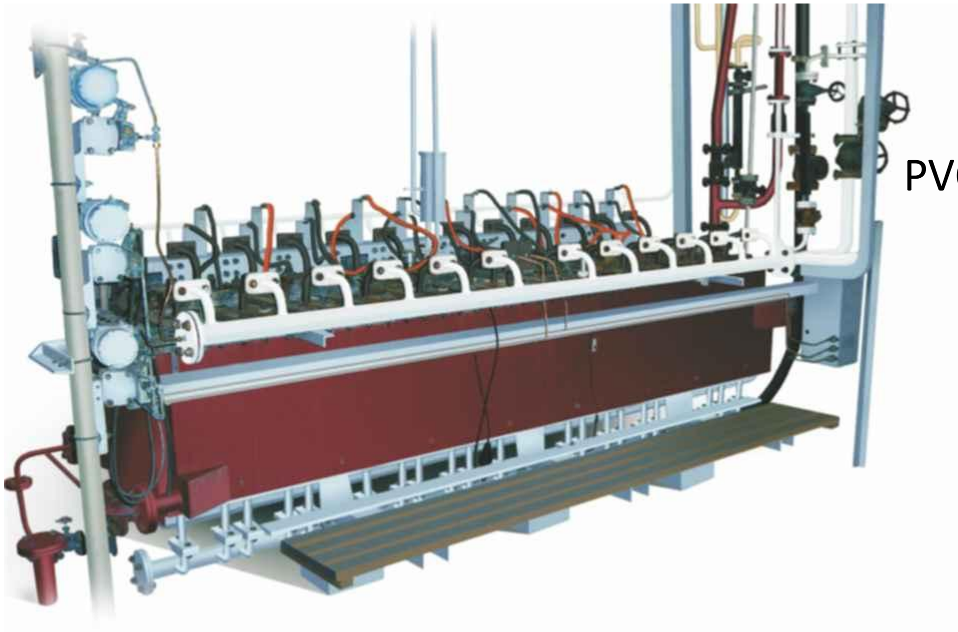
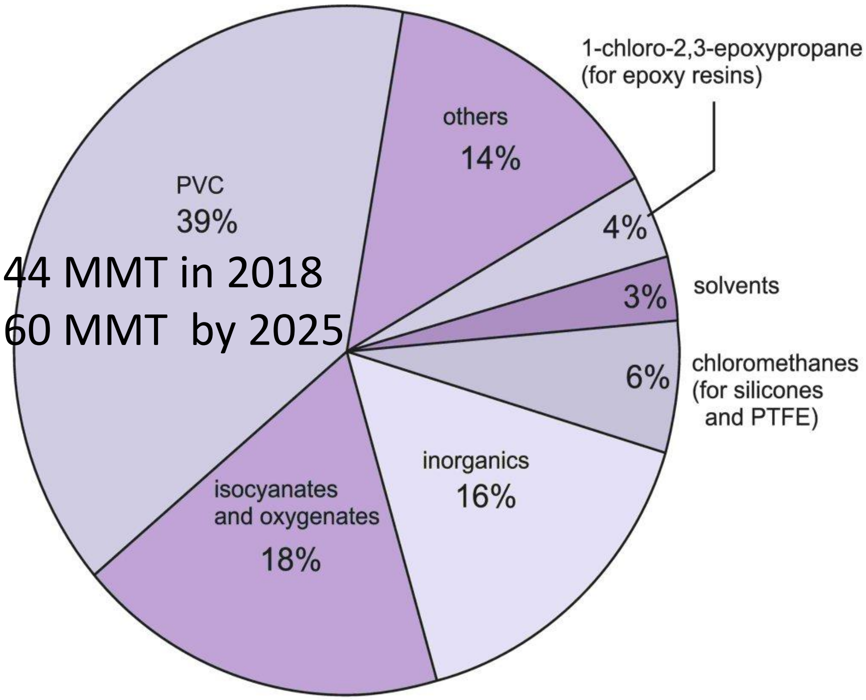
# World Production of halogens



Fluorine




PVC 44 MMT in 2018
60 MMT by 2025

Chlorine

| | |
|---|---|
| World $F_2$ | 20, 000 tonnes |

| | |
|---|---|
| World $Cl_2$ | 56 ,000,000 tonnes |

| | |
|---|---|
| World $Br_2$ | 556,000 tonnes |

| | |
|---|---|
| World $I_2$ | 19,000 tonnes |

**Every kilogram (roughly one litre by volume) of seawater has approximately 35 grams of dissolved salts (predominantly sodium(Na+) and chloride (Cl−) ions).**

| Salt Ion | Ions in Seawater | % |
|---|---|---|
| Chloride ($Cl^-$) | 18.980 | 55.04 |
| Sodium ($Na^+$) | 10.556 | 30.61 |
| Sulfate ($So_4^{2-}$) | 2.649 | 7.68 |
| Magnesium ( $Mg^{2+}$) | 1.272 | 3.69 |
| Calcium (Ca2$^+$) | 0.400 | 1.16 |
| Potassium ($K^+$) | 0.480 | 1.10 |
| Bicarbonate ($HCO^{3-}$) | 0.140 | 0.41 |
| Bromide ($Br^-$) | 0.065 | 0.19 |
| Boric acid ($H_3BO_3^-$) | 0.026 | 0.07 |
| Strontium ($Sr^{2+}$) | 0.013 | 0.04 |
| Floride ($F^-$) | 0.001 | <0.01 |
| Other ions | <0.001 | <0.01 % |

Earth's oceans together contain about 2.6 x $10^{16}$ metric tons of chlorine

- Chlorine is not only abundant in our oceans; it is the sixth most abundant element in Earth's crust.

•Chlorine has the highest electron affinity (348.6 kJ/mol) and the third highest electro-negativity (3.16) of all the reactive elements. The Cl-Cl bond dissociation energy (58 kcal/mol) is the highest among dihalogen molecules.

•Chlorine gas and many of its compounds are chemicals useful in water purification. $Cl_2$ reacts with water giving a mixture of HCl and HClO and the latter is responsible for breaching the bacterial cell wall and killing of the bacteria

•Gastric juices of stomach of human beings have 0.3 to 0.4 % hydrochloric acid. White blood cells kill bacteria by producing HClO (hypochlorus acid) inside their cells.

•Naturally occurring chlorine is a mixture of its two stable isotopes $^{35}Cl$ and $^{37}Cl$ with natural abundances of 75.8% and 24.3% respectively.

•It is used in the manufacture of house hold bleaches, disinfectants, mostly chlorinated phenols for killing bacteria and is used for bleaching paper pulp. Chlorine is also used for the manufacture of chlorates and it is important in organic chemistry, forming compounds such as chloroform, carbon tetrachloride, polyvinyl chloride, and neoprene.

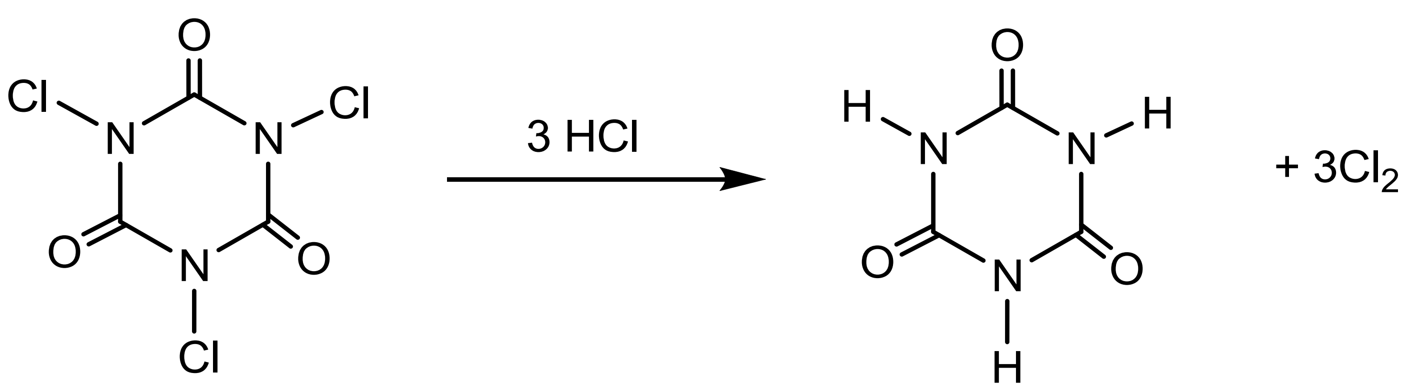
•Chlorine chemistry is essential for the manufacture of about 93% of the top-selling drugs.

•Polychlorinated dibenzodioxins, known as PCDDs are some of the most toxic compounds known to mankind which are also formed during burning of organo chlorine compounds.

•From its first use as a germicide to prevent the spread of "child bed fever" in the maternity wards of Vienna General Hospital in Austria in 1847, chlorine has been one of society's most potent weapons against a range of life-threatening infections, viruses, and bacteria for over 150 years

# Laboratory synthesis of chlorine

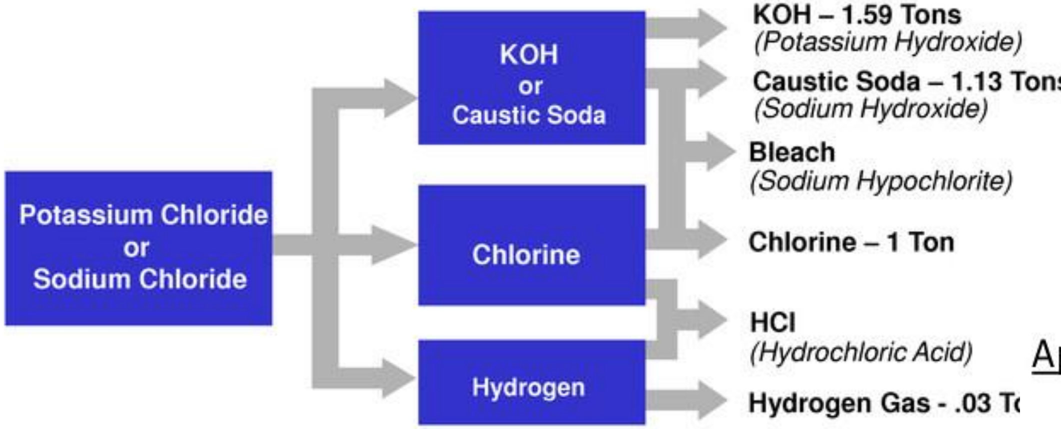
There are many methods of synthesizing chlorine gas in the laboratory and almost all of them use hydrochloric acid. A reaction of HCl with $KMnO_4$, $MnO_2$, $PbO_2$, $Pb_3O_4$, $O_2$, NaClO(aq) readily gives $Cl_2$ but often with water vapor. The most efficient method used nowadays is by the reaction of trichloroisocyanuric acid (TCCA or TCICA) with hydrochloric acid, the former being a highly stable free flowing and high melting white powder.



# Chlor Alkali Process

**Raw Materials**

BRINE + ELECTROLYSIS = PRODUCTS




$2NaCl + 2H_2O \longrightarrow 2NaOH + H_2 + Cl_2$

$Cl_2 + 2OH^- \longrightarrow ClO^- + Cl^- + H_2O$

$3Cl_2 + 6OH^- \longrightarrow ClO_3^- + 5\,Cl^- + 3H_2O$

**Application:**

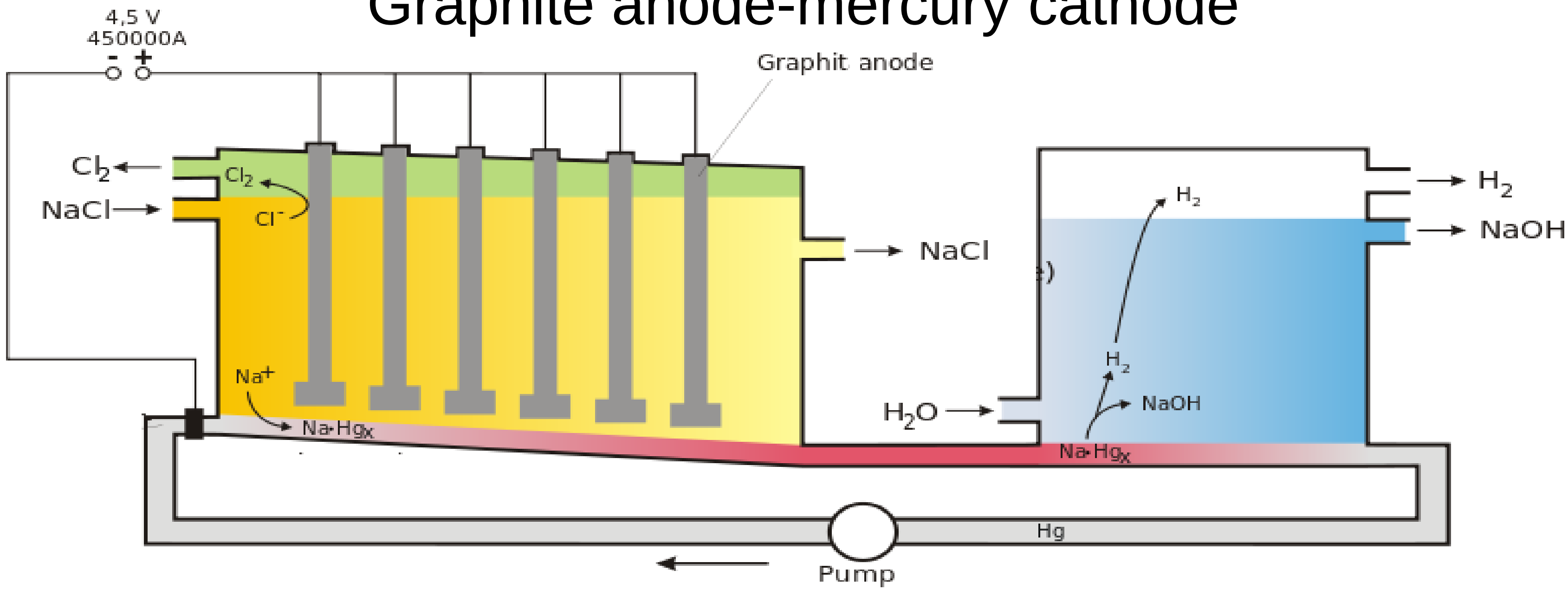
Chlor-alkali process: Chlor for chlorine and Alkali for sodium hydroxide.

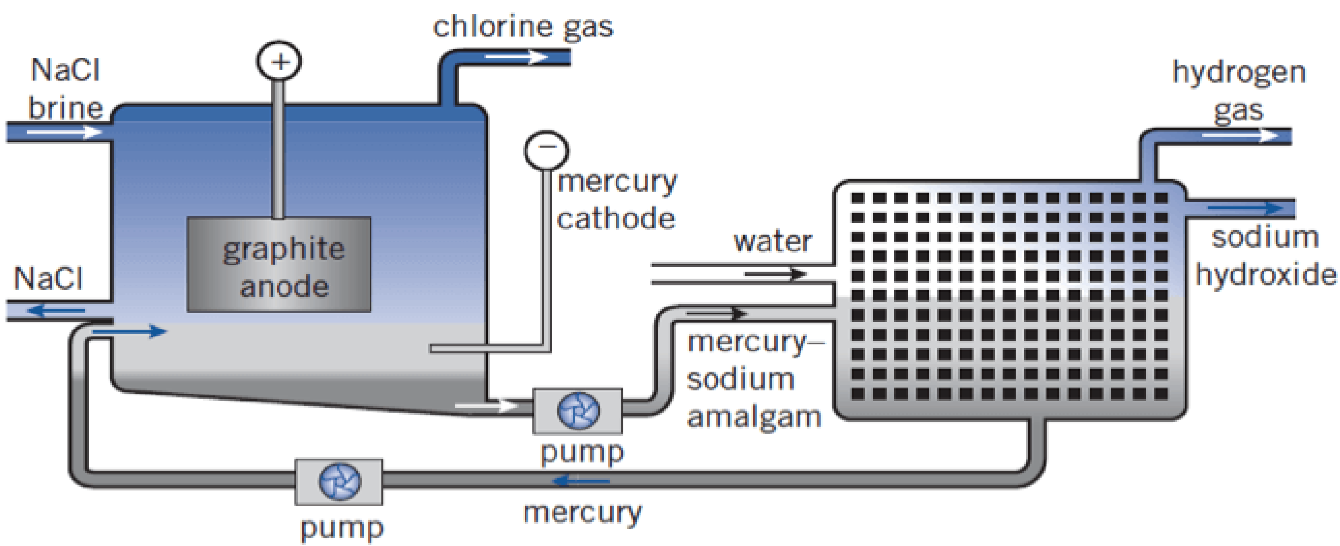
**At cathode**
- $H_2$ Gas is evolved
- Fuel
- Margarine
- ammonia

**At anode**
- $Cl_2$ Gas is evolved
- Water treatment
- PVC
- CFC's
- Disinfectants
- pesticides

**Near cathode**
- NaOH is formed
- Degreasing metal
- Soap
- Papermaking
- Artificial fibers

# Castner-Kellner Process
# Graphite anode-mercury cathode

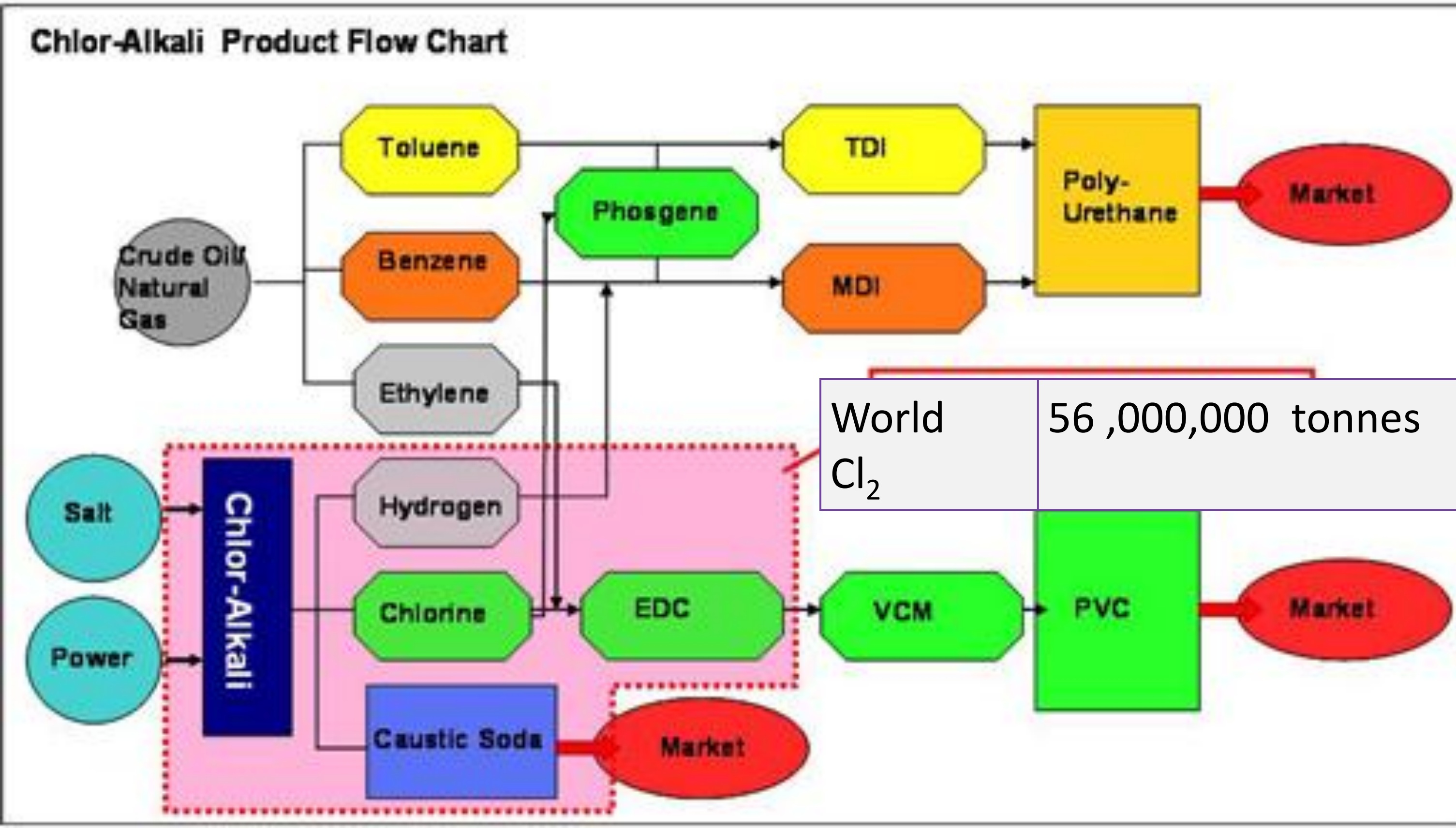


# Minamata Bay was heavily polluted in the 1950s and 1960s by wastewater

The Chisso Corporation's factory in Minamata, particularly by methylmercury.

