

Dr. Pampa Guha  
Dept. of Chemistry  
Assistant Professor  
City College, Kolkata

**CU syllabus –**

## **DSE-B-1: INORGANIC MATERIALS OF INDUSTRIAL IMPORTANCE**

**Chemical explosives: (4 Lectures)**



Origin of explosive properties in organic compounds, preparation and explosive properties of lead azide, PETN, cyclonite (RDX). Introduction to rocket propellants

## Hazard symbol



## Some Disasters -

- Bhopal Tragedy – 1984, also referred to as the Bhopal gas tragedy
- **Chernobyl disaster – 1986** – It is considered the worst nuclear power plant accident in history, both in terms of cost and casualties
- ammonium nitrate disaster in The Lebanese capital Beirut.

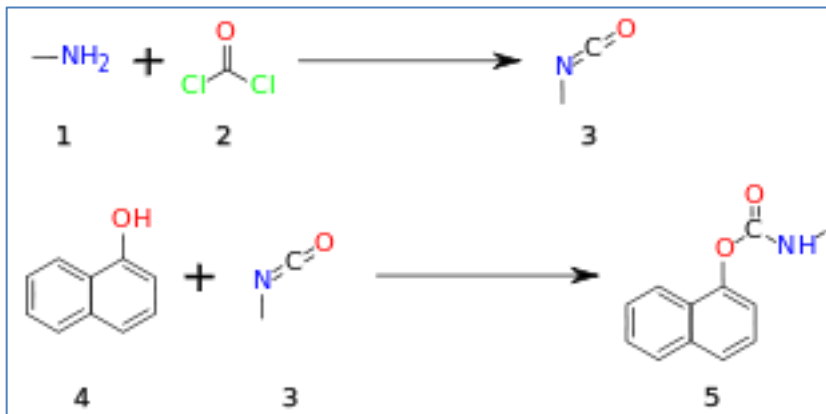
## Ammonium nitrate disaster in the Lebanese capital Beirut

- Ammonium nitrate does not burn on its own. Instead, it acts as a source of oxygen that can accelerate the combustion (burning) of other materials.
- Ammonium nitrate prills provide a much more concentrated supply of oxygen than the air around us. This is why it is effective in mining explosives, where it's mixed with oil and other fuels.
- At high enough temperatures, however, ammonium nitrate can violently decompose on its own. This process creates gases including nitrogen oxides and water vapour.
- An ammonium nitrate explosion produces massive amounts of nitrogen oxides. Nitrogen dioxide ( $\text{NO}_2$ ) is a red, bad-smelling gas. Images from Beirut reveal a distinct reddish colour to the plume of gases from the blast.

## Bhopal disaster -

The **Bhopal disaster**, also referred to as the **Bhopal gas tragedy**, was a gas leak incident on the night of 2–3 December 1984 at the Union Carbide India Limited (UCIL) pesticide plant in Bhopal, Madhya Pradesh, India.

It is considered among the world's worst industrial disasters. Over 500,000 people were exposed to methyl isocyanate (MIC) gas.



Methylamine (1) reacts with phosgene (2) producing methyl isocyanate (3) which reacts with 1-naphthol (4) to yield carbaryl (5).

## **Explosion -**

- An explosion can be generally defined as a process of the sudden expansion of matter to a volume much larger than the initial one.
- An explosion is a type of spontaneous chemical reaction that, once initiated, is driven by both a large exothermic change (great release of heat) and a large positive entropy change (great quantities of gases are released) in going from reactants to products
- It constituting a thermodynamically favorable process in addition to one that propagates very rapidly.
- Explosions are usually associated with loud noise, clouds of black smoke, and scattering, they differ in nature, in particular in the physical nature of the energy of explosion and in the way it is released

## Explosive -

**An explosive is a reactive substance that contains a large amount of energy stored in chemical bonds that can produce an explosion if released suddenly, usually accompanied by the production of light, heat, sound, and pressure.**

In other words, **chemical substances or mixtures of chemical substances that can, under the influence of some external energy (thermal, mechanical, etc.), undergo highly exothermic chemical reactions resulting in gaseous products, strongly bonded species like carbon monoxide, carbon dioxide, and (di)nitrogen, which contain strong double and triple bonds having bond strengths of nearly 1 MJ/mole, are called explosives or explosive substances.**

Most commercial explosives are organic compounds containing  $-\text{NO}_2$ ,  $-\text{ONO}_2$  and  $-\text{NHNO}_2$  groups that, when detonated, release gases.

