

CHEMICAL REACTIONS

Lecture 6



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RECAP

- **chemical reaction** is a process in which one or more substances are **converted** to one or more different substances
- substances are either chemical elements or compounds
- **chemical reactions** involve **breaking** chemical **bonds** between **reactant** molecules and **forming** new **bonds** between atoms in product particles
- number of atoms before and after the chemical change is the same but the number of molecules will change

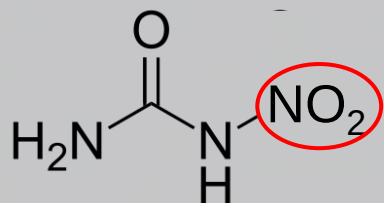
TODAY's LECTURE

chemical reactions of OME importance

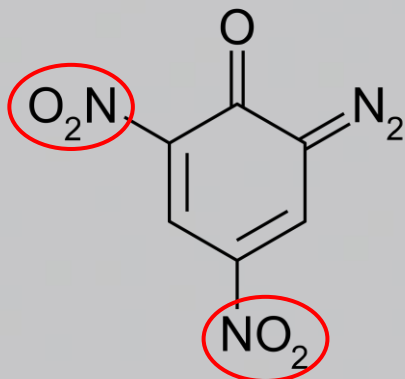
1. Nitration and Nitrolysis
2. Reduction – Oxidation (Redox)
3. Combustion, detonation (decomposition products)



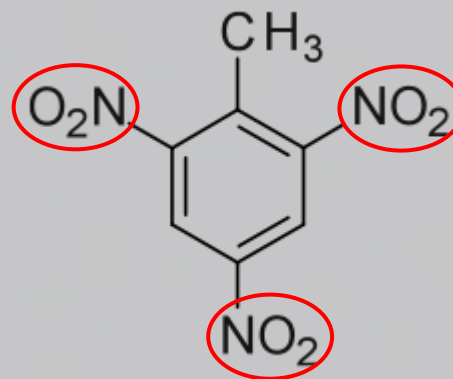
NO₂ GROUP IN EXPLOSIVE COMPOUNDS



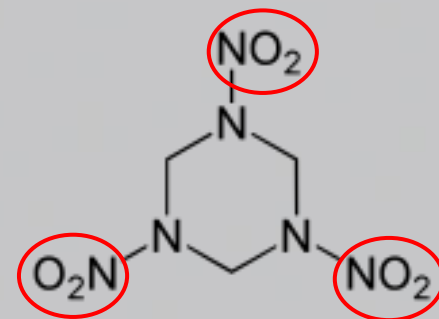
Nitrourea



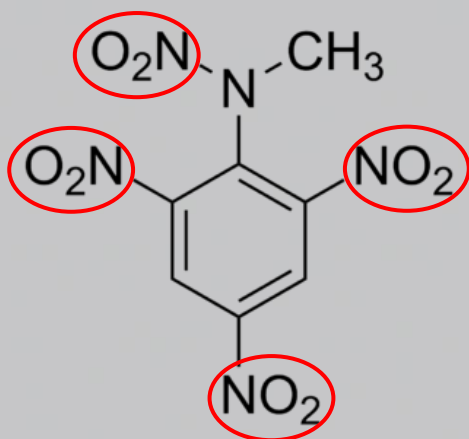
Diazodinitrophenol
(DDNP)



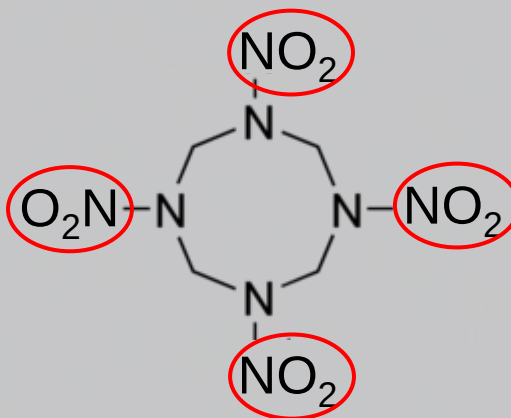
Trinitrotoluene
(TNT)



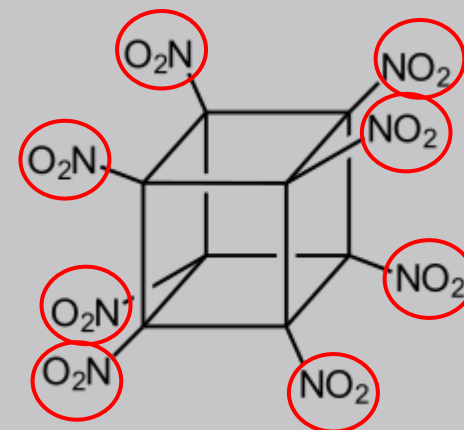
RDX



2,4,6-
Trinitrophenylmethylnit
ramine (tetryl)



Octogen
(HMX)



Octanitrocubane



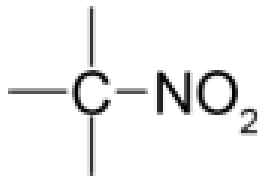
MOLECULAR EXPLOSIVES

In order to improve the burn rate and hence the performance of explosives, **molecular explosives have the fuel and oxidiser atoms on the same molecule** (example TNT).

Molecular explosives can be classified according to where the NO_2 groups are located in the molecule. There are three categories:

C-nitration

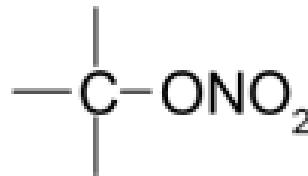
nitro
compound



nitro group
attached to
carbon atom

O-nitration

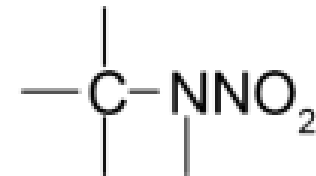
nitrate ester



nitro group
attached to
oxygen atom

N-nitration

nitramine

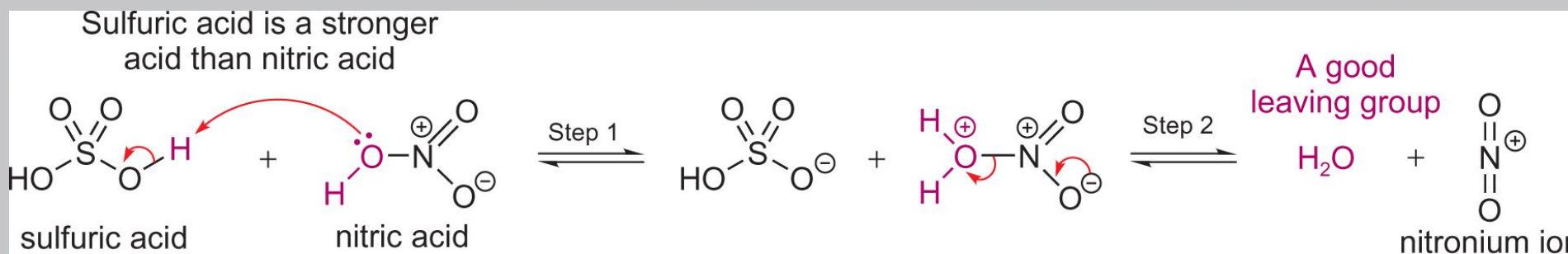


nitro group
attached to
nitrogen atom



NITRONIUM ION, ${}^+\text{NO}_2$

The nitronium ${}^+\text{NO}_2$ ion can be generated by the reaction of concentrated nitric acid, HNO_3 , with concentrated sulfuric acid H_2SO_4