The highly toxic compound bio accumulated in fish and shellfish in the bay which, when eaten by the people living around the bay, gave rise to Minamata disease. More than 10,000 people were affected.



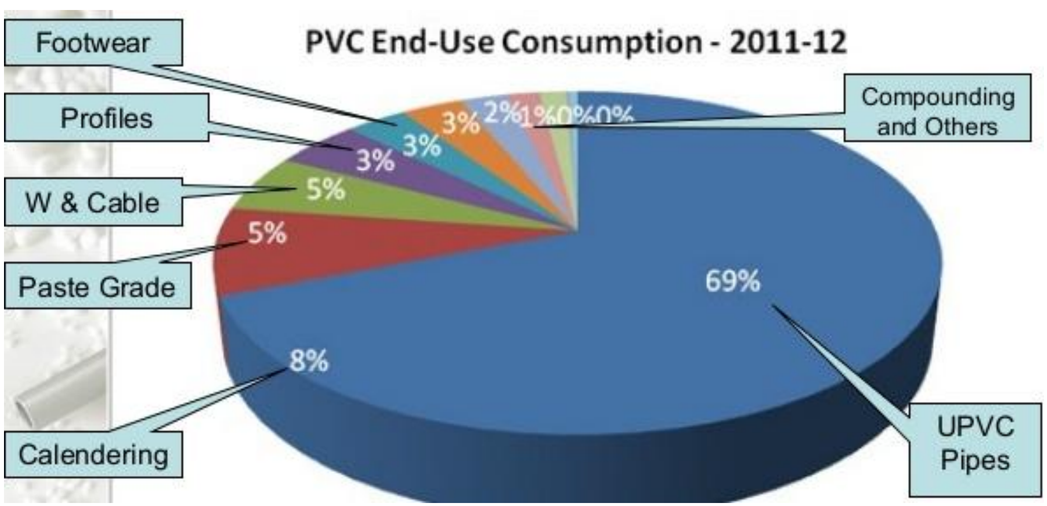

| | |
|---|---|
| World $Cl_2$ | 56 ,000,000 tonnes |

Toluene Di Isocynate

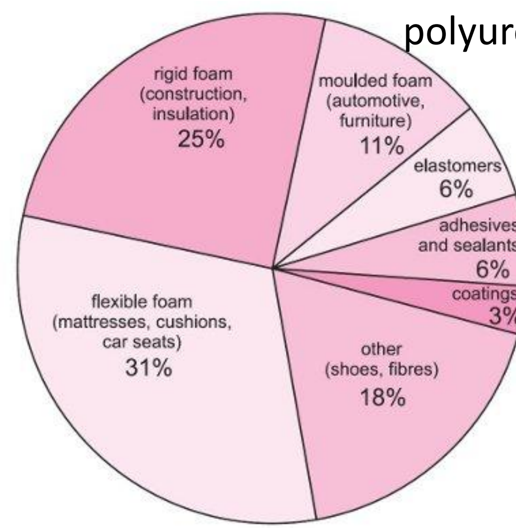
Methylene Diphenyl di Isocynate


Ethylene Di Chloride

Vinyl chloride monomer




polyurethane



# Halogen displacement reactions

One of the unique reactions of halogens is the displacement reaction in which a more reactive halogen will displace a lesser reactive halogen from its salt dissolved in water. In practice these reactions are carried out for chlorine, bromine and iodine as fluorine gas is too reactive to handle and reacts with water explosively. Selective evolution of $Br_2$ from a mixture of NaCl and NaBr by passing chlorine is one of the industrial uses of this reaction.

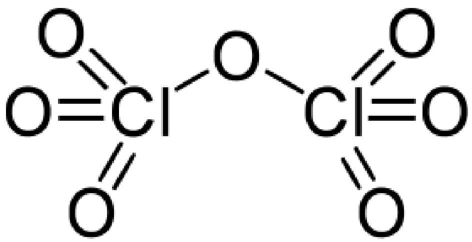
$$Cl_2 + 2\,NaBr \xrightarrow[H_2O]{} 2\,NaCl + Br_2$$

$$Cl_2 + 2\,NaI \xrightarrow[H_2O]{} 2\,NaCl + I_2$$

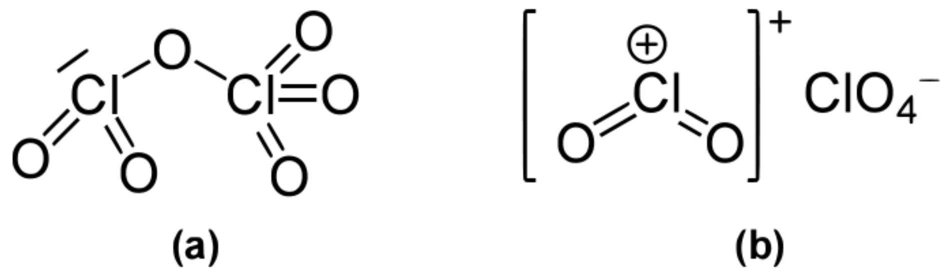
$$Br_2 + 2\,NaI \xrightarrow[H_2O]{} 2\,NaBr + I_2$$

**Chlorine: Unique properties**

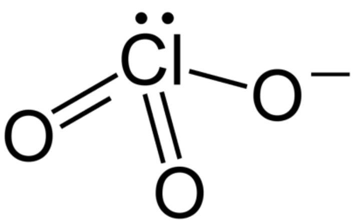
Chlorine shows oxidation states 7, 6, 5, 4, 3, 2, 1, 0, −1 and is also a good oxidizing agent.



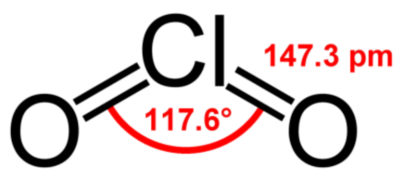
Dichlorine heptoxide



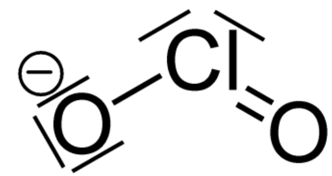

Dichlorine hexoxide



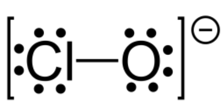
Chlorate



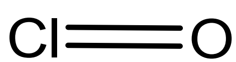

Chlorine dioxide



Chlorite



hypochlorite

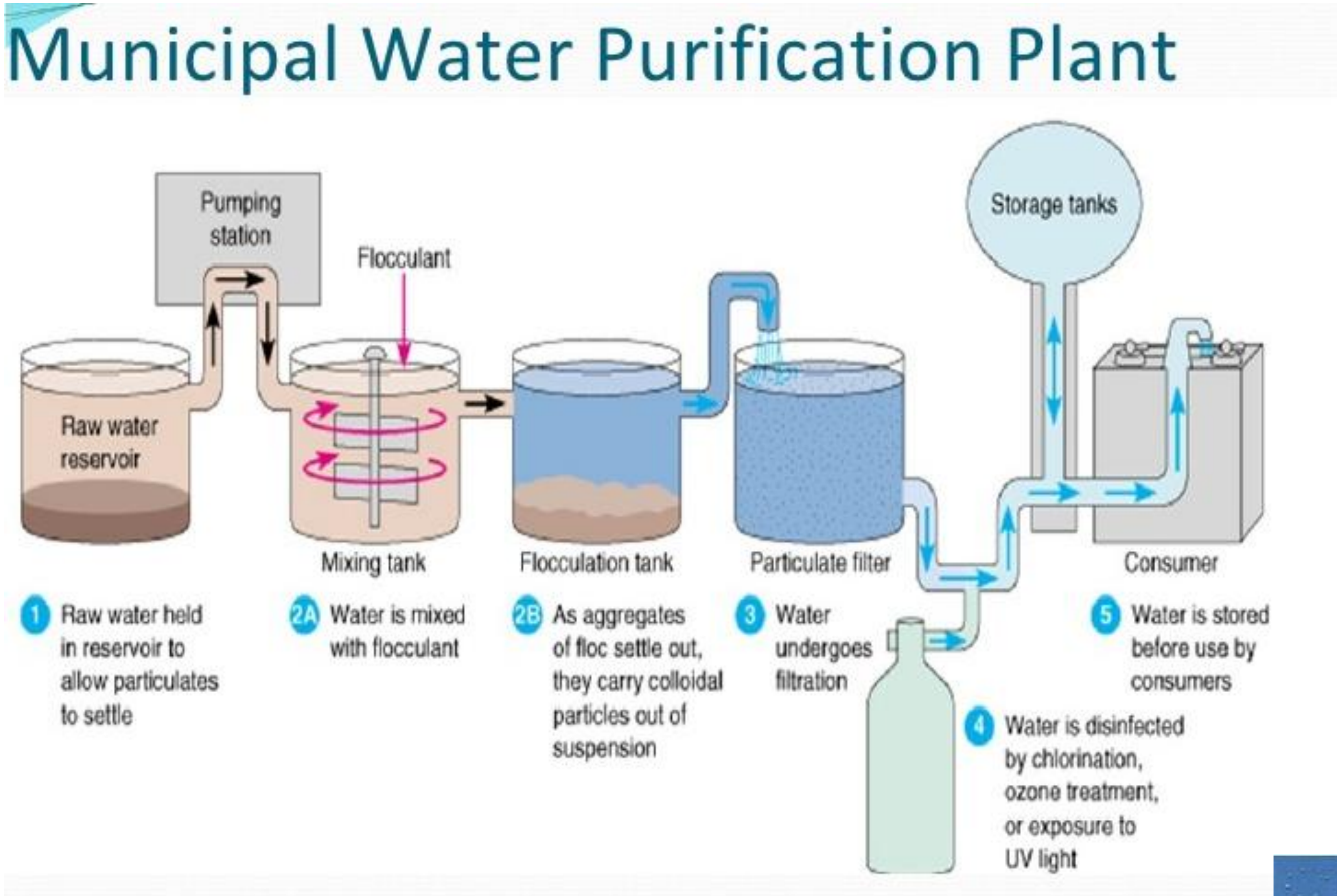


Chlorine monoxide

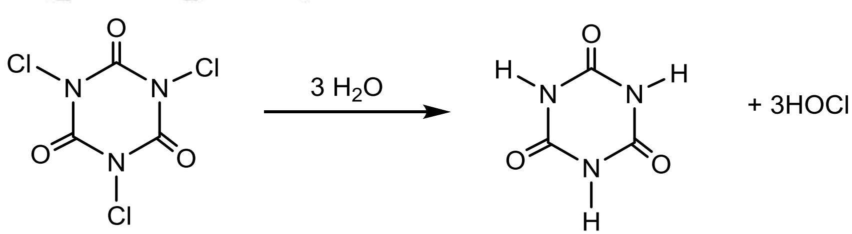
Chlorine

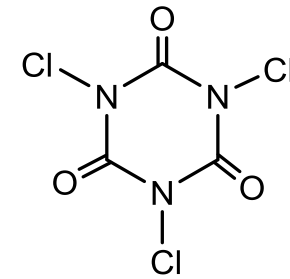
Chloride

# Chlorine gas in water purification




$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

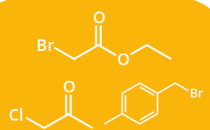


TCICA: Swimming pool chlorine tablets

# CHEMICAL WARFARE ☠ WORLD WAR I

WORLD WAR I IS SEEN AS THE DAWN OF MODERN CHEMICAL WARFARE, WITH A VARIETY OF DIFFERENT CHEMICAL AGENTS BEING EMPLOYED ON A LARGE SCALE, RESULTING IN APPROXIMATELY 1,240,000 NON-FATAL CASUALTIES, AND 91,000 FATALITIES. A VARIETY OF POISONOUS GASES WERE USED THROUGHOUT THE CONFLICT, WITH EACH HAVING DIFFERING EFFECTS UPON VICTIMS.



## TEAR GASES

(ethyl bromoacetate, chloroacetone & xylyl bromide)

### SMELL & APPEARANCE

Both ethyl bromoacetate and chloroacetone are colourless to light yellow liquids with fruity, pungent odours. Xylyl bromide is a colourless liquid with a pleasant, aromatic odour.

### EFFECTS

Tear gases are what is known as 'lachrymatory agents' - they irritate mucous membranes in the eyes, mouth, throat & lungs, leading to crying, coughing, breathing difficulties, and temporary blindness.

### FIRST USED

**1914** In August 1914, the French forces used tear gas grenades against the German army, to little effect.

### ESTIMATED CASUALTIES

**0** fatal These gases were used to incapacitate enemies rather than to kill; symptoms commonly resolved within 30 minutes of leaving the affected area.

## CHLORINE

$Cl_2$

### SMELL & APPEARANCE

Chlorine is a yellow-green gas with a strong, bleach-like odour. Soldiers described its smell as 'a distinct mix of pepper and pineapple'.

### EFFECTS

Chlorine reacts with water in the lungs, forming hydrochloric acid. It can cause coughing, vomiting, and irritation to the eyes at low concentrations, and rapid death at concentrations of 1000 parts per million.

### FIRST USED

**1915** Used by German forces at Ypres in April 1915. British forces used it for the first time at Loos in September.

### ESTIMATED CASUALTIES

**>1,100** number of fatalities in first use of chlorine at Ypres

Chlorine was devastating as troops were initially unequipped to deal with it. Later, gas masks limited its effectiveness.



## PHOSGENE & DIPHOSGENE

(carbonyl dichloride & trichloromethane chloroformate)

### SMELL & APPEARANCE

Phosgene is a colourless gas with a musty odour comparable to that of newly mown hay or grass. Diphosgene is a colourless, oily liquid.

### EFFECTS

React with proteins in lung alveoli, causing suffocation. Cause coughing, difficulty breathing and irritation to the throat & eyes. Can cause delayed effects, not evident for 48hrs, including fluid in the lungs & death.

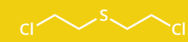
### FIRST USED

**1915** In December 1915, the German forces used phosgene against the British at Ypres.

### ESTIMATED CASUALTIES

**85%** of all gas-related fatalities in WWI

It's estimated 85% of all gas-related fatalities in World War I resulted from phosgene and disphosgene, which were both used to fill artillery shells.



## MUSTARD GAS

(bis(2-chloroethyl) sulfide)

### SMELL & APPEARANCE

When pure, mustard gas is a colourless and odourless liquid, but it's used as a chemical agent in impure form. These are yellow-brown in colour and have an odour resembling garlic or horseradish.

### EFFECTS

Powerful irritant and vesicant (blistering agent) that can damage the eyes, skin, & respiratory tract. Causes chemical burns on contact with skin. Forms intermediates that react with DNA leading to cell death.

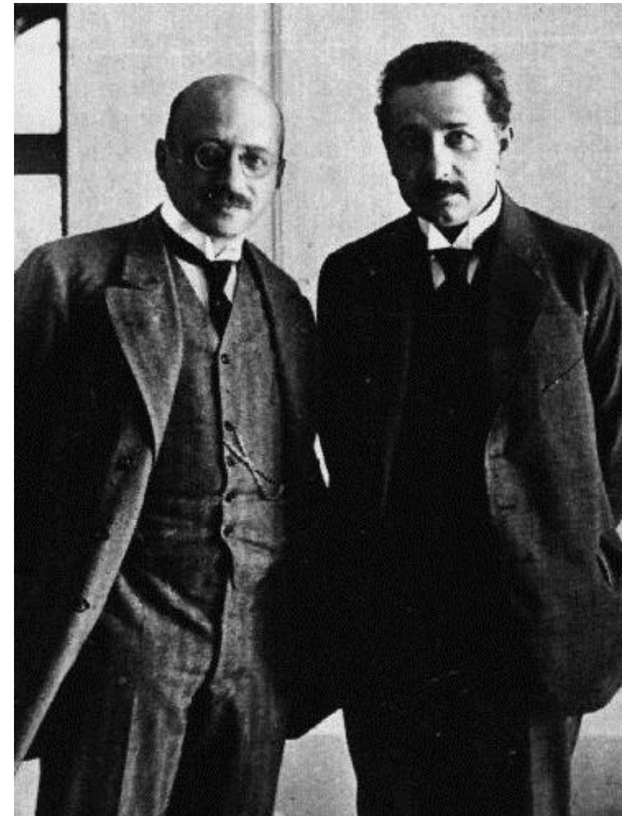
### FIRST USED

**1917** On 12th July 1917, German forces used mustard gas against the British at Ypres.

### ESTIMATED CASUALTIES

**2-3%** mortality rate of mustard gas casualties

The mortality rate of mustard gas casualties was low, but its effects were debilitating, and patients required elaborate care.



