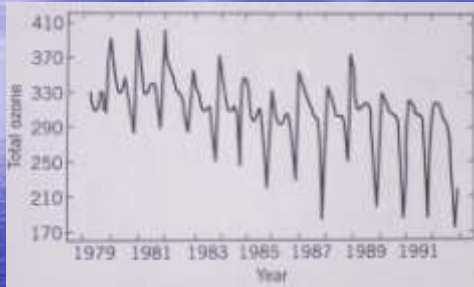
US scientists relying on TOMS (Total Ozone Mapping Spectrometer) measurements from space claim to observe nothing

## Scientific Evidence

1983: British scientists observe 30% reduction in ozone layer. US scientists claims no reduction.

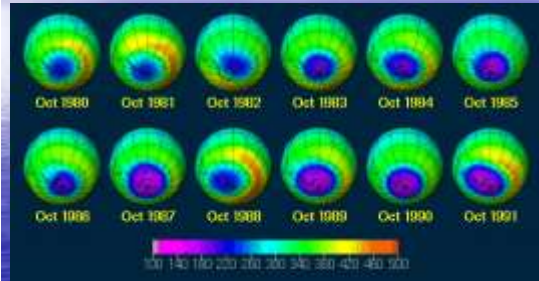
1985: British observe 50% reduction. US claims no reduction. US re-tests and confirms. WHY THE SCIENTIFIC SNAFUS??

### Total ozone



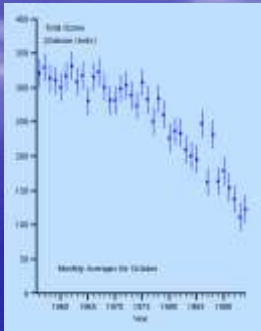
Total ozone measured above Antarctica, in Dobson Units. From Horel and Geisler, 1996

### TOMS Data (corrected)



October Average for Total Ozone over Antarctica, 1955-1995

Based on British measurements from weather balloons



### Understanding the Science

1986: DuPont scientists continue to argue that tropospheric ozone (smog) will migrate up and "fill the ozone hole" in the stratosphere

Why doesn't this theory fly?

### Location of Stratosphere

- Exosphere — 400 km
- Thermosphere — 300 km
- Mesosphere — 50 km
- Stratosphere — 40 km
- Troposphere — 10 km



### Montreal Protocol Landmark

- 1987: 2 yrs of intensive research reveal that ozone hole is anthropogenic
- 1988: UN hold meeting in Montreal 45 Nations sign to reduce CFC use by 50% by year 2000.  
Developing countries' efforts would be 'subsidized'

## Two steps forward...

1990-Follow up meetings result in:

1992:Industrialized nations: total ban by 2000

Developing nations: ban by 2010, with assistance from developed nations

US agrees to complete phaseout by 1996;  
DuPont to halt production by 1997

1995:Rowland and Molina receive Nobel Prize

## One step back...

1995:Congress challenges ozone science:  
Junk science gains credibility  
despite scientific consensus of  
anthropogenic causes of O<sub>3</sub> depletion

1996:Ban begins but black market for CFCs  
appear

WHY?

CFC substitutes (HFC) break down faster, but  
still pose problems for ozone depletion

## CFC's are not alone!!!

### Methyl Bromide

- What is it?
- Challenges to Montreal Protocol

## Methyl Bromide

A periodic table of elements with a red arrow pointing to Bromine (Br) in the halogen group. The table is titled 'Methyl Bromide' and shows the standard periodic table layout with element symbols and names.

## Uses of Methyl Bromide

60 million lbs /yr in US

- Agricultural (75%)
  - Strawberries
- Stored products (11%)
- Flame retardants (6%)
- Pest management (6%)
  - Termite removal
- Chemical production (2%)