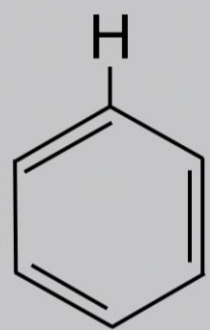


1. H_2SO_4 donates a **proton, H^+** , to HNO_3
2. Protonated **OH** group on HNO_3 leaves as water, H_2O , producing nitronium ion, ${}^+\text{NO}_2$, which is a strong **electrophile**

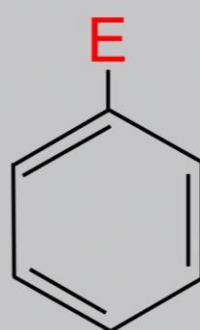


ELECTROPHILIC AROMATIC SUBSTITUTION

- organic reaction in which an atom that is attached to an aromatic system (usually hydrogen) is replaced by an **electrophile**
- one of the most important electrophilic aromatic substitutions is aromatic nitration
 - **electrophilic**, because we're adding an electron-poor species (electrophile)
 - to an **aromatic** compound (benzene)
 - **substitution**, because we're breaking C-H and forming C-E, where E is our electrophile (-NO₂ in this case)



benzene
(other aromatic)



electrophilic aromatic
substitution product

key bonds
formed

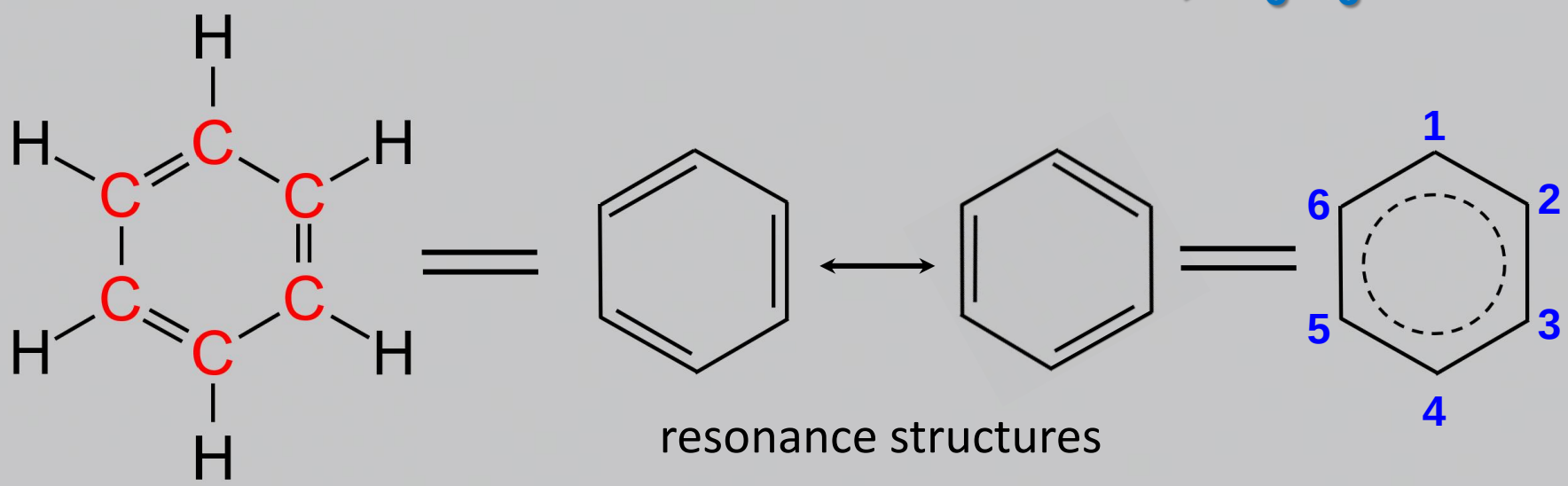
C - E

key bonds
broken

C - H

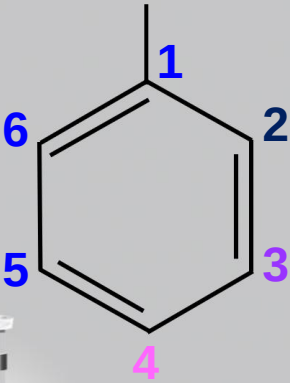


CHEMICAL STRUCTURE OF BENZENE, C₆H₆

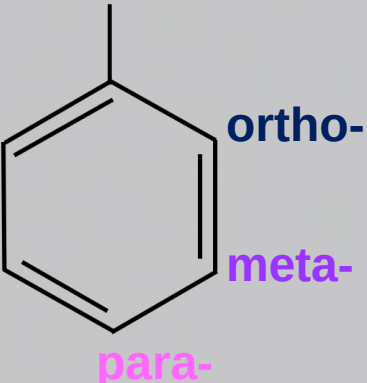