# Halogen free radicals

| Dihalogen | Bond dissociation energy kJ/mol E | Bond distance pm | Caluclated wavelength of light capable of breaking the bond λ |
|---|---|---|---|
| F2 | 159 | 143 | 752 |
| Cl2 | 243 | 199 | 492 |
| Br2 | 193 | 228 | 620 |
| I2 | 151 | 266 | 792 |

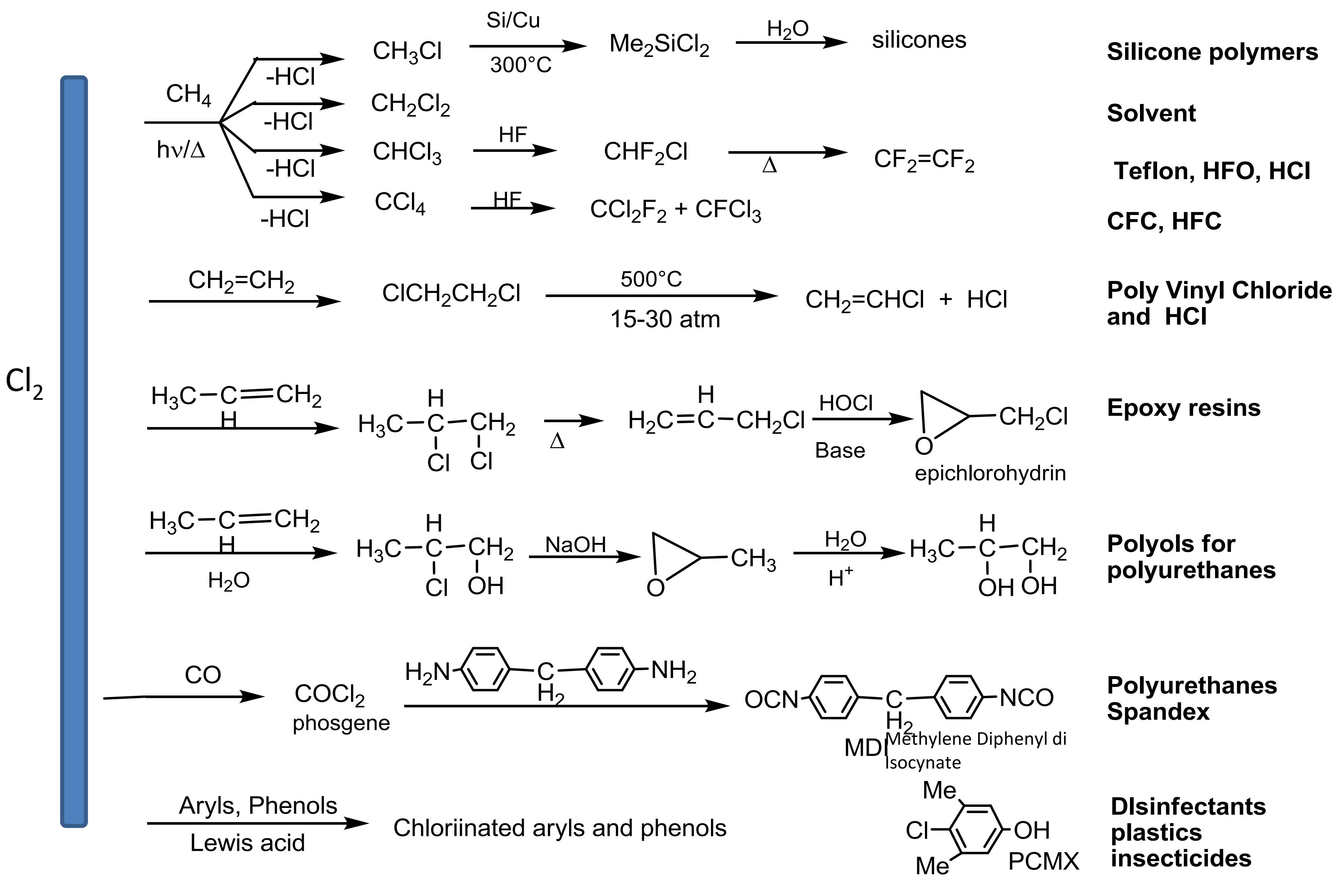
$$E = hv = Na \times {}^{hc}/_{\lambda}$$

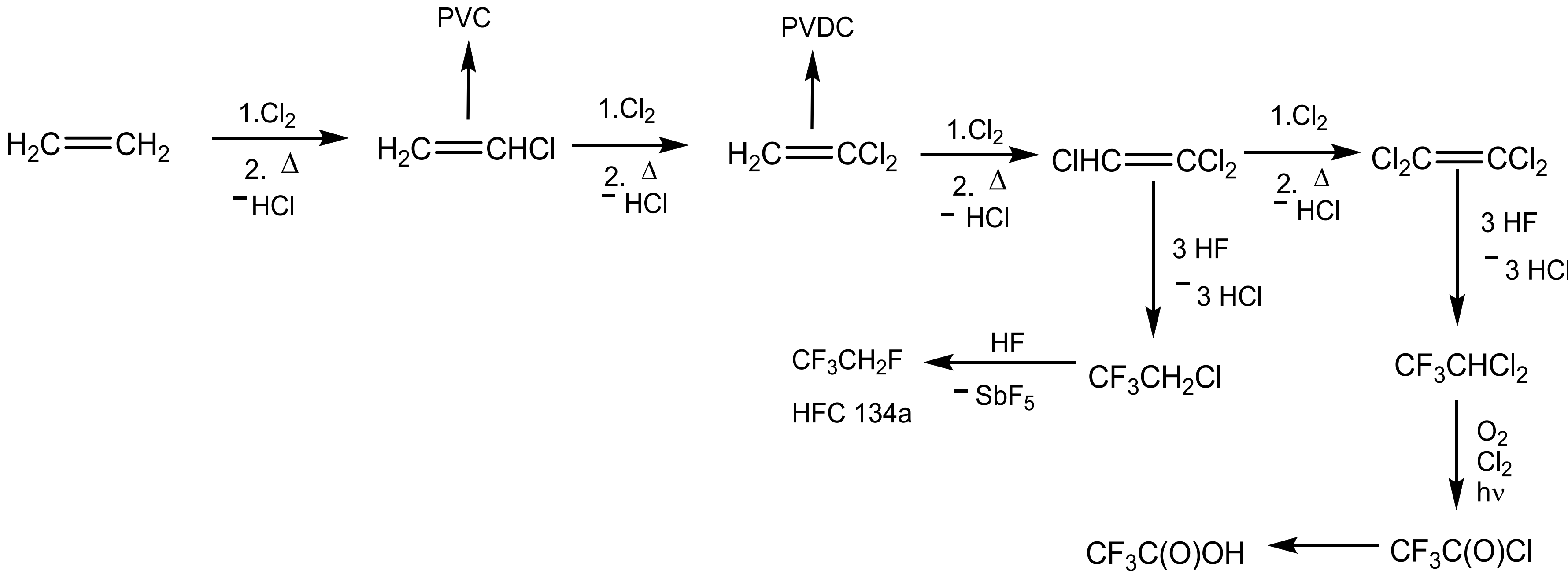
$$\frac{6.023 \times 10^{23} \times 3.0 \times 10^{8} \times 6.626 \times 10^{-34}}{E}$$

| Color | Wavelength |
|---|---|
| violet | 380–450 nm |
| blue | 450–495 nm |
| green | 495–570 nm |
| yellow | 570–590 nm |
| orange | 590–620 nm |
| red | 620–750 nm |

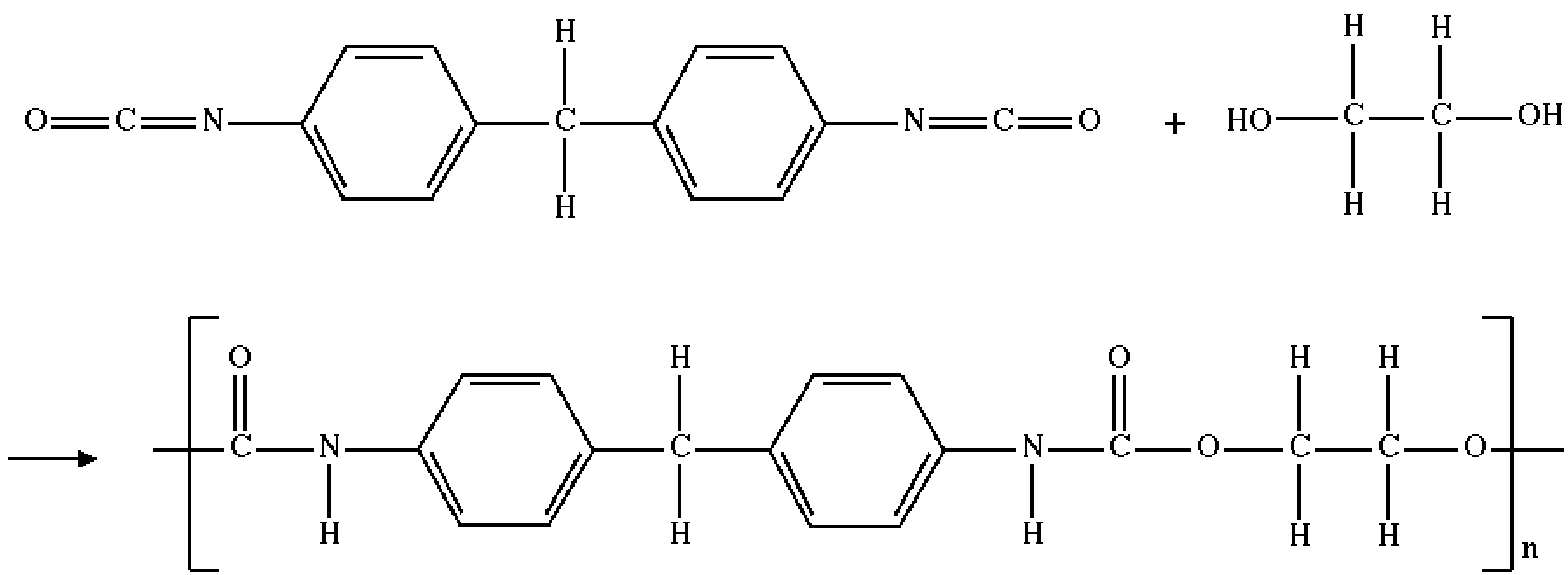
The reactions of fluorine, chlorine, bromine, and iodine with methane are quite different. Fluorine is the most reactive. If no precautions are taken, a mixture of fluorine and methane explodes. The reaction between methane and chlorine is easily controllable and occurs with UV, while bromine reaction happens with incandescent light bulb. Iodine, on the other hand, does not react with methane as the reaction is thermodynamically not favoured.

| Reaction ΔG (Kcal/mol) | F2 | Cl2 | Br2 | I2 |
|---|---|---|---|---|
| $CH_4 + X_2 \longrightarrow CH_3X + HX$ | -103 | -25 | -16 | +13 |

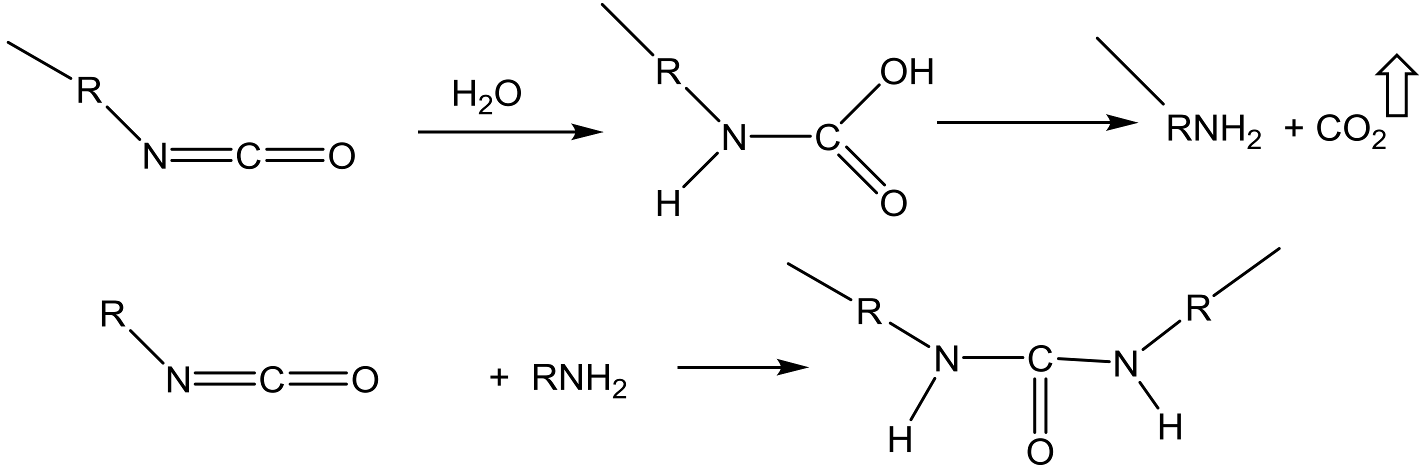

Cl2
CH4
hν/Δ
-HCl
-HCl
-HCl
-HCl
CH3Cl
Si/Cu
300°C
Me2SiCl2
H2O
silicones
Silicone polymers
CH2Cl2
Solvent
CHCl3
HF
CHF2Cl
Δ
CF2=CF2
Teflon, HFO, HCl
CCl4
HF
CCl2F2 + CFCl3
CFC, HFC
CH2=CH2
ClCH2CH2Cl
500°C
15-30 atm
CH2=CHCl + HCl
Poly Vinyl Chloride and HCl
H3C−C(H)=CH2
H3C−CH(Cl)−CH2Cl
Δ
H2C=C(H)−CH2Cl
HOCl
Base
CH2Cl
O
epichlorohydrin
Epoxy resins
H3C−C(H)=CH2
H2O
H3C−CH(Cl)−CH2OH
NaOH
CH3
O
H2O
H+
H3C−CH(OH)−CH2OH
Polyols for polyurethanes
CO
COCl2
phosgene
H2N
C
H2
NH2
OCN
NCO
MDI
Methylene Diphenyl di Isocynate
Polyurethanes Spandex
Aryls, Phenols
Lewis acid
Chloriinated aryls and phenols
Me
Cl
OH
Me
PCMX
DIsinfectants plastics insecticides


PVC
PVDC
1.Cl2
2. Δ
- HCl
3 HF
- 3 HCl
HF
- SbF5
O2
Cl2
hν
CF3CH2F
HFC 134a
CF3CH2Cl
CF3CHCl2
CF3C(O)OH
CF3C(O)Cl

18%

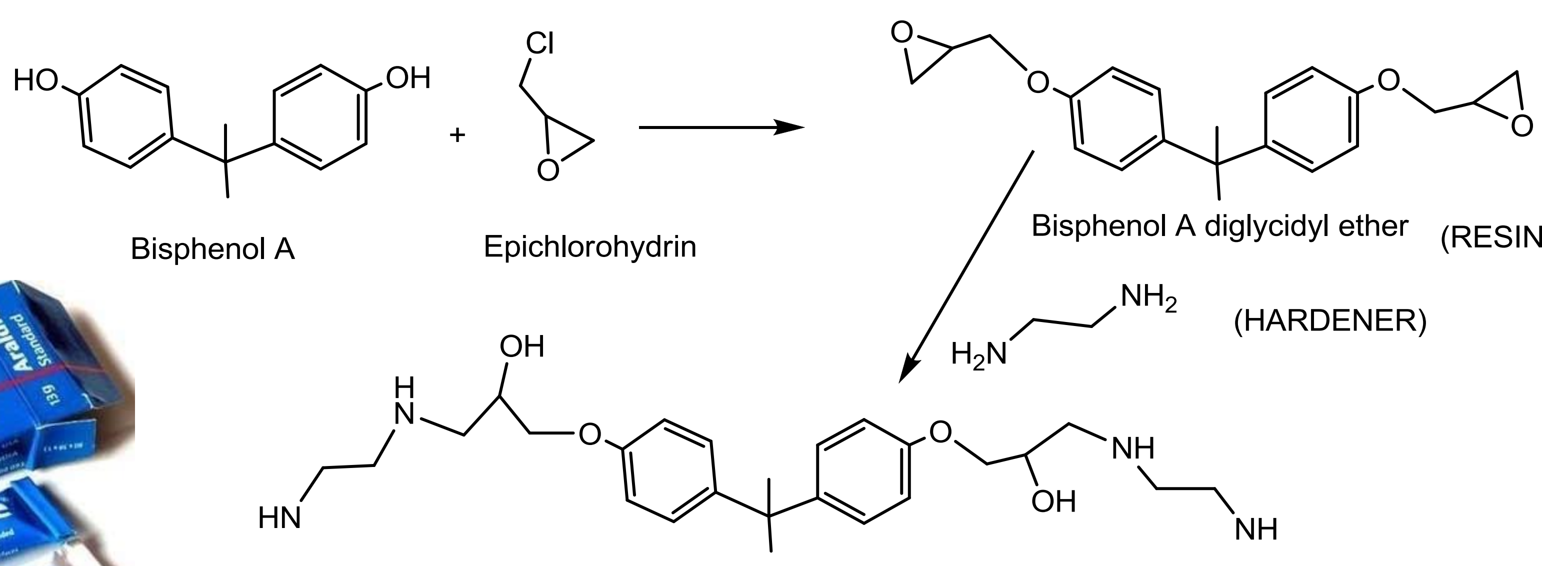


How foam is formed in polyurethanes: Blowing agents

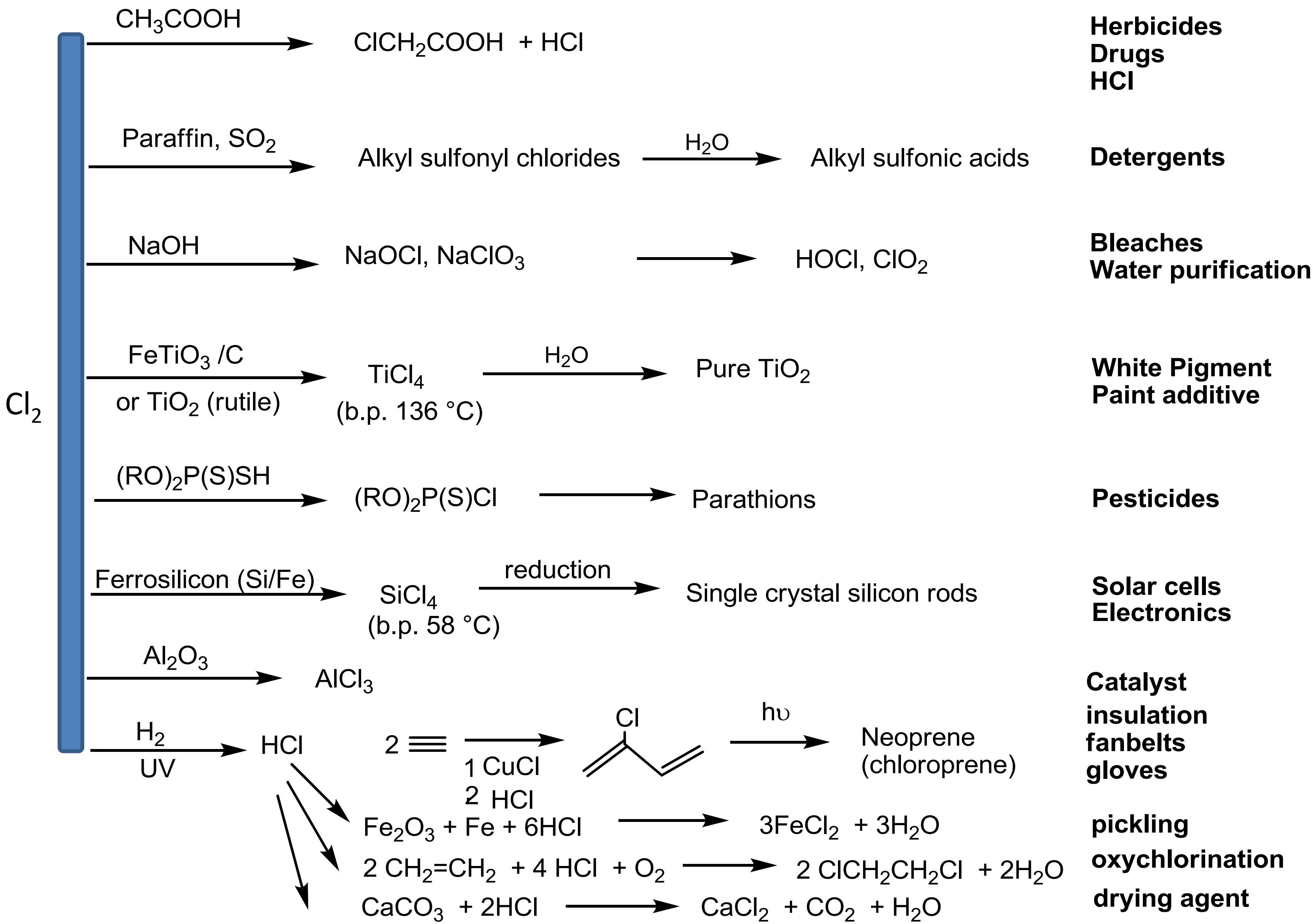



External blowing agents , CFC, HFC, HCFC, HFO, Hydrocarbons (Pentane) etc

4%




Hardened eposy resin



Cl2
CH3COOH
ClCH2COOH + HCl
Herbicides
Drugs
HCl
Paraffin, SO2
Alkyl sulfonyl chlorides
H2O
Alkyl sulfonic acids
Detergents
NaOH
NaOCl, NaClO3
HOCl, ClO2
Bleaches
Water purification
FeTiO3 /C
or TiO2 (rutile)
TiCl4
(b.p. 136 °C)
H2O
Pure TiO2
White Pigment
Paint additive
(RO)2P(S)SH
(RO)2P(S)Cl
Parathions
Pesticides
Ferrosilicon (Si/Fe)
SiCl4
(b.p. 58 °C)
reduction
Single crystal silicon rods
Solar cells
Electronics
Al2O3
AlCl3
Catalyst
H2
UV
HCl
2
1 CuCl
2 HCl
Cl
hυ
Neoprene
(chloroprene)
insulation
fanbelts
gloves
Fe2O3 + Fe + 6HCl
3FeCl2 + 3H2O
pickling
2 CH2=CH2 + 4 HCl + O2
2 ClCH2CH2Cl + 2H2O
oxychlorination
CaCO3 + 2HCl
CaCl2 + CO2 + H2O
drying agent