## Basic characteristics of explosives -

- (1) It is a chemical compound or mixture ignited by heat, shock, impact, friction, or a combination of these conditions.
- (2) Upon ignition, it decomposes rapidly in a detonation.
- (3) There is a rapid release of heat and large quantities of high-pressure gases that expand rapidly with sufficient force to overcome confining forces
- (4) The energy released by the detonation of explosives produces four basic effects; (a) rock fragmentation; (b) rock displacement; (c) ground vibration; and (d) air blast.



The sources of the explosion energy are various: chemical, nuclear, thermal, electric, kinetic energy, energy of elastic compression etc

When a particular source of explosion energy is considered, three fundamental types of explosion can be distinguished: **physical, chemical, and nuclear explosions**.

- i) Physical explosions - electrical discharges, steam explosion, volcanic explosion etc.
- ii) Nuclear explosions - thermonuclear reactions on the Sun's surface
- iii) Chemical explosions - explosions produced as a consequence of a chemical reaction in which the chemical energy of a substance, or mixture of substances, is rapidly released causing a sudden expansion of the air (expansive shock wave). The velocity at which the shock wave front travels through the detonating explosive is called velocity of detonation.

An explosion of a chemical explosive is essentially an irreversible process in which the explosive is converted into the final, mainly gaseous, products.

➤ The velocity at which the shock wave front travels through the detonating explosive is called **velocity of detonation**.

### **Deflagration and detonation** -

These are two ways energy may be released. If the combustion process propagates outward at subsonic speeds (slower than the speed of sound), it's a **deflagration**. If the explosion moves outward at supersonic speeds (faster than the speed of sound), it's a **detonation**

➤ The velocity of detonation influences the destructive power of the explosive's deflagration/detonation, in such a way that **“detonations traveling at supersonic speeds will be more destructive”**

## Classification of Explosives



I.



**Propellants or low explosives** are combustible materials, containing within themselves all oxygen needed for their combustion, which burn but do not explode, and function by producing gas which produces an explosion. Under normal conditions, low explosives undergo [deflagration](#) at rates that vary from a few centimeters per second to approximately 400 metres per second.

It is possible for them to deflagrate very quickly, producing an effect similar to a [detonation](#). This usually occurs when ignited in a confined space. Explosives of this class differ widely among themselves in the rate at which they deliver their energy.

There are slow powders and fast powders for different uses.

*Examples:* [black powder](#), [smokeless powder](#).

### **High energy explosives –**

High energy explosives detonate creating a supersonic shock wave that propagates usually exceeding 4000 m/s. Three classes are typically subdivided for high explosives according to their sensitivity to explode: primary, secondary and tertiary explosives

**Primary explosives** are extremely sensitive to different weak stimuli (such as heat, spark or friction) by which detonation initiates. In general, primary explosives are not particularly powerful. Because of these properties, they are usually used in little amounts as detonators of secondary high explosives. Some typical primary explosives are mercury fulminate, silver fulminate, **lead azide**, cuprous acetylide, lead picrate, lead styphnate, diazodinitrophenol, tetrazoles, NG, TATP and HMTD.

**Secondary explosives** are practically insensitive to weak stimuli and they usually require the input of a strong shock to detonate. Most secondary explosives are exceptionally powerful (with velocities of detonation that exceed 6000 m/s). Secondary explosives include the most common explosives used in the military field such as **RDX**, **PETN**, **HMX**, **TNT**, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), tetryl, picric acid, CL20 and NC.

**Tertiary explosives** is an extra group, sometimes added in the classification, to include and separate those insensitive explosives widely used for mining and demolition purposes, which have lower velocities of detonation than military secondary explosives. ANFO, ANAI and dynamite compositions are common examples of tertiary explosives.

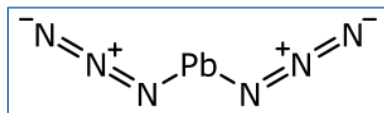
## **Low energy explosives -**

Low energy explosives deflagrate creating a subsonic wave front that does not reach the speed of sound. The explosion that low explosives may produce is a consequence of the overpressure generated inside a container by the accumulation of gas products from deflagration. Because of the progressive production of these gas products during their deflagration, low explosives are mostly used as propellants, either in pyrotechnics, space rockets or ammunition for firearms. Smokeless powder, black powder and flash powder are typical examples of low explosives.