Derivatives of benzene: carbon atoms in ring are numbered and named

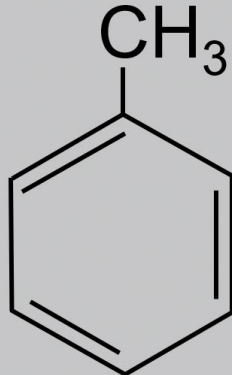




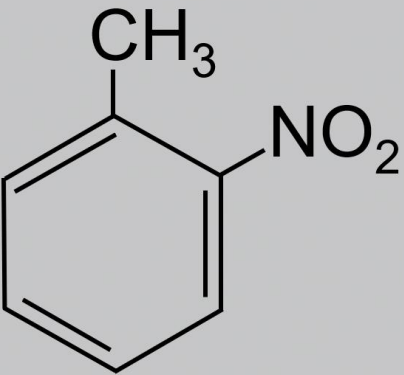
1,2 – ortho
1,3 – meta
1,4 – para



ortho-
meta-
para-



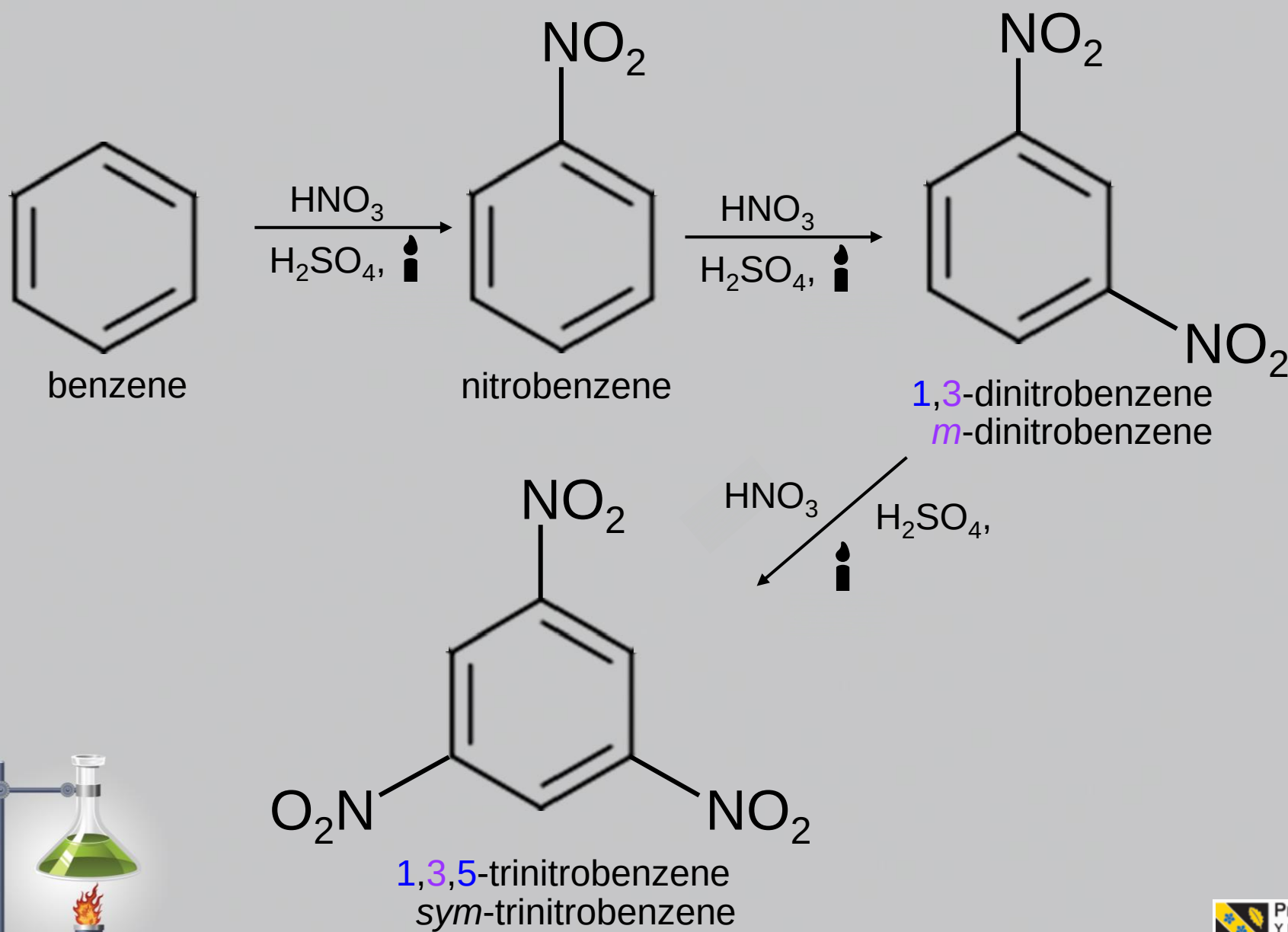
methylbenzene
toluene



1-methyl-2-nitrobenzene
2- nitrotoluene
o-nitrotoluene

C-NITRATION OF BENZENE

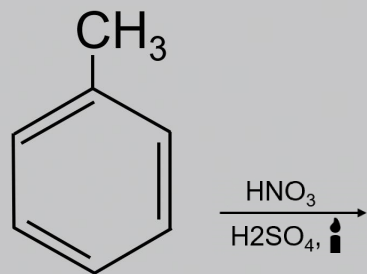
the nitro group, NO₂, is
meta directing



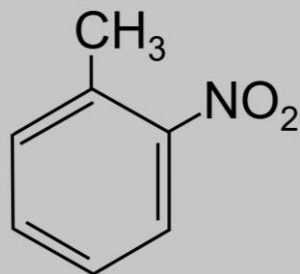
C – NITRATION OF TOLUENE

-CH₃ is *ortho* and *para* directing

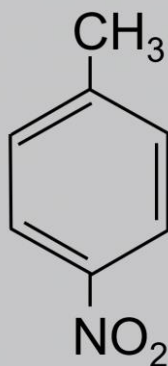
-NO₂ is *meta* directing



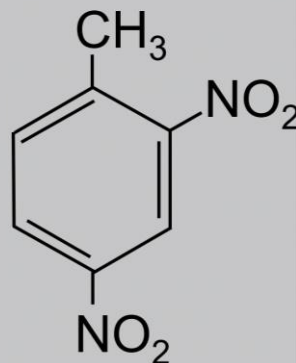
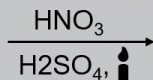
methylbenzene
toluene



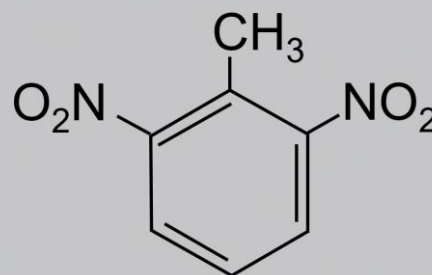
2-nitrotoluene
o-nitrotoluene



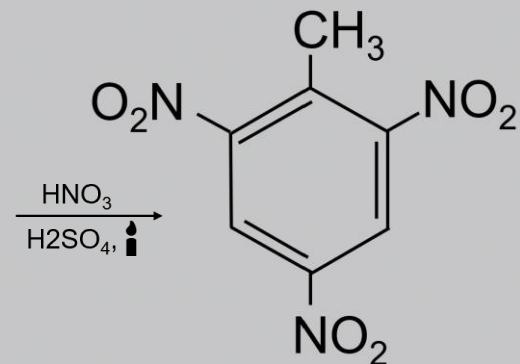
4-nitrotoluene
p-nitrotoluene



2,4-dinitrotoluene



2,6-dinitrotoluene



2,4,6-trinitrotoluene
TNT

ISOMERS

ISOMERS

Isomers are compounds having different elements but the same chemical formula in different arrangements.