The Rochow Muller Process

$CH_3OH + HCl \rightarrow CH_3Cl$

$$CH_3Cl + Si/Cu\ (9:1) \xrightarrow{300\ °C} (CH_3)_nSiCl_{4-n}$$

| $Me_2SiCl_2$ | MeH $SiCl_2$ | $MeSiCl_3$ | $Me_3SiCl$........... |
|---|---|---|---|
| 80% | 3% | 8% | 3% |

**The first chain reaction discovered was a chemical chain reaction. It was discovered in 1913 by Max Bodenstein, who saw a mixture of chlorine and hydrogen gases explode when triggered by ultra violet light of 490-470 nm or stronger. The chain reaction mechanism was fully explained in 1918 by Walther Nernst.**

$$Cl_2 + h\nu \rightarrow 2Cl \qquad \text{initiation}$$

$$\left.\begin{array}{l} Cl + H_2 \rightarrow HCl + H \\ H + Cl_2 \rightarrow HCl + Cl \end{array}\right\} \text{propagation}$$

$$\left.\begin{array}{l} Cl + wall \rightarrow 1/2Cl_2 \\ Cl + Cl + M \rightarrow Cl_2 + M \\ H + O_2 + M \rightarrow HO_2 + M \end{array}\right\} \text{termination}$$

1. Initiation reaction

$$Cl_2 \xrightarrow{h\nu} 2\ Cl\bullet$$

2. Chain propagation

$$Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet$$

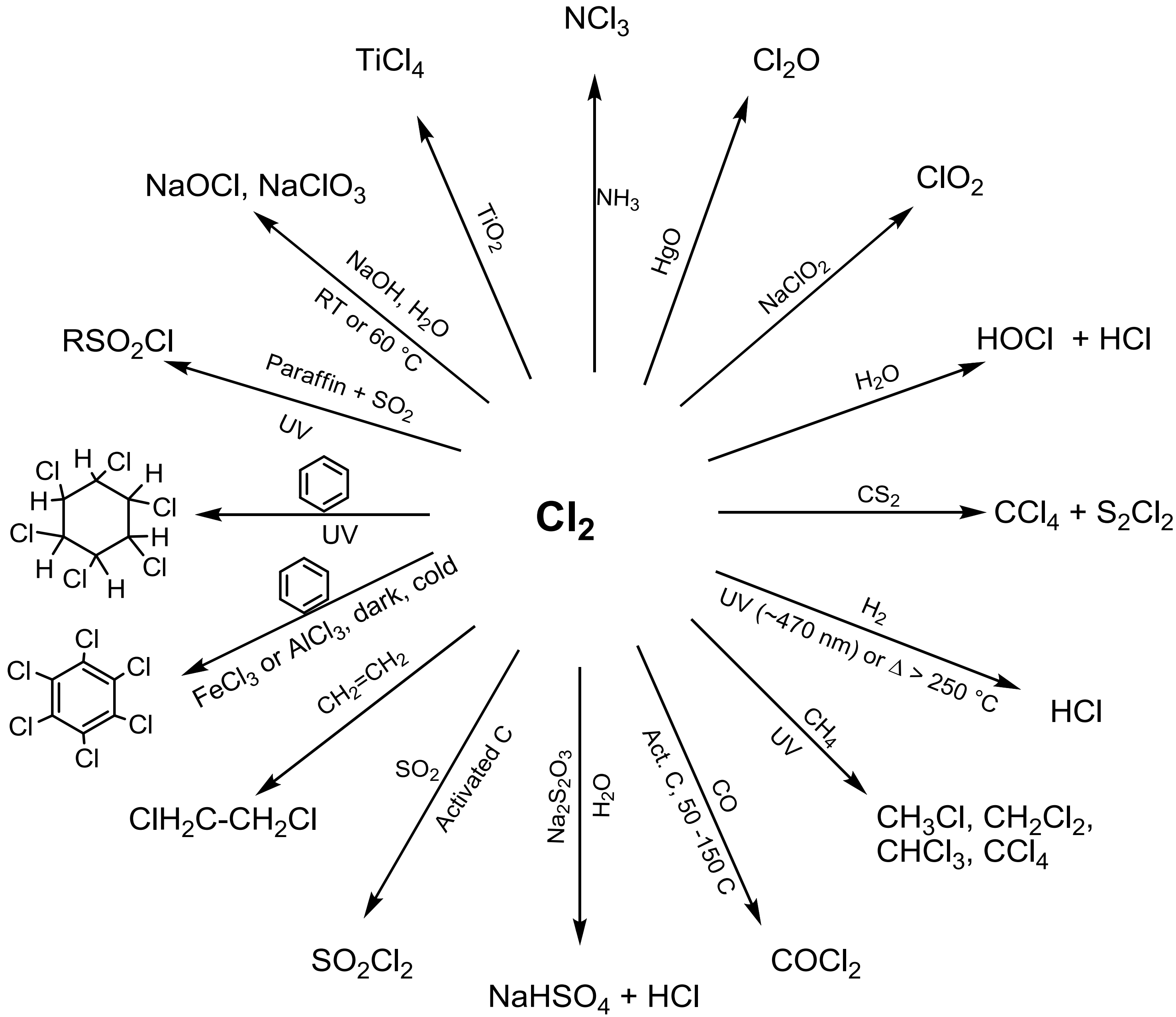
$$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$$

3. Chain termination reactions

$$Cl\bullet + Cl\bullet \rightarrow Cl_2$$

$$CH_3\bullet + CH_3\bullet \rightarrow CH_3-CH_3$$

$$Cl\bullet + CH_3\bullet \rightarrow CH_3Cl$$

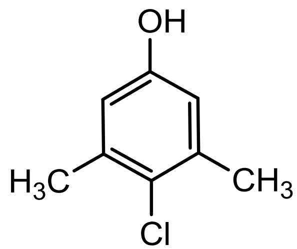


Cl2
NCl3
NH3
TiCl4
TiO2
Cl2O
HgO
ClO2
NaClO2
NaOCl, NaClO3
NaOH, H2O
RT or 60 °C
HOCl + HCl
H2O
RSO2Cl
Paraffin + SO2
UV
CCl4 + S2Cl2
CS2
UV
H
Cl
FeCl3 or AlCl3, dark, cold
HCl
H2
UV (~470 nm) or Δ > 250 °C
CH2=CH2
ClH2C-CH2Cl
CH4
UV
CH3Cl, CH2Cl2,
CHCl3, CCl4
SO2
Activated C
SO2Cl2
Na2S2O3
H2O
NaHSO4 + HCl
CO
Act. C, 50 -150 C
COCl2

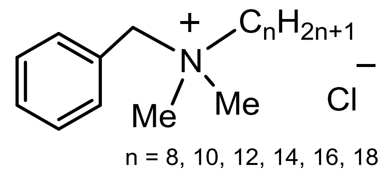
# Chlorine based Disinfectants and antiseptics

$NaClO$
Sodium hypochlorite

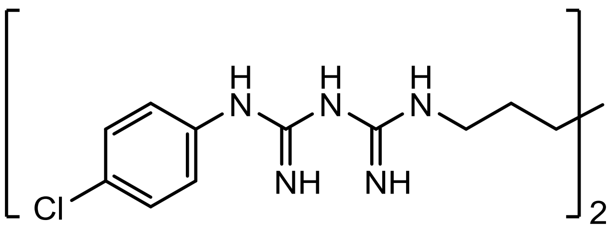
$Ca(ClO)_2$
Calcium hypochlorite



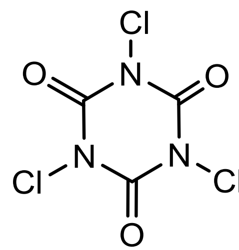
Para-Chloro-Meta-Xylenol



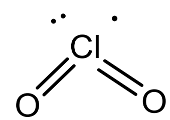
Benzalkonium chloride

Chlorhexidine



TCICA



Chlorine dioxide






# Antoine-Germain Labarraque

Catguts are strings of high tensile strength made out of processed sheep intestines. In 1820, the French *Society for Encouraging National Industry* offered a prize of 1500 francs for discovering a method which could prevent the putrefaction of catguts. **Antoine-Germain Labarraque,** a French chemist and pharmacist received this coveted prize as he showed that chlorinated bleaching solutions ( $NaClO$, $Ca(ClO)_2$) not only removed the smell of putrefaction of animal tissue decomposition, but also retarded the decomposition thus helping the catgut industry. His bleaching and disinfecting solution was named *Eau de Javel* (Javel water) and later as *Eau de Labarraque.*

King Louie the XVIII of France, (reinstated as king after his brother and wife were guillotined during French revolution) died in 1824 and at that time he was severely affected by gangrene of both his legs. During his last days, his legs were emanating foul odour due to decaying flesh and after death it was unbearable for those standing near the dead body. Labarraque was called in to find a way to remove the bad smell so that the king can be given a decent burial. He solved the issue by covering the dead body with a cloth soaked with his *chloro sodaic* solution

# Ignaz Semmelweis


**The life of Ignaz Semmelweis- 1818-1865**
**Saviour of Mothers**

**Statue in Budapest**

Even before Robert Koch and Louis Pasteur came out with their germ theory

ON THE

**DISINFECTING PROPERTIES**

OF

*LABARRAQUE'S PREPARATIONS*

OF

**CHLORINE;**

Particularly in preventing Putrefaction; in purifying Unwholesome Water and Tainted Provisions; in correcting the atmosphere of Sick Chambers; in removing the noxious effluvia of Water Closets, Work Shops, Drains, Stables, Slaughter Houses, Prisons, Holds of Ships, &c. in destroying the Infection of Small Pox, Measles, Scarlet Fever, Plague, &c.

ALSO IN

*MEDICAL AND SURGICAL PRACTICE,*

AND IN

THE DISEASES OF HORSES,

WITH AN

**APPENDIX BY THE TRANSLATOR.**

*Translated from the French,*

By JAMES SCOTT, Surgeon.

*THIRD EDITION.*

"We think Mr. Scott has done the Public a material service by translating this little Treatise; and we recommend it, therefore, with pleasure, to the notice of our Readers." *Lancet*, Vol. 9, Page 179.

**London:**

Printed for J. Scott, by W. Glendinning, 25, Hatton Garden; and Published by S. Highley, 174, Fleet Street.

1828.

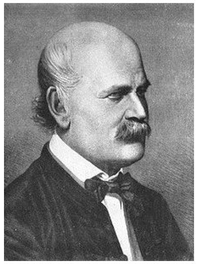
GENERAL ARTICLE

## Chlorine and the Chemistry of Disinfectants*

A Fascinating Journey—18th Century to the COVID Times

*N. Dastagiri Reddy and Anil J. Elias*

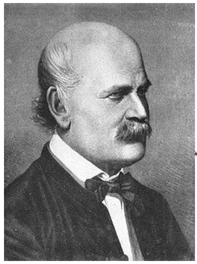
**Resonance : Journal of Science Education**
**March 2021**



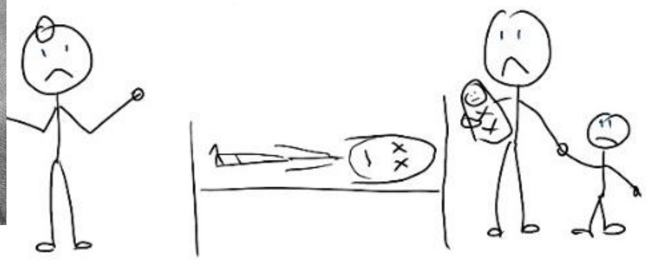
Dr Ignaz Semmelweis, in 1847 was working in the maternity department of the Vienna Lying-in Hospital, Austria. There were two obstetrical clinics dealing with childbirth in this hospital. One was manned by midwives and student midwives and the other was managed by medical students and doctors. The surprising observation Semmelweis made was that death of mothers due to puerperal fever ('childbed fever', a common reason for death of mothers during childbirth) was three times more in the clinic manned by doctors and medical students than the clinic manned by midwives! He even noticed that even women who gave birth at homes or streets were less affected by childbed fever. So the medical students and doctors were the culprits! His keen observation lead to the finding that the medical students were also practicing their surgical skills on cadavers/dead bodies in the autopsy room while attending to women giving childbirth. He concluded that the medical students carried "cadaverous particles" on their hands from the autopsy room to the patients they examined in the first obstetrical clinic. This explained why the student midwives in the second clinic, who were not engaged in autopsies and had no contact with corpses, saw a much lower mortality rate.

***Semmelweis being the hospital superintendant ordered that all doctors and house surgeons should wash their hands using a solution of chlorinated lime (Bleaching powder) between autopsy work and the examination of patients. He did this because he knew the effect of chlorine water from a previous work and found that this chlorine water worked best to remove the putrid smell of autopsy tissue.***

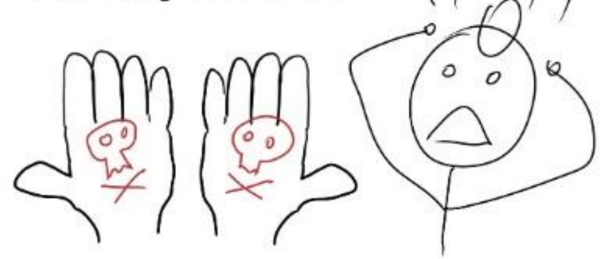
The practice of washing hands with chlorinated lime (solution of bleaching powder) immediately reduced the incidence of death by puerperal fever and finally to 0%. Semmelweis, confident with the success of his method started advocating the use of chlorinated lime or chlorine water to prevent childbed fever and death.



Mothers Were Dying



A Shocking Aha-Moment



Chlorine Hand Wash Strictly Requested

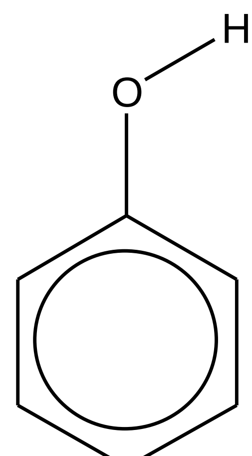
However … Rejected By Medical Authorities


Semmelweis was angry and upset by the indifference shown by the medical community and even wrote angry letters to well known European obstetricians, at times even calling them irresponsible murderers. His contemporaries thought he was mad, and in 1865, he was put in a mental asylum by his own colleagues. After two weeks, he died there of blood poisoning at the age of 47, possibly due to being severely beaten by guards as he tried to escape.

*That is why even now during Corona times we are asked to wash our hands with soap water or use sodium hypochlorite solution for disinfecting !!!*

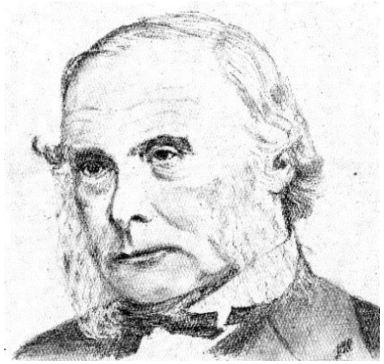
It is reputed that phenol's germ-killing power first came to notice in a bizarre way. Sailors who underwent amputations at sea appeared to have a higher survival rate than patients in hospital. This seemed to be due to the practice at sea of dipping the stump into molten tar to seal the wound. Tar contains, among other things, phenol

Captain Mackra, and the Pirate with a wooden leg.

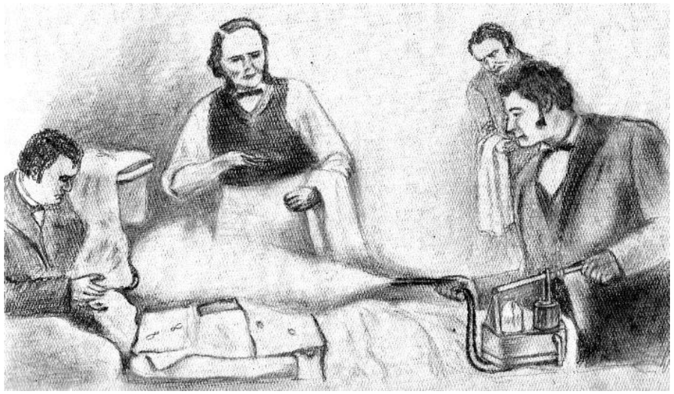



Adapted from Chemistry in the cupboard; RSC chemistry, UK , 2010

# Joseph Lister and Phenol as a disinfectant



The antiseptic property of phenol was discovered by a British surgeon Sir Joseph Lister. **Joseph Lister** wrote in the British medical journal, Lancet "*In the course of the year 1864, I was much struck with an account of the remarkable effects by carbolic acid upon the sewage of the town of Carlisle-preventing all odour from the lands irrigated with the refuse material but as it was stated, destroying the entozoa which usually infest cattle fed upon such pastures*"



Lister proposed in 1867 to surgeons that phenol should be rubbed on surgical instruments and hands of surgeons, and the bandages for covering the wounds should be soaked in it. He even suggested that while surgery is in progress, the operation theatre should be sprayed with phenol and phenol had to be sprayed also on the surgeons, to ward off germs.

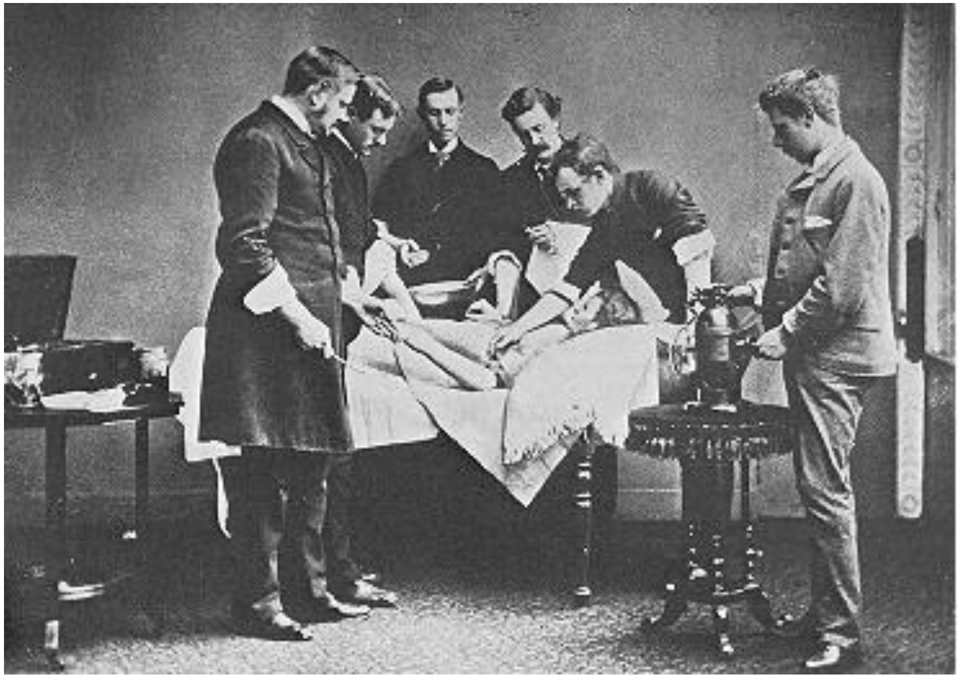
**Johann Mikulicz** from Breslau, Poland in 1897, began the practice of using a face mask for the first time. Mikulicz described his face mask as "*a piece of gauze tied by two strings to the cap, and sweeping across the face so as to cover the nose and mouth and beard*". This method of controlling the infection that gave importance to keeping all germs away, as opposed to destroying them with chemicals was taken up by doctors elsewhere in Europe.

## The Story of Dettol

### Antiseptics and disinfectants

Before the mid-1800s, major surgery was often a death sentence. Amputations of damaged limbs were carried out as a last resort but patients frequently died from post-operative infections.

This changed in the 1860s when Joseph Lister developed antiseptic surgery using carbolic acid to sterilise wounds and instruments. Lister was aware of the germ theory of infections developed by Louis Pasteur and others, and knew that carbolic acid (which we now call phenol) was able to kill germs

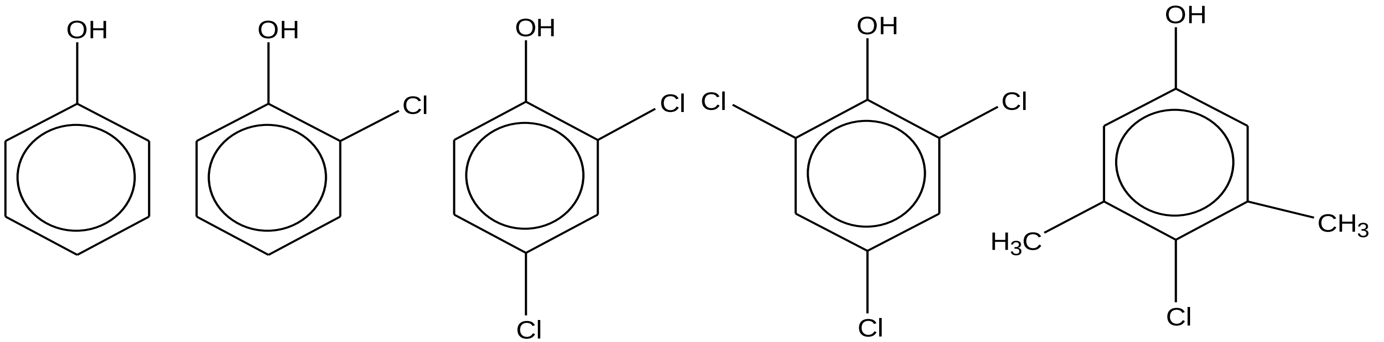


Adapted from Chemistry in the cupboard; RSC chemistry, UK , 2010

## Structure activity relationships

Phenol is effective at killing germs but is otherwise a far from ideal antiseptic as it causes nasty skin burns. One technique used by pharmaceutical chemists when faced with this sort of situation is to synthesise a number of compounds related to the substance that is known to be effective. This is in the hope that one or more of these compounds will be as active, or better, than the original but with fewer side effects (such as skin burning). Even better is the possibility of establishing a structure-activity relationship. This is a pattern which links some structural feature of the molecule with its pharmacological efficiency

- **the more methyl groups attached to a benzene ring, the better the germ-killing power, or**
- **the more electronegative a substituent, the less harmful to the skin.**




1 4 13 23 280

Increasing germ-killing power

Adapted from Chemistry in the cupboard; RSC chemistry, UK , 2010

In fact the structure-activity relationships that have been established for derivatives of phenol are:

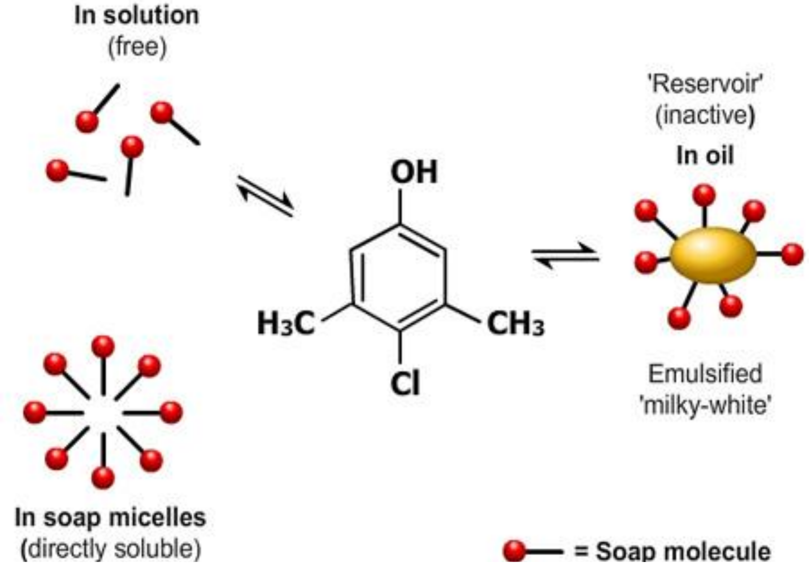
•the −OH group is required for activity;

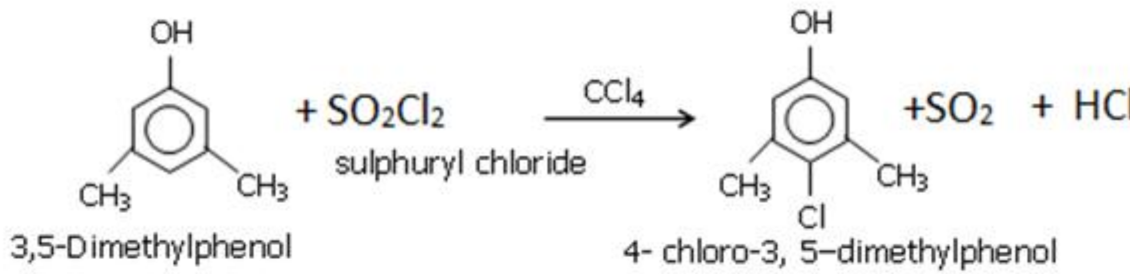
•activity increases with a halogen in the 4- position (ie opposite the −OH group in the ring);
•activity increases with alkyl substituents of increased chain length;
•increased substitution makes the compound less water-soluble; and
•increased substitution decreases toxicity to humans when taken by mouth.

Phenol is already an effective germicide, so a greater killing power is not really needed. What the greater efficiency of 4-chloro-3,5-dimethylphenol means is that much smaller concentration can be used and therefore fewer side-effects will be expected.

The active germ-killing ingredient in Dettol is in fact 4-chloro-3,5-dimethylphenol, also known by its non-systematic name *para*-chloro-*meta*-xylenol or PCMX

# Para chloro meta xylenol- PCMX


| Chemical Name | CAS No | Proportion (%w/w) |
|---|---|---|
| Chloroxylenol | 88-04-0 | 4.8 ( %w/v ) |
| Pine Oil | 8002-09-3 | <10 |
| Isopropyl alcohol | 67-63-0 | 10 - 30 |
| Other ingredients classified as not hazardous according to NOSCH | | to 100 |

Adapted from Chemistry in the cupboard; RSC chemistry, UK , 2010

**How does PCMX kill bacteria?**

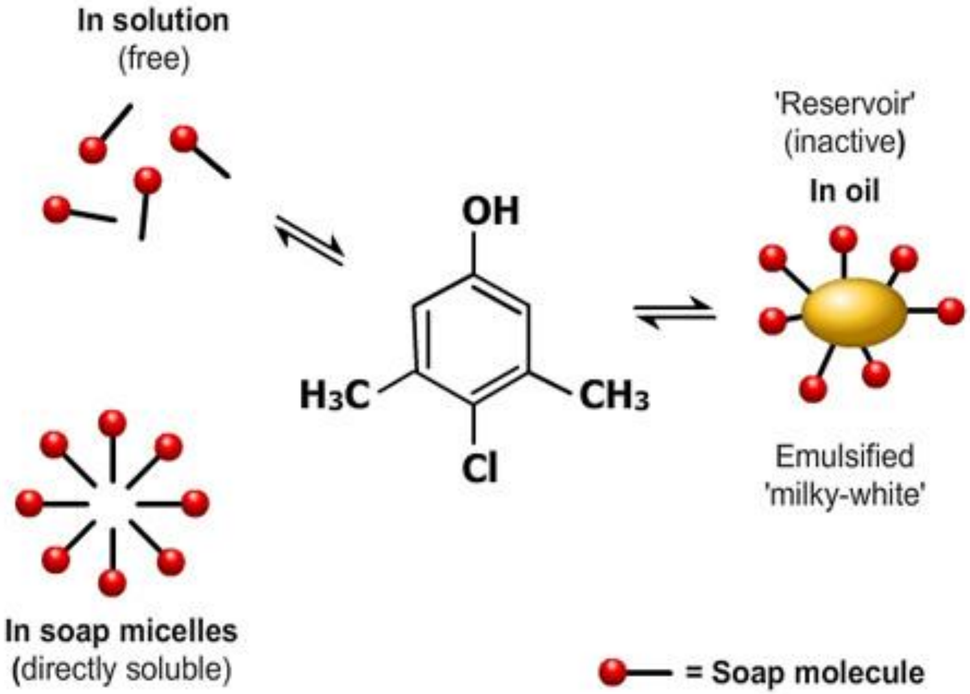
The detailed biochemistry of the action of PCMX and other phenol-based antibacterial agents is complex. However, very simply, they are understood to work by the −OH group of the molecule binding to proteins present on the cell membrane of bacteria, disrupting the cell membrane and allowing the contents of the cell to leak out.

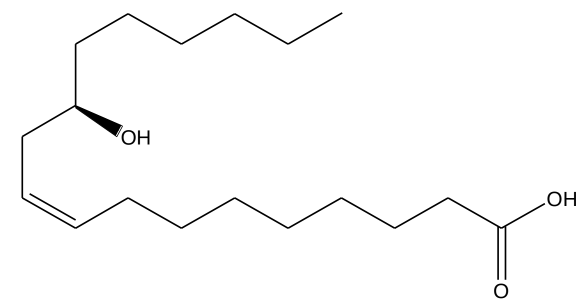
This allows more PCMX to enter the cell, binding further with proteins and enzymes, and effectively shutting down the cell's functions. At high concentrations of PCMX, the proteins and nucleic acids in the cell are coagulated and cease to function, leading to rapid cell death.

The p$K_a$ value is a measure of the strength of an acid. The larger the p$K_a$ value, the weaker the acid.

- PCMX p$K_a$ = 9.7; $K_a$ = 1.99 x $10^{-10}$ mol $dm^{-3}$
- phenol p$K_a$ = 9.9; $K_a$ = 1.28 x $10^{-10}$ mol $dm^{-3}$
- ethanol p$K_a$ = 15.9; $K_a$ = 7.9 x $10^{-15}$ mol $dm^{-3}$

In the phenoxide ion, $PhO^-$, the negative charge is spread over the benzene ring due to overlap of a p-orbital on the oxygen atom with the delocalised π-system of the benzene ring,




The soap used in Dettol is made from castor oil which contains ricinoleic acid

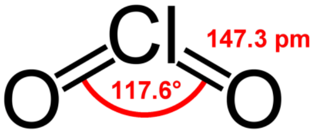
**On dilution in water, however, a cloudy liquid forms. This consists of droplets of pine oil containing dissolved PCMX. These are held dispersed in water by a layer of soap molecules arranged with their tails in the pine oil and their heads in the water, Figure 13. These droplets are big enough to scatter light, hence the cloudiness of the suspension which is called an emulsion. The PCMX in the droplets of pine oil is not available to kill bacteria - it is the free aqueous PCMX that does this. However, an equilibrium exists between the emulsified PCMX in the droplets and free PCMX dissolved in the water. As PCMX is used up in killing bacteria, more is released from the droplets to keep the aqueous PCMX concentration essentially constant.**

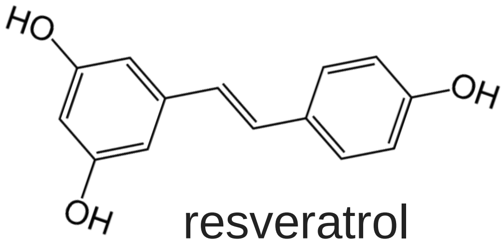
Adapted from Chemistry in the cupboard; RSC chemistry, UK , 2010

# Chlorine Dioxide

Best alternative for chlorine in industry and household use where one does not want harmful organochlorine side products to be formed during disinfection, purification etc. One of the most important qualities of chlorine dioxide is its high water solubility, especially in cold water. Chlorine dioxide does not hydrolyze when it enters water; it remains a dissolved gas in solution.

Chlorine dioxide has been termed as a chlorine free bleaching and water treatment agent. It is quite soluble in water (8g/lit) which is ten times more than the solubility of $Cl_2$ in water. Unlike $Cl_2$, it does not react with water. Its reaction in water is not pH dependent. For bleaching wood pulp it has been preferred over $Cl_2$ as it is a more selective oxidizer and less harmful side products are formed when it reacts. It does not chlorinate but only oxidize ( $ClO_2 \rightarrow ClO_2^-$ ) and that too more selective than ozone. In wine industry it is used instead of chlorine to prevent formation of chlorinated phenols



resveratrol

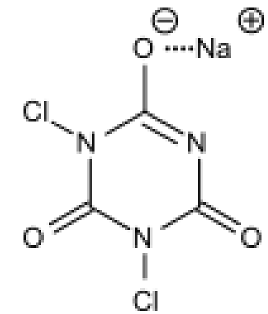
## Chlorine dioxide $ClO_2$

This yellowish-green gas crystallizes as bright orange crystals at −59 °C and boils at 11 °C. As one of several oxides of chlorine, it is a potent and useful oxidizing agent used in water treatment and in bleaching. The molecule $ClO_2$ has an odd number of valence electrons, and therefore, it is a paramagnetic radical. **It can explode at gas-phase concentrations greater than 30% volume in air decomposing into chlorine and oxygen.** The decomposition can be initiated by light, hot spots, chemical reaction, or pressure shock. Thus, chlorine dioxide gas is never handled in concentrated form.

| Compound | Reaction with $Cl_2$ | Reaction with $ClO_2$ |
|---|---|---|
| Water | HClO and HCl | No reaction |
| $CH_3CHO$ | $Cl_3CCHO$ | $H_3CC(O)OH$ |
| $NH_3$ | $NH_2Cl$, $NHCl_2$, $NCl_3$ | No reaction |
| $R_3N$ | $R_3NCl$+ | Oxidative dealkylation $R_2NH_2^+$, RCHO, $HClO_2$ |
| Cyanide | $(ClCN)_3$, Cyanuric chloride | $CNO^-$ ( below pH 10) or $CO_2$ +$N_2$ ( above pH10) |
| $H_2S$ | Colloidal Sulfur | $SO_4^{2-}$ |
| RSH | $RSO_2Cl$ or RSSR | Sulfonic acid and Sulfonates |
| Phenol | trichlorophenol | benzoquinone |
| Bromide | Bromine | No reaction |

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

| | Chlorine Dioxide (Potable Aqua) | Chlorine NaDCC (Oasis Plus) |
|---|---|---|
| **Cryptosporidium** | Highly Effective | Highly Effective |
| **Giardia** | Highly Effective | Highly Effective |
| **Viruses** | Highly Effective | Highly Effective |
| **Bacteria** | Highly Effective | Highly Effective |
| **Protozoa (most)** | Highly Effective | Highly Effective |
| **pH required** | Any pH | 5.5- 9 |
| **Water Temperature** | Above 64 deg. F | Above 64 deg. F |
| **Treatment Time** | 4 hours- (30 min. min.) | 10 Minutes |



Sodium dichloro Isocyanurate NaDCC ( has better water solubility than TCICA)

$$NaOCl + H_2O \rightarrow HOCl + NaOH$$

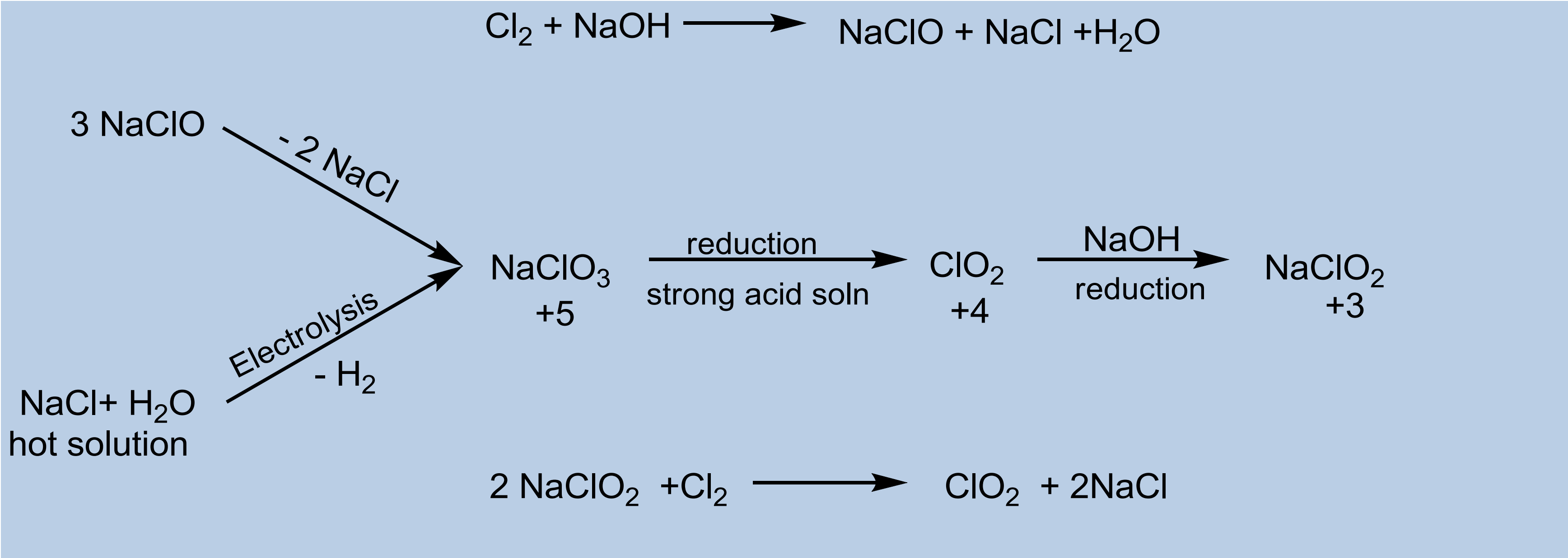
Sodium hypochlorite dispersion in water

$$NaCl_2(NCO)_3 + 2H_2O \leftrightarrow 2HOCl + NaH_2(NCO)_3 .$$

NaDCC dissolution in water

| Compound | Reaction with $Cl_2$ | Reaction with $ClO_2$ |
|---|---|---|
| Water | HClO and HCl | No reaction |
| action | Oxidation by ‘O’ | Oxidation by removal of e- |