number of atoms

Isomers have the same number of atoms.

type of elements

Isomers are composed of different elements.

number of atoms

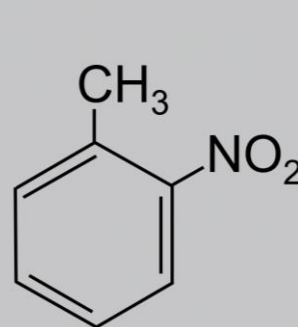
Isomers may have similar or different structures.

presence

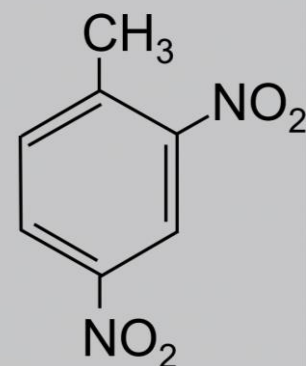
Isomerism can be seen in organic molecules (ex: hydrocarbon) and inorganic molecules (ex: silane).

major types

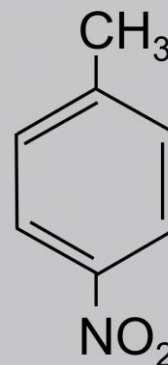
Isomers include mainly structural isomers and stereoisomers.



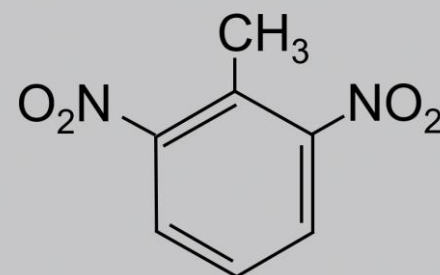
2-nitrotoluene



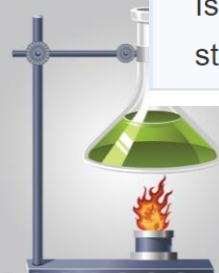
2,4-dinitrotoluene



4-nitrotoluene

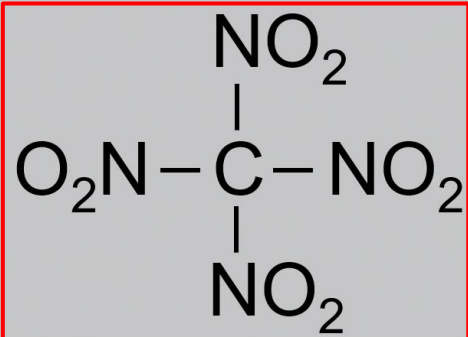
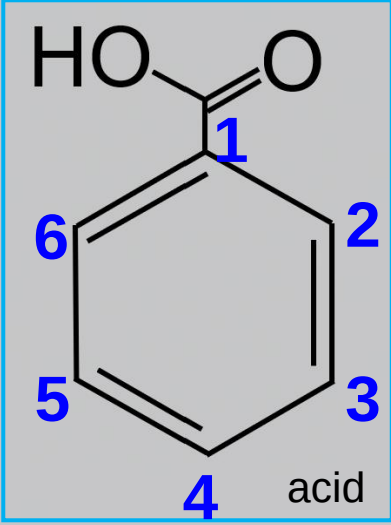
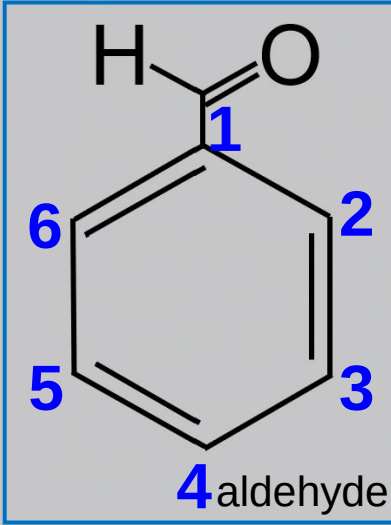
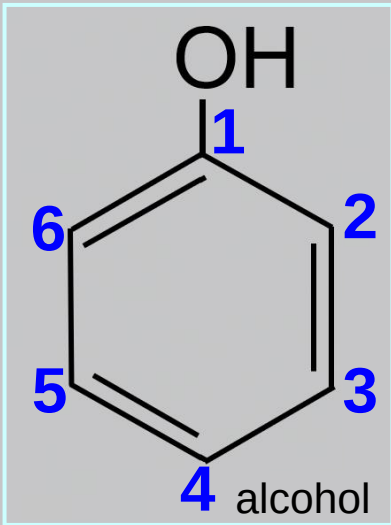
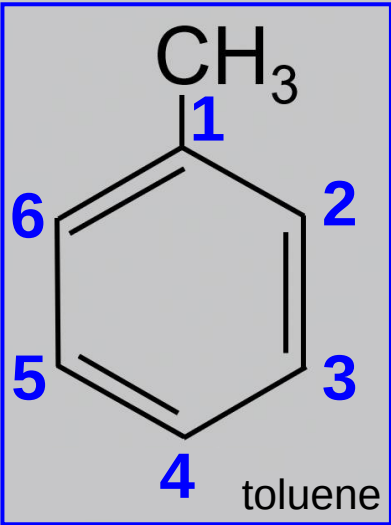