**Chlorine Dioxide $ClO_2$**




$$2NaClO_3 + 2\,NaCl + 2H_2SO_4 \longrightarrow 2\,ClO_2 + Cl_2 + 2Na_2SO_4 + 2H_2O$$

$$6NaClO_3 + CH_3OH + 4H_2SO_4 \longrightarrow 6\,ClO_2 + CO_2 + 2Na_3H(SO_4)_2 + 5H_2O$$

$$NaClO_2 + 1/_2\,Cl_2 \longrightarrow ClO_2 + NaCl$$

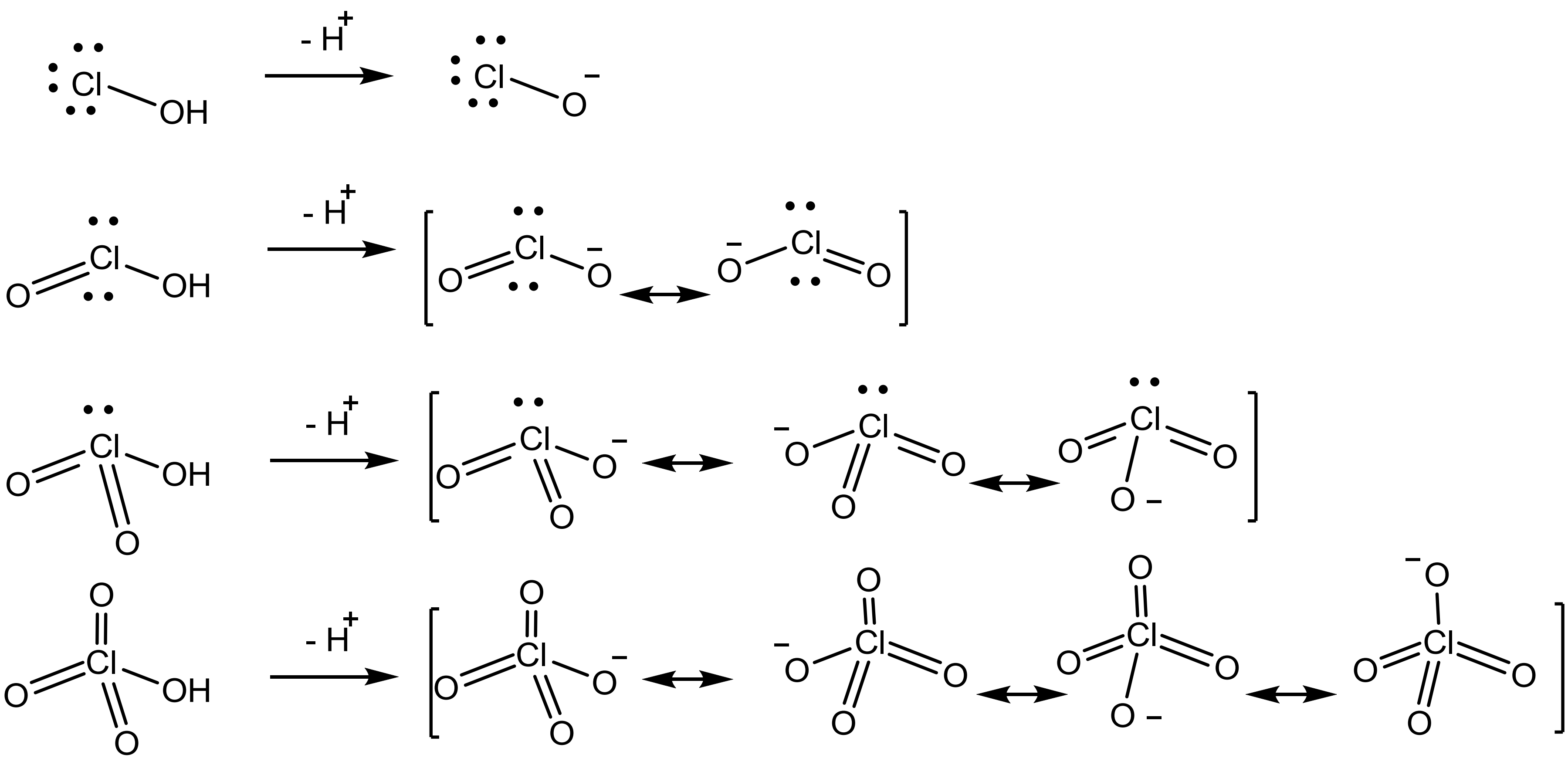
$$5\,NaClO_2 + 4HCl \longrightarrow 4\,ClO_2 + 5\,NaCl + 2H_2O$$

Since $ClO_2$ is difficult to handle and is also an explosive ,for all practical purposes it is generated from $NaClO_{2.}$ $NaClO_{2.}$ is produced worth over 18 million USD per year.

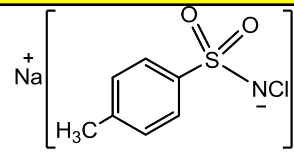
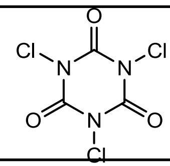
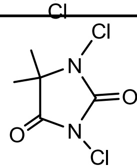
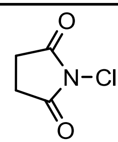
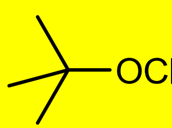
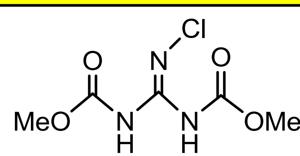
# Standard reduction potentials for halogens and halates

| | $E^0$ |
|---|---|
| $Cl_2(g) + 2e \longrightarrow 2Cl^-$ | 1.36 V |
| $Br_2(l) + 2e \longrightarrow 2\,Br^-$ | 1.09 V |
| $I_2(s) + 2e \longrightarrow 2\,I^-$ | 0.54 V |
| $2\,ClO_3^- + 12H^+ + 10e \longrightarrow Cl_2(g) + 6\,H_2O$ | 1.49 V |
| $2\,BrO_3^- + 12H^+ + 10e \longrightarrow Br_2(l) + 6\,H_2O$ | 1.48 V |
| $2\,IO_3^- + 12H^+ + 10e \longrightarrow I_2(s) + 6\,H_2O$ | 1.20 V |
| $ClO_2(l) + e \longrightarrow ClO_2^-$ | 0.95 V |

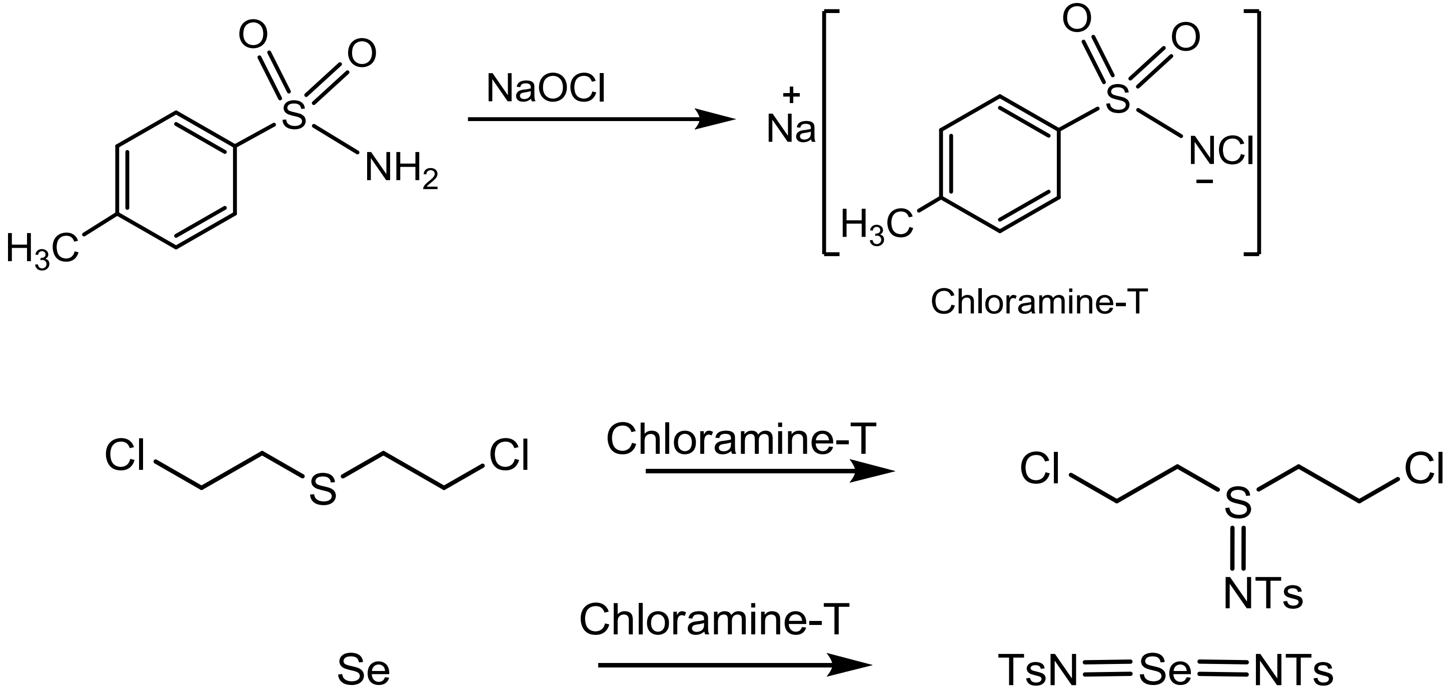
| **Oxidation state** | **Chlorine** | **Bromine** | **Iodine** | **Name of the acid** |
|---|---|---|---|---|
| +1 | $HClO$ | $HBrO$ | $HIO$ | Hypohalous |
| +3 | $HClO_2$ | - | - | Halous |
| +5 | $HClO_3$ | $HBrO_3$ | $HIO_3$ | Halic |
| +7 | $HClO_4$ | $HBrO_4$ | $HIO_4$, $H_5IO_6$ | Perhalic |



# Electrophilic Chlorinating Agents

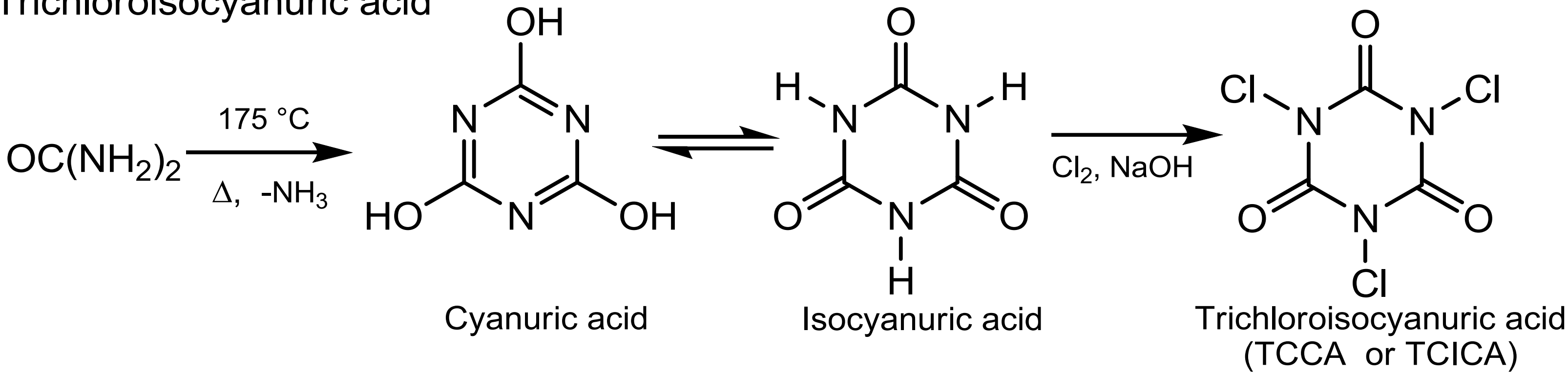
| Name/ Abbreviation | Structure | Physical constants (°C) | Advantages/ Disadvantages | Relative reactivity |
|---|---|---|---|---|
| Sulfuryl chloride | $SO_2Cl_2$ | b.p. 69.4 °C | Highly reactive, highly air sensitive, source of chlorine oxidizer | high |
| Chlorine gas | $Cl_2$ | b.p. – 34 °C | Highly reactive, Poor selectivity | high |
| Chloramine-T |  | m.p. 169 °C | Good as oxidant. Although electrophilic, products rarely have chlorine. | low |
| Trichloroisocyanuric acid [TCCA or TCICA] |  | m.p. 234 C | Inexpensive, stable can generate explosive $NCl_3$, | low |
| Dichlorodimethyl hydantoin [DCDMH or NDDH] |  | m.p. 132 °C | Inexpensive, easily degraded after chlorination, react violently with xylene | low |
| N-Chlorosuccinimide [NCS] |  | m.p. 151 °C | Expensive, high toxicology, reacts violently with alcohols | low |
| Tert butyl hypochlorite [tBuOCl] |  | b.p. 79.6° C /750 mm Hg | Decomposes during transportation; light, heat and moisture sensitive | high |
| Chloro(bismethoxycarbonyl)guanidine [Palau' chlor, CBMG] |  | m.p. 110 °C | Air stable free-flowing , functional group tolerant | low |

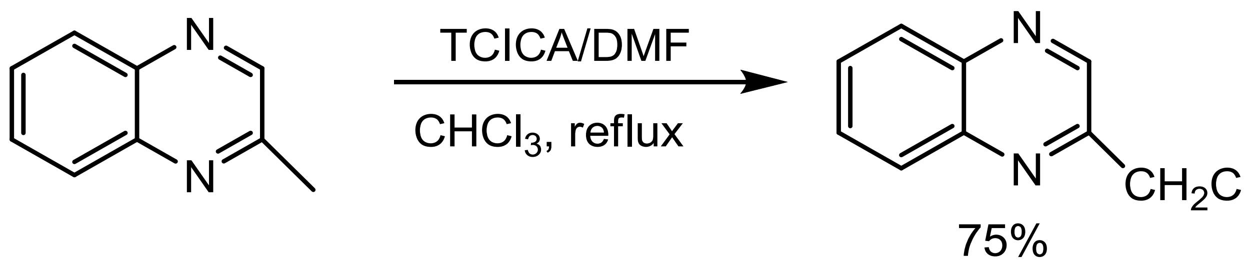
Chloramine-T

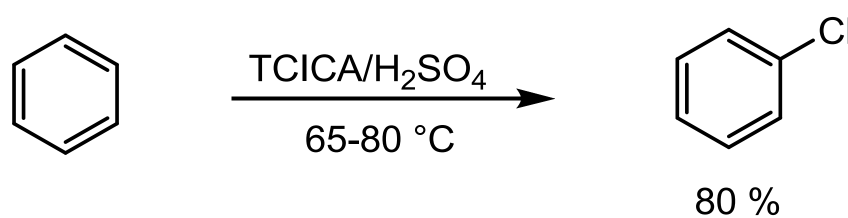



Although Chloramine-T has electrophilic chlorine present, it rarely does chlorination and often what it does is oxidation of the substrate resulting in a tosylimine

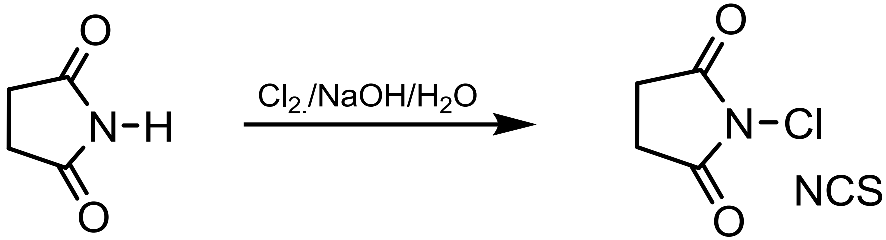
Trichloroisocyanuric acid

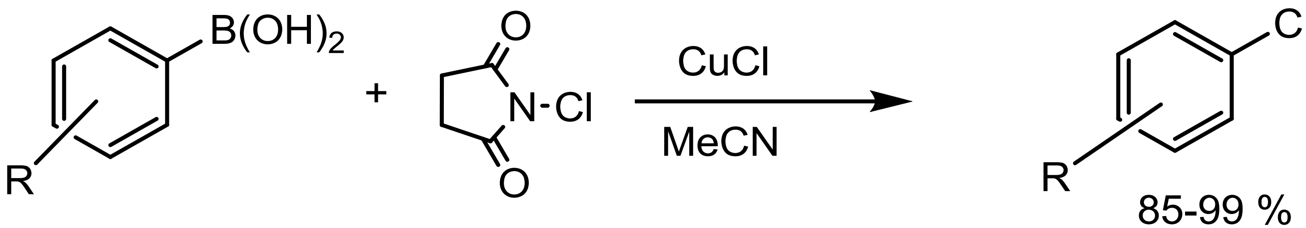


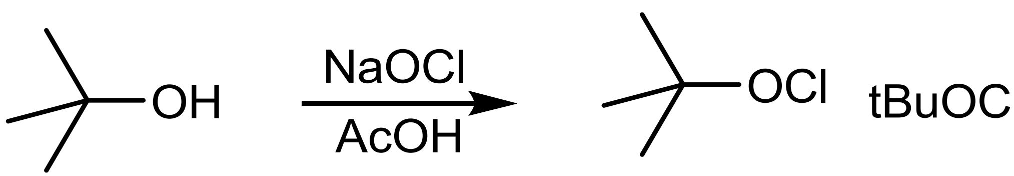



N-Chlorosuccinamide : Most Common

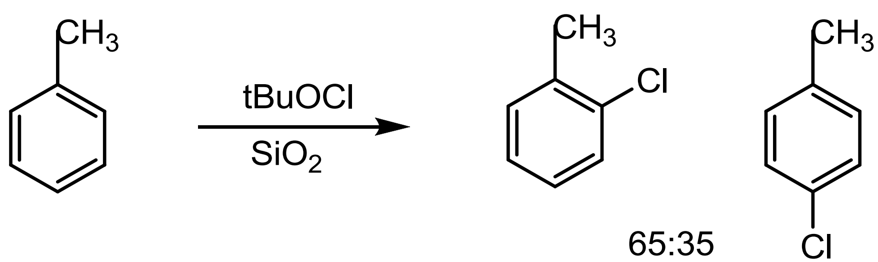


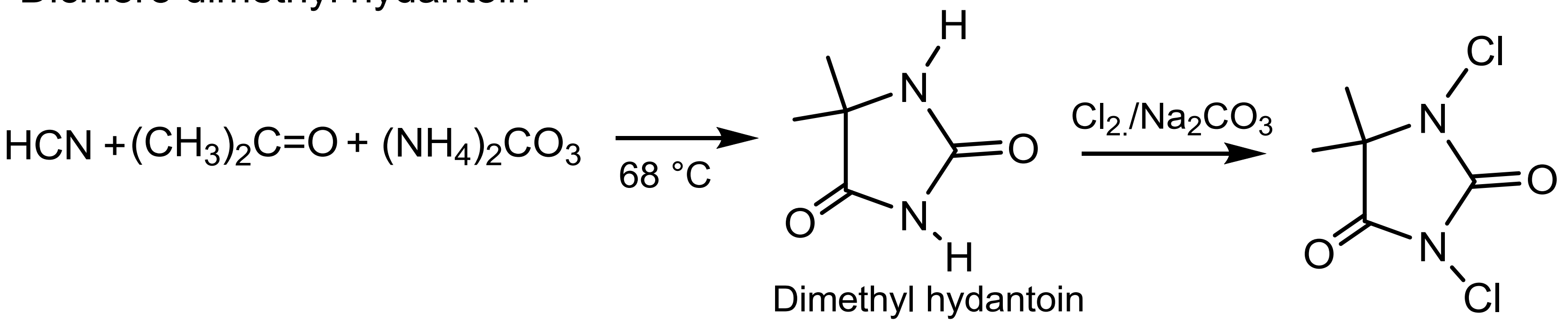

tert butyl hypochlorite



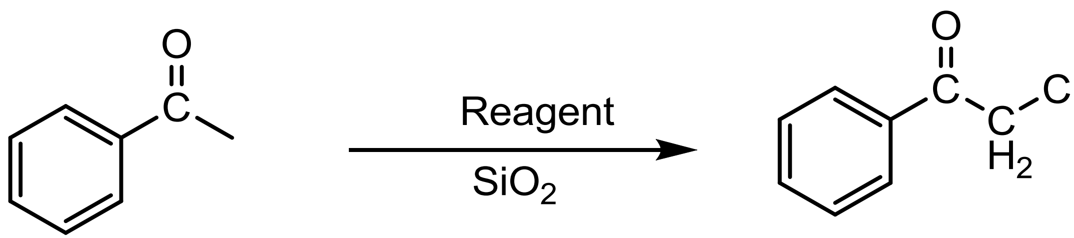

liquid b.p. 79.6 °C/750 mm Hg



# Dichloro dimethyl hydantoin



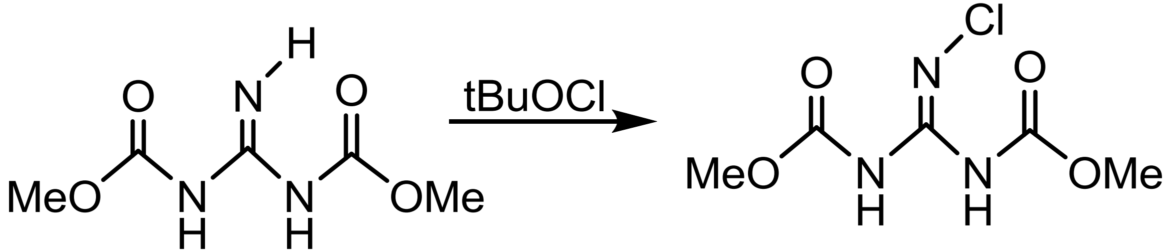

DCDMH or DDH




| | | |
|---|---|---|
| Reagent | DCDMH | 95% |
| | NCS | 70% |

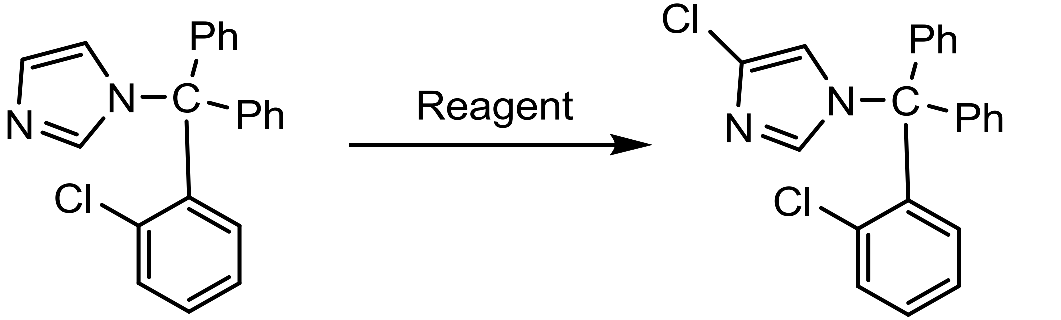
# 2014 : Chlorination of unsaturated heterocycles

Palau'chlor

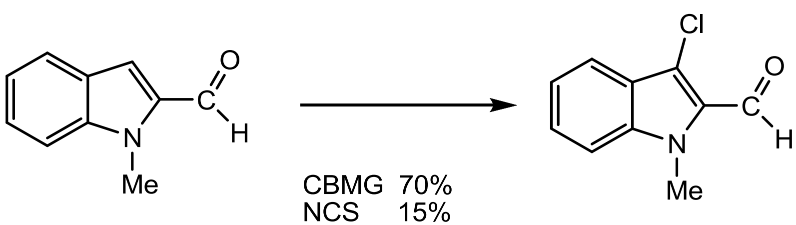


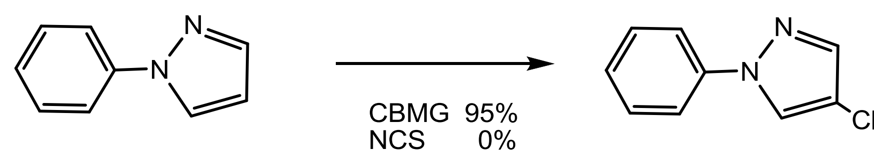

Chloro(bismethoxycarbonyl) guanidine

(CBMG)



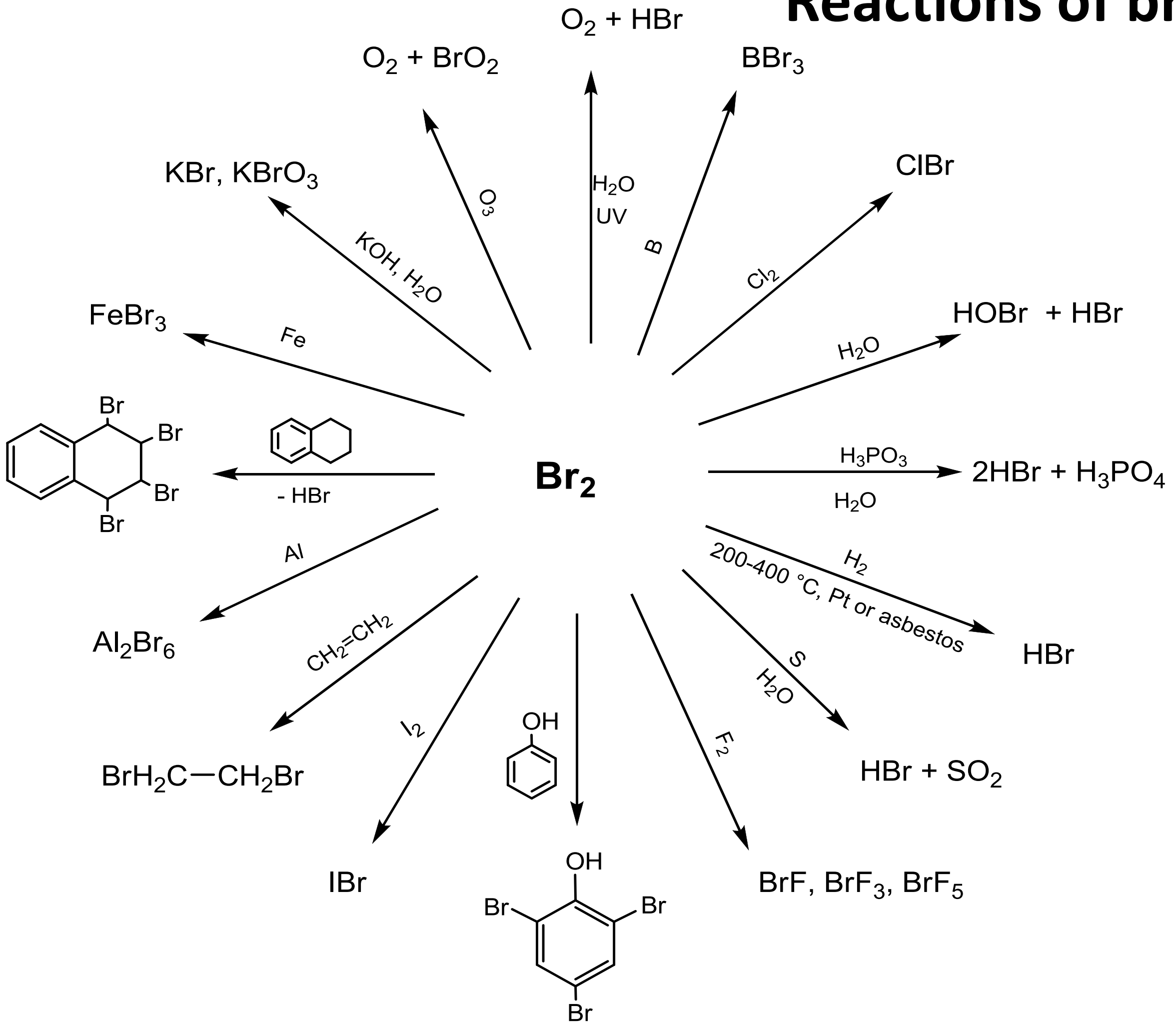

| | |
|---|---|
| NCS | 0% |
| $CuCl_2$ | 0% |
| $SO_2Cl_2$ | 31% |
| $Cl_2$ | 41% |
| TCICA | 43% |
| DCDMH | 51% |
| tBuOCl | 80% |
| CBMG | 87% |

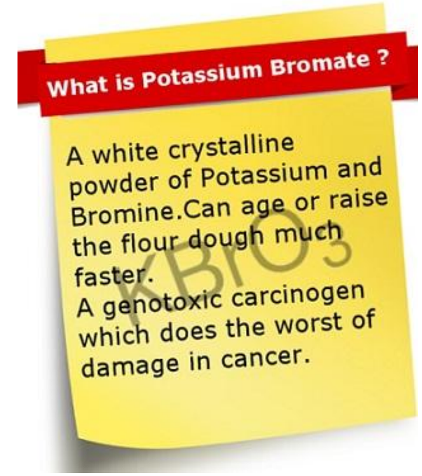



*J. Am. Chem. Soc.*, **2014**, *136* (19), pp 6908–6911

# Reactions of bromine




Potassium bromate is typically  as a flour improver mostly in the USA and is getting banned in other countries. It acts to strengthen the dough and to allow higher rising. It is an oxidizing agent (E° = 1.48 V), and under the right conditions will be completely used up in the baking bread. However, if too much is added, or if the bread is not baked long enough or not at a high enough temperature, then a residual amount will remain, which may be harmful. Potassium bromate has been banned from use in food products in the European Union, Argentina, Brazil, Canada, Nigeria, South Korea, Peru, India on 20 June 2016.

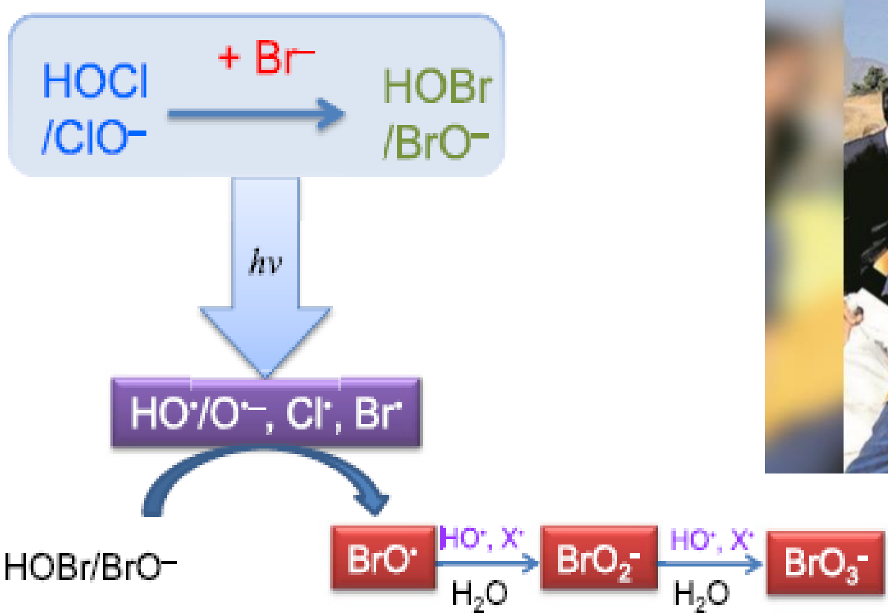
# Water reservoirs of Los Angeles

| | | | $E^0$ |
|---|---|---|---|
| $Cl_2(g) + 2e$ | $\longrightarrow$ | $2Cl^-$ | 1.36 V |
| $Br_2(l) + 2e$ | $\longrightarrow$ | $2\,Br^-$ | 1.09 V |
| $I_2(s) + 2e$ | $\longrightarrow$ | $2\,I^-$ | 0.54 V |

$$Cl_2(g) + Br^- \longrightarrow Br_2(l) + 2\,Cl^-$$

$$Br_2(l) + H_2O \longrightarrow HBrO + HBr$$

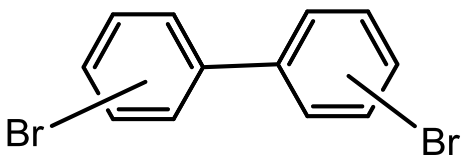
How formation of bromate in natural drinking water is prevented . When drinking water is chlorinated it oxidizes the bromide to bromate in the presence of sunlight



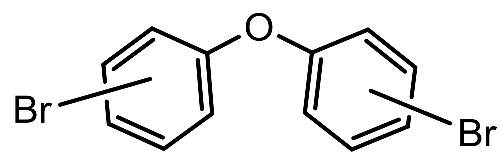

# Organobromine compounds as fire retardants

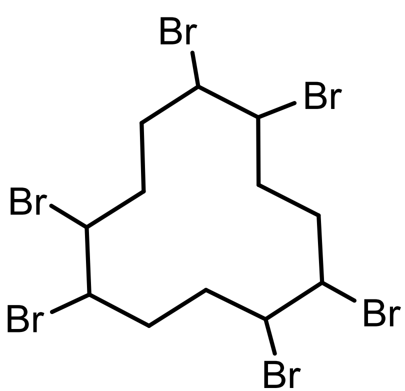
Brominated flame retardants (BFR's) either prevent a fire from starting, or slow down the progress of a fire significantly. Brominated compounds are added to materials such as polymers without altering their individual properties. One mechanism accounting for the effectiveness of brominated flame retardants is their ability to release active bromine free radicals into the gas phase as the material is decomposed in the fire. These bromine atoms effectively quench the chemical reactions occurring in the flame, reducing the heat generated and slowing or even preventing the burning process

Poly brominated biphenyls (PBB)

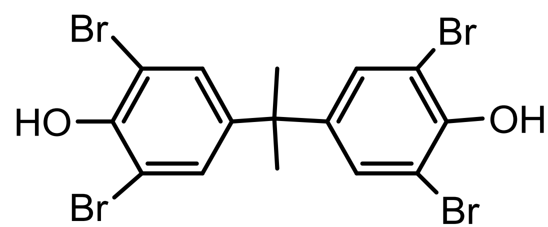



Polybrominated diphenylethers PBDE



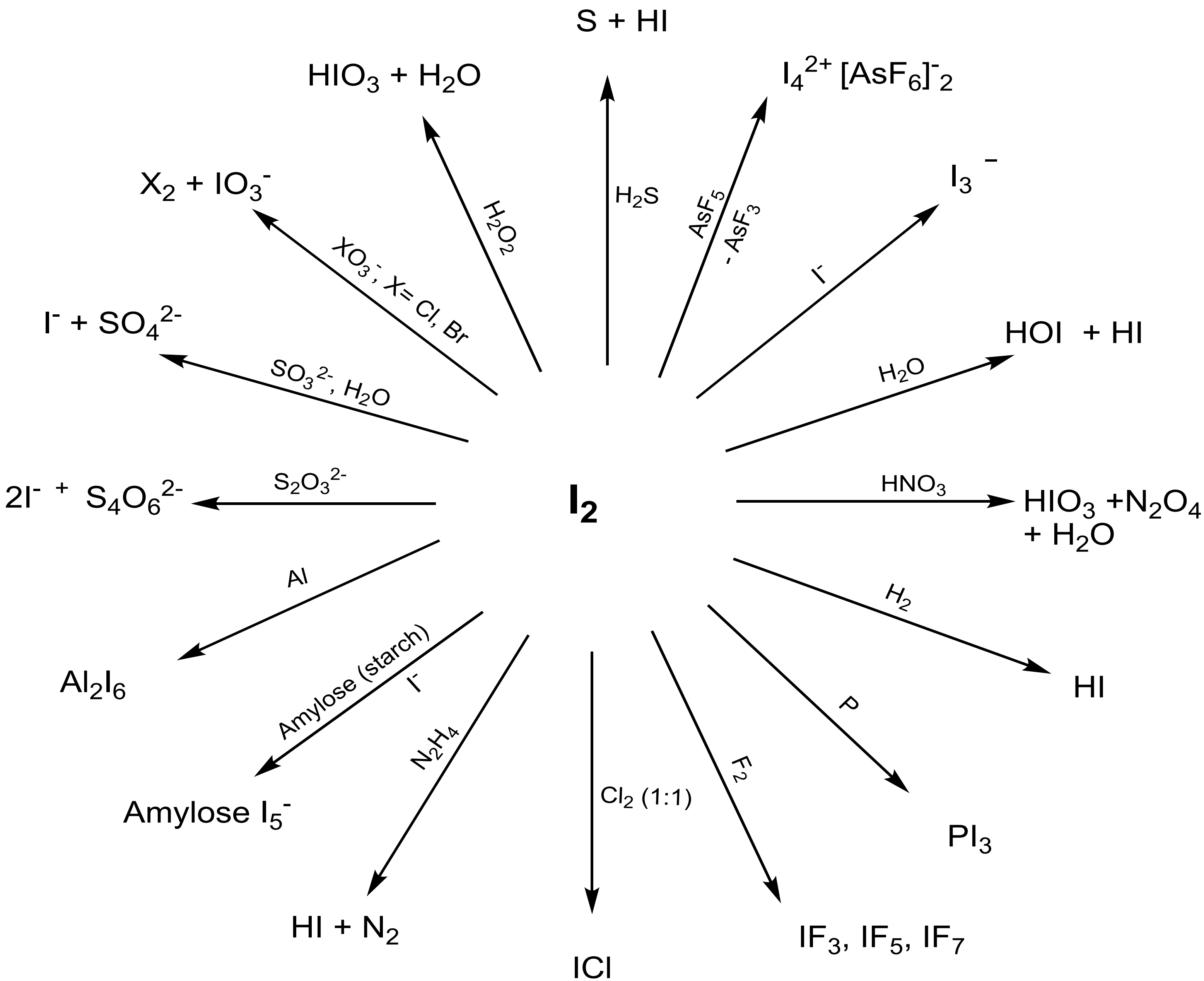




Hexabromocyclododecanes (HBCD)