2,6-dinitrotoluene



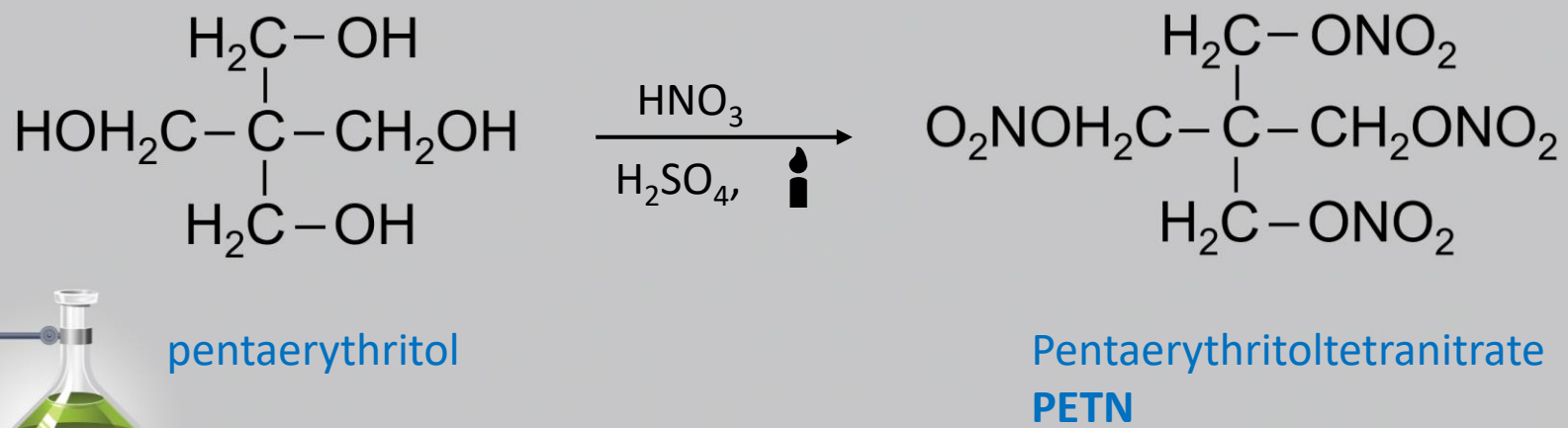
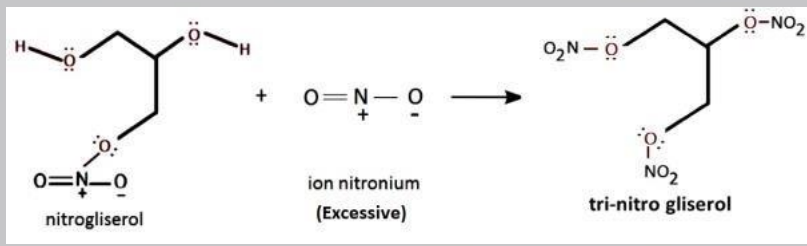
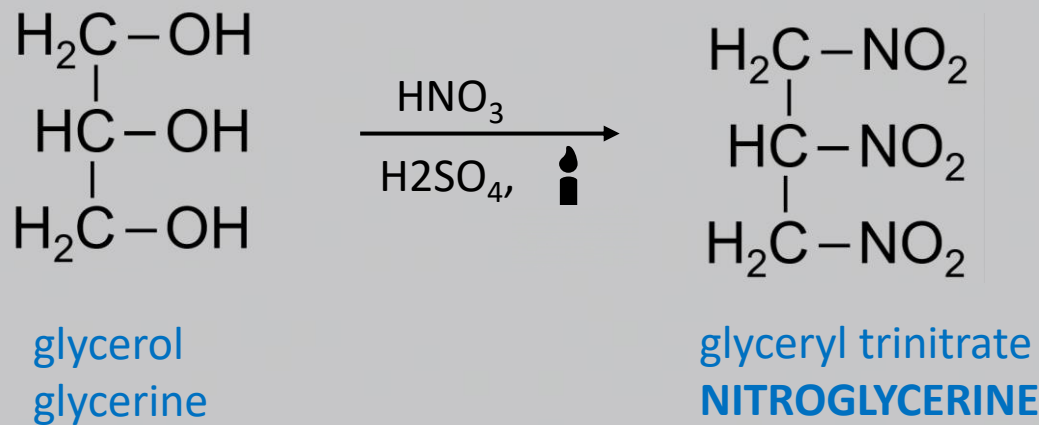
AROMATIC SUBSTITUTION

compound	approx max normal conc %	
	crude	finished
2,4,5-TNT	2.50	0.30
2,3,4-TNT	1.75	0.20
2,3,6-TNT	0.50	0.05
2,3,5-TNT	0.05	0.05
2,6-DNT	0.25	0.25
2,4-DNT	0.50	0.50
2,3-DNT	0.05	0.05
2,5-DNT	0.10	0.10
3,4 -DNT	0.10	0.10
3,5-DNT	0.01	0.01
1,3-DNT	0.02	0.02
1,3,5-TNB	0.15	0.10
2,4,6-trinitrobenzyl alcohol	0.25	0.25
2,4,6-trinitrobenzylaldehyde	0.25	0.25
2,4,6-trinitrobenzylacid	0.50	0.05
tetranitromethane	0.10	none

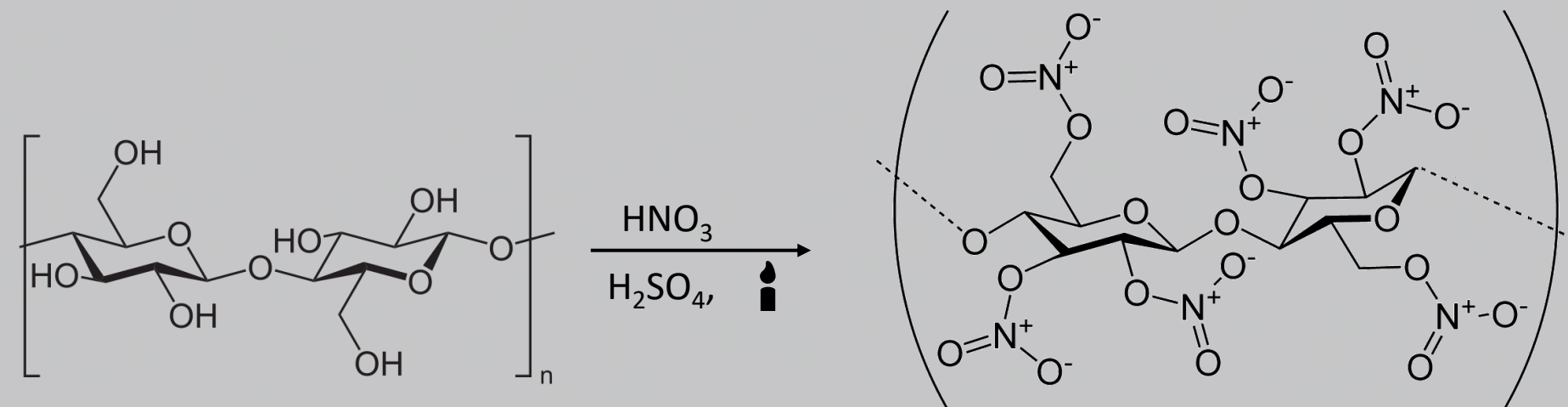


O-NITRATION

Early examples of primary high explosives



O-NITRATION



cellulose

major component of cotton

burns slowly in air

nitrocellulose

gun cotton

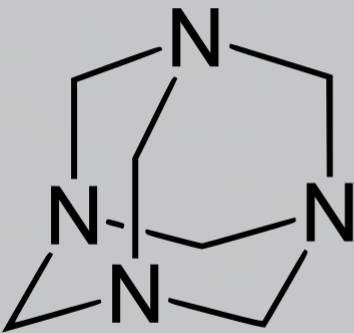
major component of modern gun powder and fireworks

burns very rapidly even without air

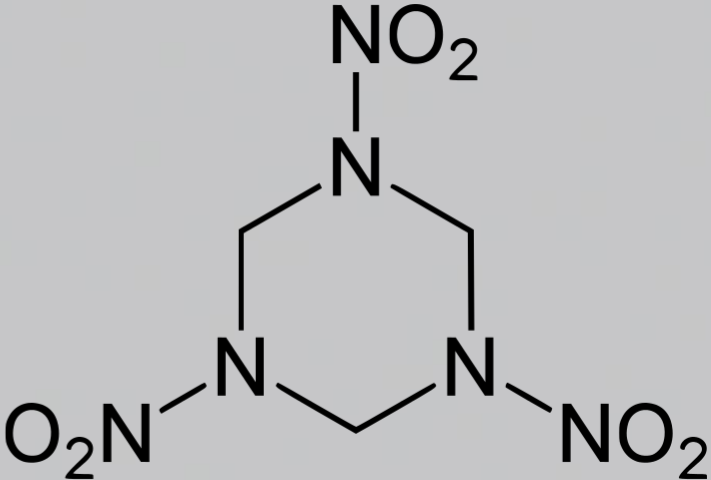
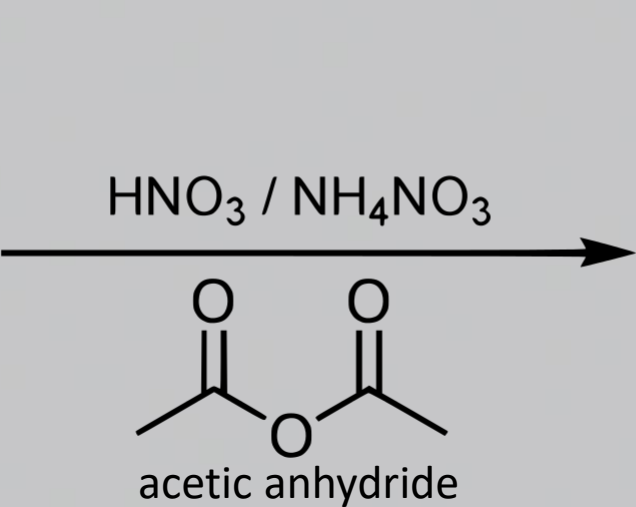


<https://www.youtube.com/watch?v=VoDAvltgUv4>

NITROLYSIS – N-NITRATION



hexamine

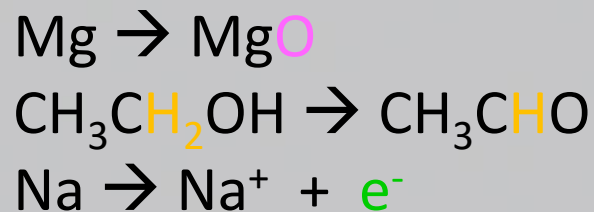


RDX – Research Department
eXplosive, hexogen

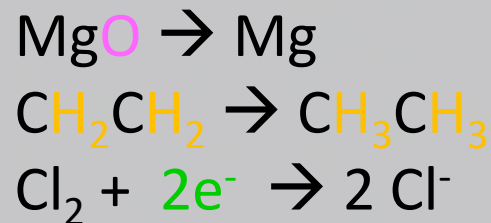


RED-OX REACTIONS

OXIDATION: substance gains oxygen
 substance loses hydrogen
 substance loses electron(s)



REDUCTION: substance loses oxygen
 substance gains hydrogen
 substance gains electron(s)



REDOX reactions always occur simultaneously

gunpowder: KNO_3 , C, S

NO_3^- **reduced** to NO and NO_2

C **oxidised** to CO and CO_2

S **oxidised** to SO_2 and SO_3



OXIDATION AND REDUCTION - REDOX

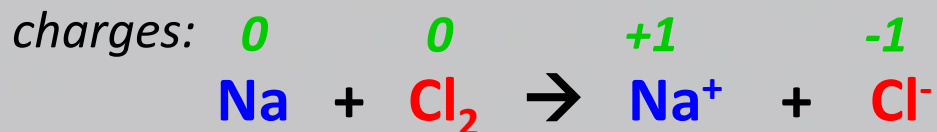
- involves a transfer of **electrons** between two species
- **reduction** and oxidation always occur together
- net charge is zero
- ion or molecule is **oxidised** when it **loses electrons** (oxidation number increases)
- ion or molecule is **reduced** when it **gains electrons** (oxidation number decreases)
- **OIL RIG** "oxidation is loss" and "**reduction** is gain"
- ion or molecule that **accepts electrons** is called the **oxidizing agent** (by **accepting electrons** it **oxidizes** other species)
- ion or molecule that **donates electrons** is called the **reducing agent** (by **giving electrons** it **reduces** the other species)
- what is oxidized is the reducing agent and what is **reduced** is the **oxidizing agent** (disproportionation reactions - **oxidizing** and **reducing** agents are the same element or compound)



REDOX REACTIONS OF IONIC COMPOUNDS

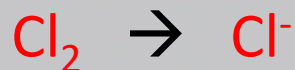


1. Recognise the RED and OX processes (can be done by the analysis of oxidation states (charges))



charge on Na increased
Na lost an electron

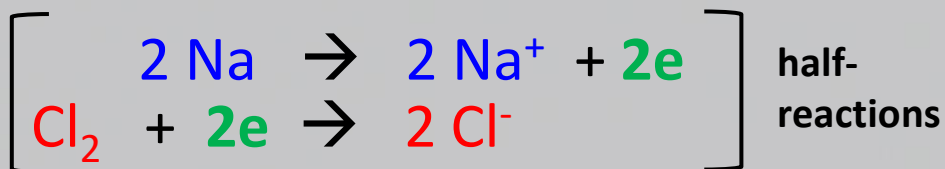
OXIDATION



charge on Cl decreased
Cl gained electron

REDUCTION

2. Balance the atoms and charges: conservation of MASS and CHARGES



OXIDATION NUMBER – ‘FAKE CHARGE’