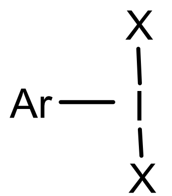

Tetrabromobisphenol A (TBBPA)

# Reactions of iodine

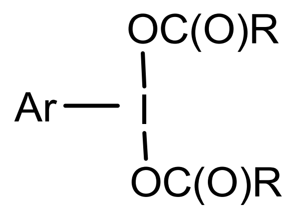


# Hypervalent organoiodine compounds

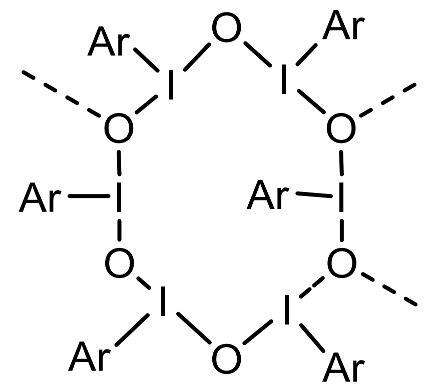
I(III)




X= F, Cl
Dihaloiodoarenes

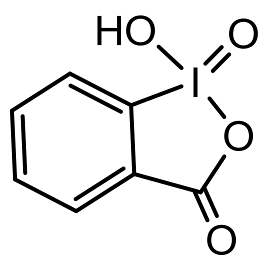



R= Me, $CF_3$
Bis(acyloxy)iodoarenes

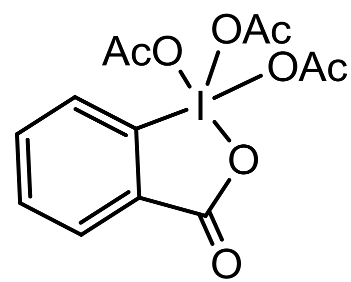



Iodosylarenes $(ArIO)_n$

I(V)

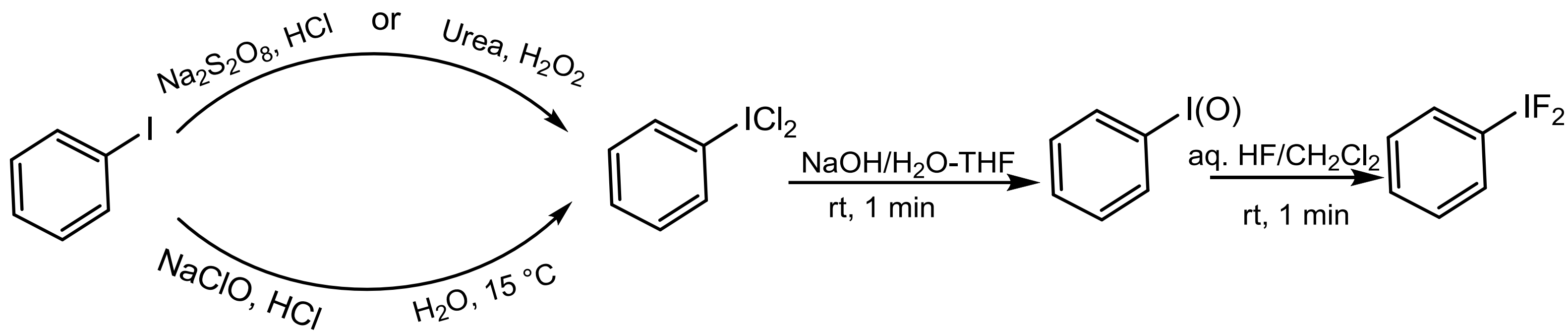


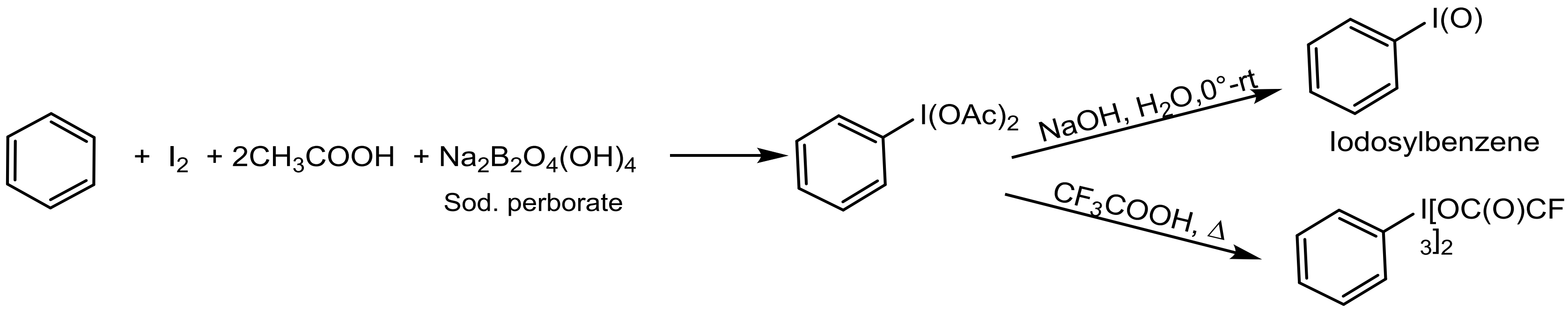

2-iodoxybenzoic acid (IBX)

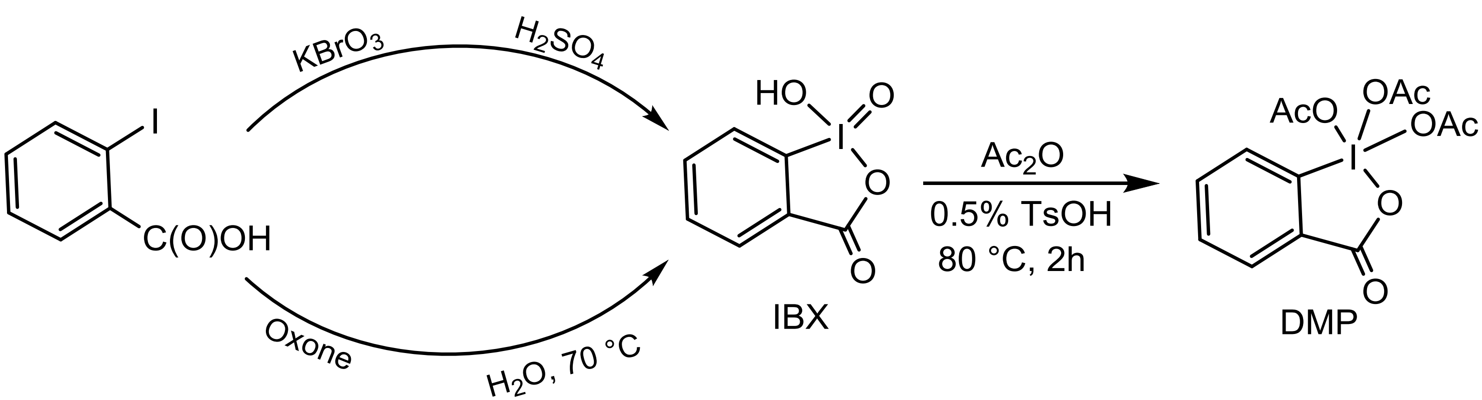



Dess-Martin Periodinane (DMP)

# Synthesis of hypervalent organoiodine compounds

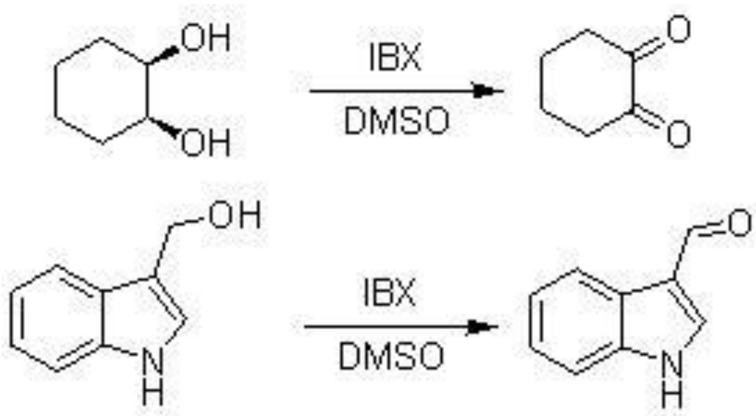


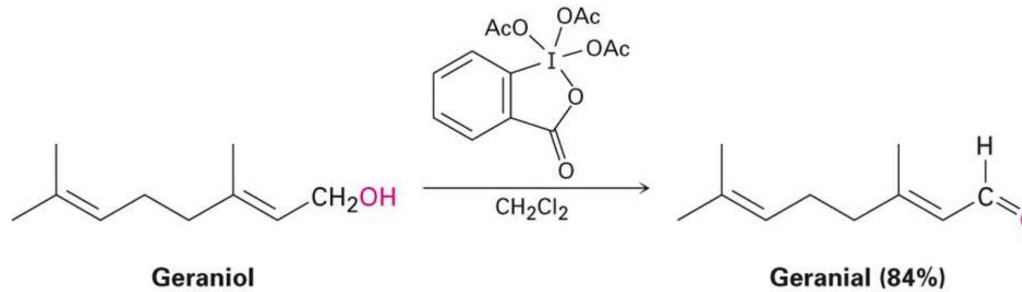




Oxone = $2KHSO_5$-$KHSO_4$-$K_2SO_4$

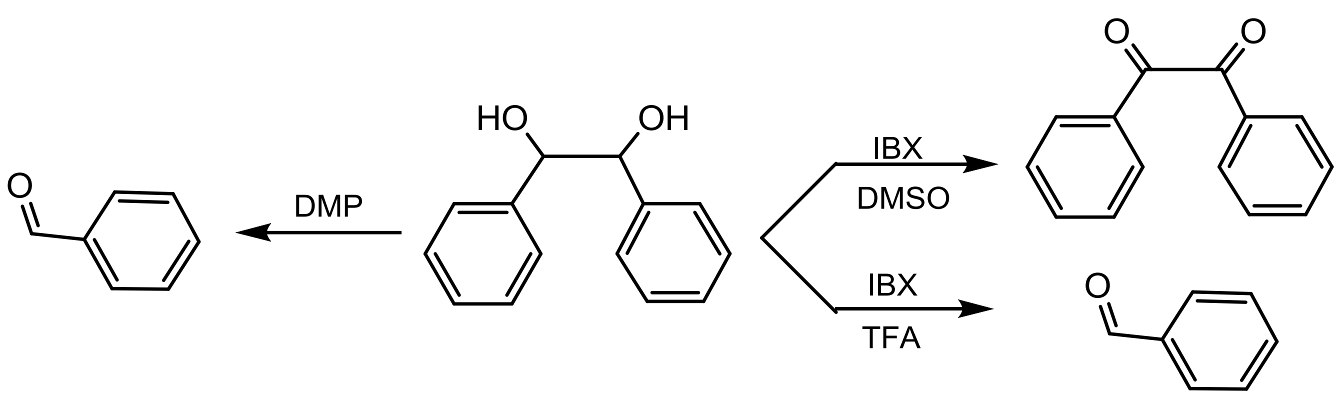
# Difference in the reactivity of IBX and DMP



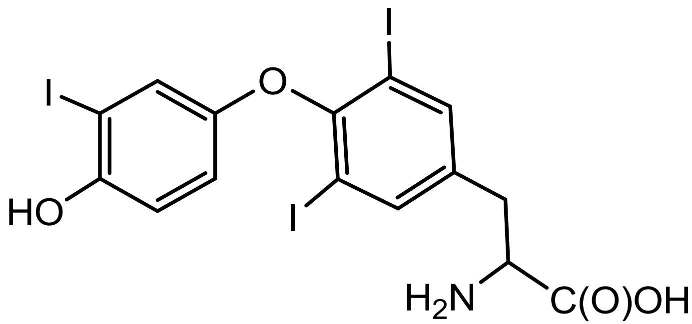



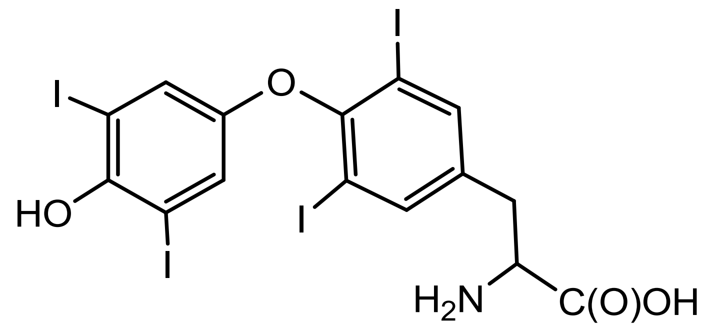

IBX poor solubility –only DMSO

DMP good solubility aromatic & chlorinated solvents

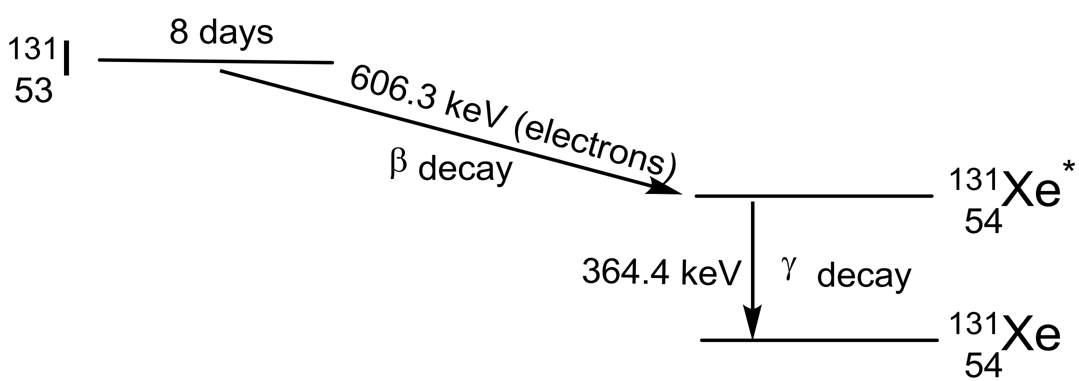


The thyroid gland produces two tyrosine based hormones namely **triiodothyronine** ($T_3$) and its prohormone **thyroxine** ($T_4$) having three and four iodine atoms in their structure. These hormones are primarily responsible for **regulation of metabolism**. A deficiency of iodine leads to decreased production of $T_3$ and $T_4$, resulting in enlargement of thyroid glands; a disease known as goitre.



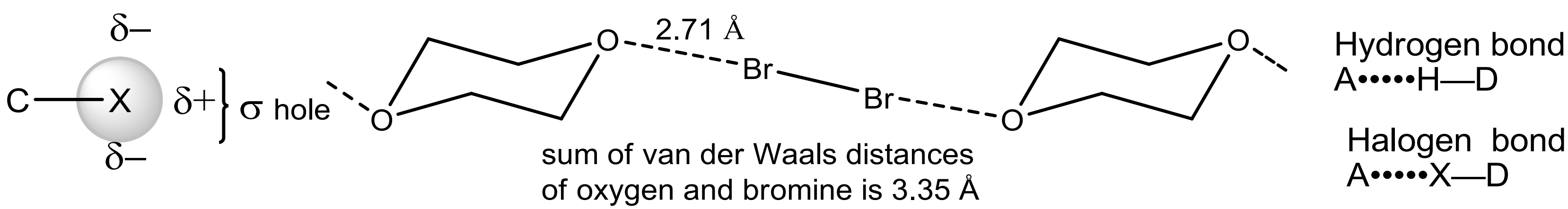


**Iodine-131** is the most feared fission product after the atomic bomb explosions or an accident like Chernobyl or Fukushima. The danger comes from its volatility thus being present in the air and high radioactivity. If breathed, it concentrates on the thyroid glands and is the cause of cancers of this sensitive gland that uses iodine to make thyroxine.



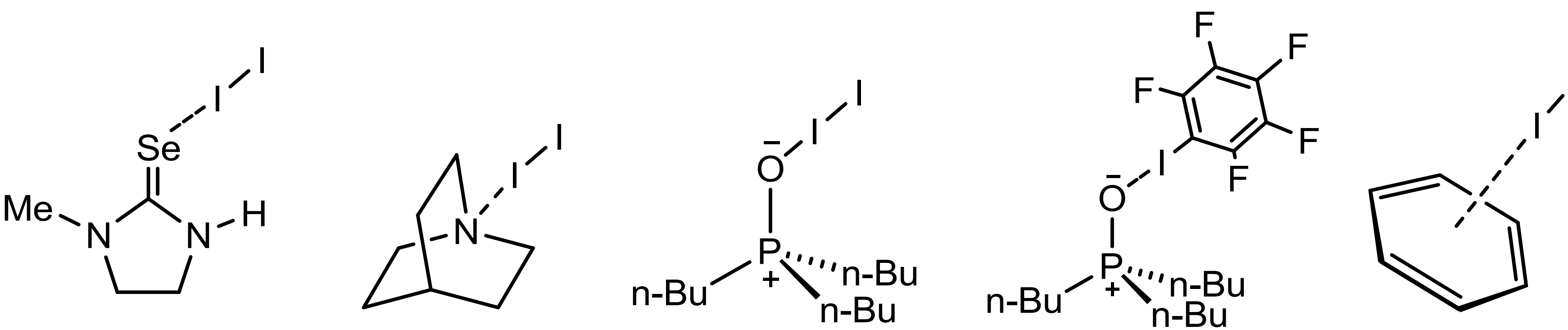
# The halogen bond

Similar to the well-known hydrogen bond, there exists a weak bond involving halogens and other electron donor atoms. Odd Hassel, the Norwegian Nobel prize recipient of 1969, showed in 1954 that molecular complexes in the molar ratio 1:1 of dioxane and bromine associated with polarisation induced $Br^{\delta+}\cdots O^{\delta-}$ interactions. The electron density on a halogen atom is anisotropically distributed when it is involved in a covalent bond with same or other atoms. For example, in a carbon–halogen covalent bond, there is positive polarisation in the region of the halogen atom that is furthest away from the carbon atom. The equatorial region of the halogen atom is consequently negatively polarised as the overall charge on the atoms should be zero.[33] By this way, the positively polarised region of the halogen (electrophilic region) is able to initiate an electrostatic contact with a negatively polarised (nucleophilic region) atom or electronegative species. The region of lower electron density is also called a σ hole.




The strength of the halogen bond has been estimated roughly to be in the range of 0–10 kcal/mol comparable to medium hydrogen bonds (3–14 kcal/mol) or dipole–dipole interactions (1–12 kcal/mol). The typical distance of interaction has been found to be around 20% reduction of the van der Waals radii of the donor and acceptor atoms.

The typical distance of interaction has been found to be around 20% reduction of the van der Waals radii of the donor and acceptor atoms. When compared to hydrogen bonds, the unique features of halogen bonds are directionality (AXD angle ~ 180°), hydrophobicity, tunability and variable size of the donor atoms. Some examples of halogen bond involving iodine with energies varying in the 0–10 kcal/mol are depicted below.




8.9 kcal/mol 7.2 kcal/mol 3.8 kcal/mol 1.5 kcal/mol 0.2 kcal/mol