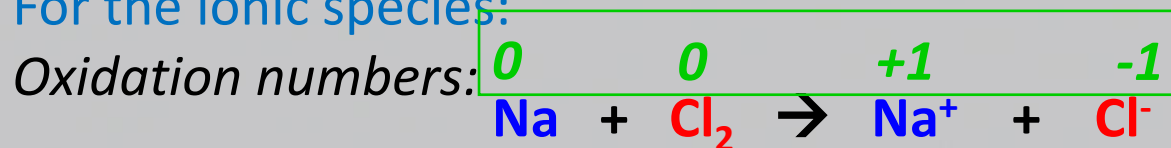
a **number** assigned to a compound or atom to show how many **electrons** were lost or gained in order to form a bond with another atom

an imaginary **charge** that the atom would have if all of the bonds to the atom were completely ionic

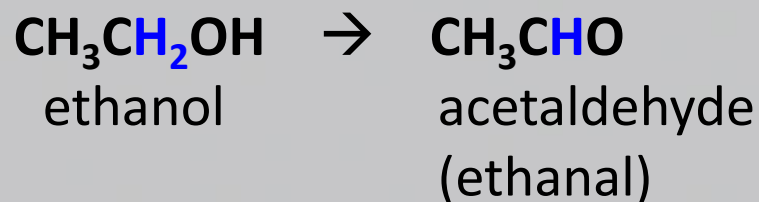
oxidation increases the **oxidation number** and **reduction** decreases the **oxidation number**

For the ionic species:

Oxidation numbers:



For the covalent species:

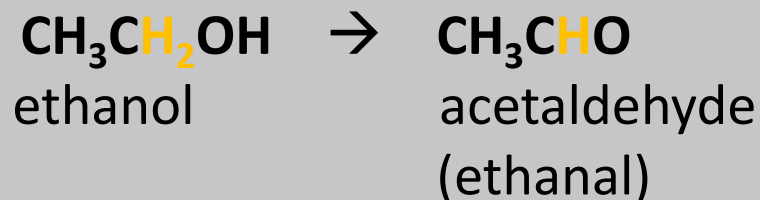


???



OXIDATION NUMBER

For the covalent species:



OXIDATION NUMBER → **'FAKE CHARGE'**

a **number** assigned to a compound or atom to show how many electrons were lost or gained in order to form a bond with another atom

The **oxidation state** of atoms in a **pure element** is **zero**

In an **uncharged compound**, the sum of all the **oxidation states** is **zero**

Average oxidation number for an atom

1. Each type of atom in a species gets an average oxidation number
2. Total oxidation number = charge on the species
3. If still not able to assign numbers, follow the rules:



ASSIGNING OXIDATION NUMBERS

The **oxidation number (state)** of atoms in a **pure element** is **zero**

In an **uncharged compound**, the sum of all the **oxidation states** is **zero**

For **monoatomic ions** **oxidation number** = **charge**

1. Metal cations: oxidation number = **charge on the cation**

group 1 metals **+1** (Na, K, ...)

group 2 metals **+2** (Mg, Ca, ...)

group 3 metals **+3** (Al, Ga)

etc

2. F **-1** (always), **halogens** **-1** (unless combined with oxygen)

3. H **+1** (except metal hydrides, -1)

4. O **-2** (except O_2^{2-} - superoxide, O_2^- - peroxide)



EXAMPLES



overall charge on this molecule is **zero**

K is +1, O is -2, N is ?

overall charge:

$$(1 \times \text{K}) + (1 \times \text{N}) + (3 \times \text{O}) = 0$$

$$(1 \times +1) + (1 \times \text{N}) + (3 \times -2) = 0$$

$$\text{N} + (1 - 6) = 0$$

$$\text{N} = +5$$



overall charge on this ion is **-2**

O is -2, S is ?

overall charge:

$$(1 \times \text{S}) + (4 \times \text{O}) = -2$$

$$(1 \times \text{S}) + (4 \times -2) = -2$$

$$\text{S} - 8 = -2$$

$$\text{S} = +6$$



overall charge on this molecule is **zero**

K is +1, O is -2, Cr is ?

overall charge:

$$(2 \times \text{K}) + (2 \times \text{Cr}) + (7 \times \text{O}) = 0$$

$$(2 \times +1) + (2 \times \text{Cr}) + (7 \times -2) = 0$$

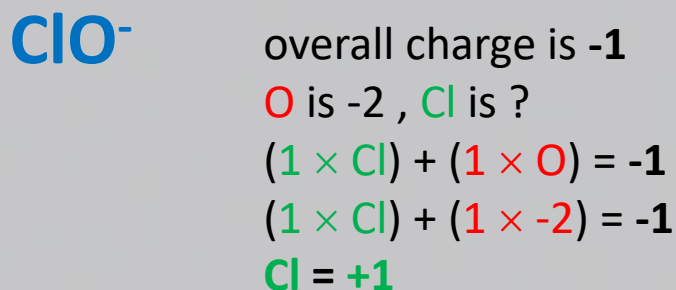
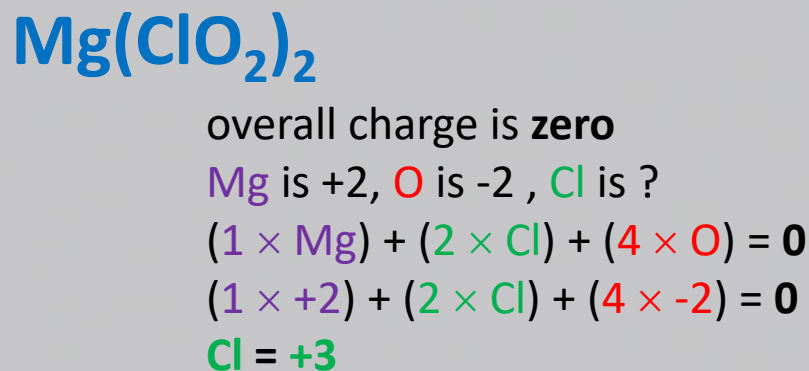
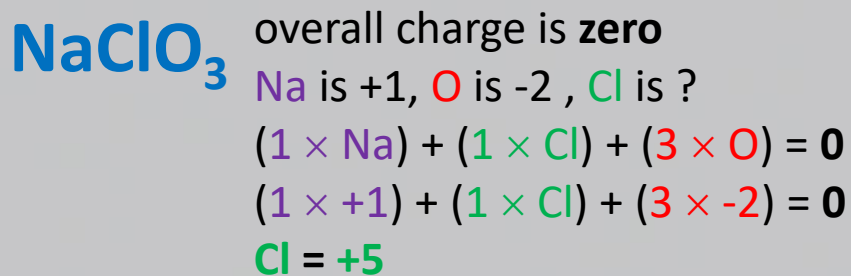
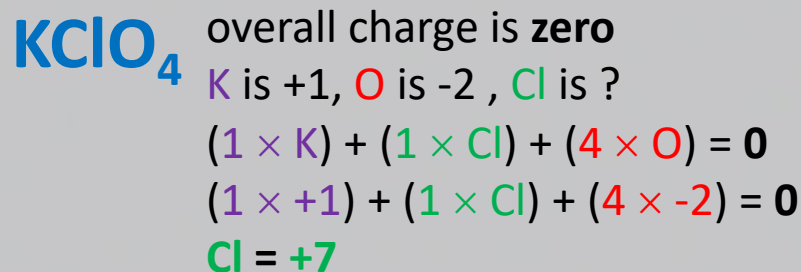
$$2 \text{Cr} + (2 - 14) = 0$$

$$\text{Cr} = +6$$



PRACTICE PROBLEM

Calculate the oxidation state of the chlorine atom, Cl, in each of the following compounds and ions:



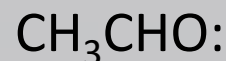
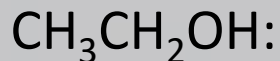
Arrange the oxyanions of chlorine in order of increasing oxidising power.



strongest oxidising agent => reduced most easily => gains electrons most easily. Ox states for chlorine in ClO⁻, ClO₂⁻, ClO₃⁻, and ClO₄⁻ are: +1, +3, +5, +7, respectively. So ClO⁻ has to gain only one electron



REDOX REACTIONS OF ORGANIC COMPOUNDS



For easier work rewrite: $\text{C}_2\text{H}_6\text{O}$

$\text{C}_2\text{H}_4\text{O}$

overall charge on this molecule is 0
H is +1, O is -2 and C is ?

overall charge on this molecule is 0
H is +1, O is -2, C is ?

$$(2 \times \text{C}) + (6 \times 1) + (1 \times -2) = 0$$

$$(2 \times \text{C}) + (4 \times 1) + (1 \times -2) = 0$$

$$\text{C} = -2$$

$$\text{C} = -1$$

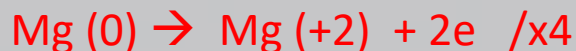
carbon lost electron

OXIDATION



REDOX REACTIONS of OME IMPORTANCE

1. FLASH REACTION: Potassium perchlorate and magnesium form coloured signal composition when transform to magnesium oxide and potassium chloride.



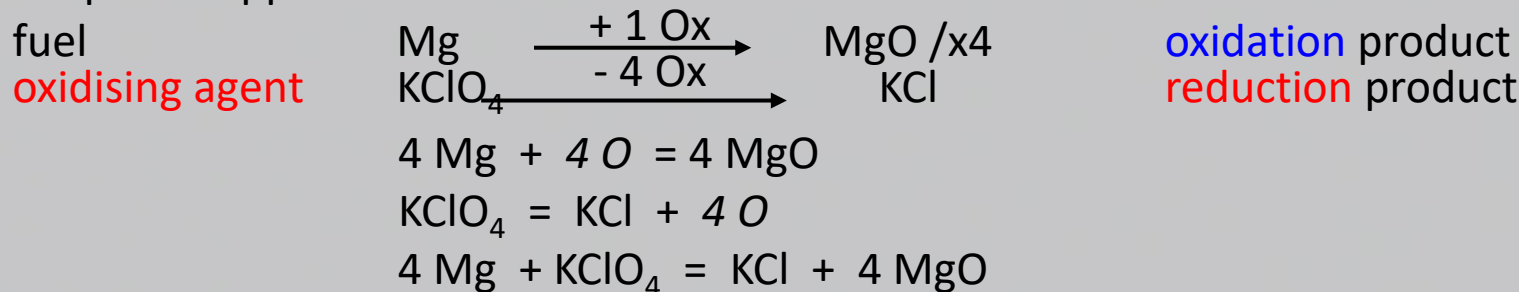
oxidation



reduction



Simplified approach:



2. SMOKE BOMB: thermal mixture of lactose, $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$, and potassium chlorate forms a coloured smoke composition. When combusted it forms carbon monoxide, solid potassium chloride and water vapour.



reduction

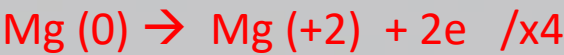
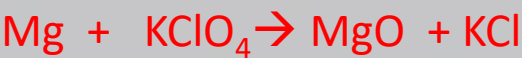


oxidation



REDOX REACTIONS of OME IMPORTANCE

2. FLASH REACTION: Potassium perchlorate and magnesium form coloured signal composition when transform to magnesium oxide and potassium chloride.



oxidation

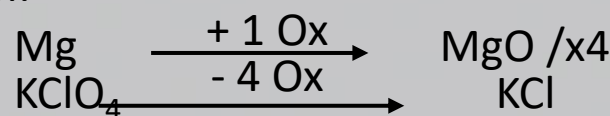


reduction

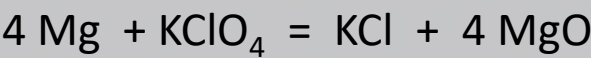


Simplified approach:

fuel
oxidising agent



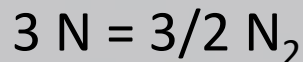
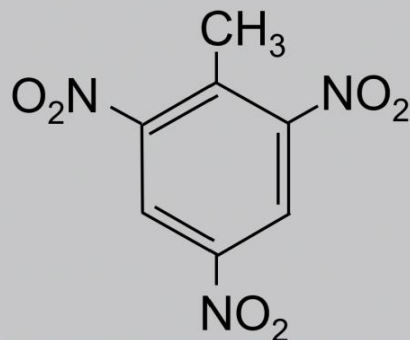
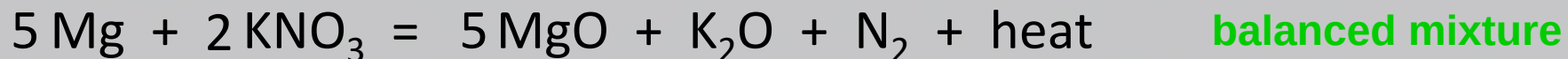
oxidation product
reduction product



REDUCING AND OXIDISING AGENTS

The **energy** in munitions derives largely from the heat-producing reaction of a **reducing agent** (fuel) with an **oxidising agent**, which might be separate ingredients or different parts of the same molecule

The most common **oxidising agents** in military applications are **oxygen** and **fluorine**



not enough oxygen !!!

fuel rich ingredient



OXIDES

Oxides are important ingredients in energetic materials because they can release oxygen to combine energetically with many other elements and compounds