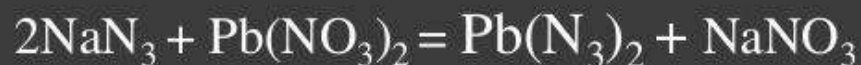
**LEAD AZIDE**



## Preparation and explosive properties of lead azide, $\text{Pb}(\text{N}_3)_2$



- It is prepared by reacting aqueous solutions of sodium azide and lead nitrate with each other.



- During the preparation, the formation of large crystals must be avoided, since the breakup of the crystalline needles may produce an explosion.
- Accordingly, technical grade product is mostly manufactured which contains 92–96%  $\text{Pb}(\text{N}_3)_2$ , and is precipitated in the presence of dextrin, polyvinyl alcohol, or other substances which interfere with crystal growth.

The order of impact sensitivity:

Alkali Azides <  $\text{TlN}_3$  <  $\text{AgN}_3$  <  $\text{Ba}(\text{N}_3)_2$  <  $\text{Pb}(\text{N}_3)_2$  < Copper Azides

The most commonly used primary explosives by the U.S. military are lead azide (used most often in detonators and blasting caps)

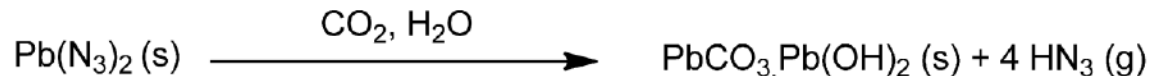
\* There is a strong correlation between non-bond NN distance and impact sensitivity in inorganic azides. The closer together the non-bonded nitrogen atoms are the more sensitive the compound. This correlation is much stronger than correlations based on enthalpy of formation, lattice energy and ionisation potential of the cations involved. Short non-bond distances minimise atomic movements to form products and are vital to sensitivity as they provide for a more rapid decomposition reaction.

\* There is some controversy on this statement.



## Reactions –

1. Lead azide is highly sensitive and usually handled and stored under water in insulated rubber containers. Its color varies from white to buff.
2. Ammonium acetate and sodium dichromate are used to destroy small quantities of lead azide.
3. The hygroscopicity of lead azide is very low. Water does not reduce its impact sensitivity
4. Lead azide has immediate deflagration to detonation transition (DDT), meaning that even small amounts undergo full detonation (after being hit by flame or static electricity).
5. Lead azide reacts with copper, zinc, cadmium, or alloys containing these metals to form other azides that is more sensitive than the original lead azide.  
lead azide does not react with aluminum, hence detonator capsules for lead azide are made of this metal.
6. Lead azide reacts with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to produce basic lead carbonate and highly toxic hydrazoic acid ( $\text{HN}_3$ ).  $\text{HN}_3$  can react with exposed copper metal surface in pipes and wires, thus generating the highly sensitive and deadly copper azide ( $\text{Cu}(\text{N}_3)_2$ ). Several fatal military accidents over the years have been associated with this species.

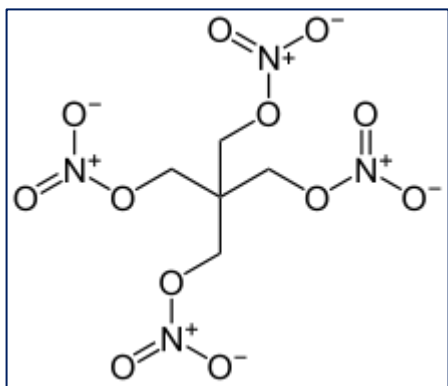


## CAUTION!!!

- Caution should be exercised when using azides. Both organic and inorganic azides can be heat- and shock-sensitive and can explosively decompose with little input of external energy.
- Exposure to small amounts of sodium azide can result in rapid breathing, restlessness, dizziness, weakness, headache, nausea, vomiting, rapid heart rate, red eyes, clear drainage from the nose, coughing, skin burns, and blisters.
- Do not use halogenated solvents (such as methylene chloride or chloroform) for sodium azide reactions, as this can result in the formation of potentially explosive diazidomethane and triazidomethane, respectively.
- Do not concentrate azide-containing reaction mixtures through rotary evaporation or distillation.
- Do not use metal spatulas for weighing and transferring azides.
- Do not expose organic azides to ground glass joints as this may cause the azide to decompose explosively.

# PENTAERYTHRITOL TETRANITRATE

PETN



**PETN** has the chemical formula  $C_5H_8N_4O_{12}$ . It is the [nitrate ester](#) of [pentaerythritol](#), and is structurally very similar to [nitroglycerin](#). Penta refers to the five [carbon atoms](#) of the [neopentane](#) skeleton.

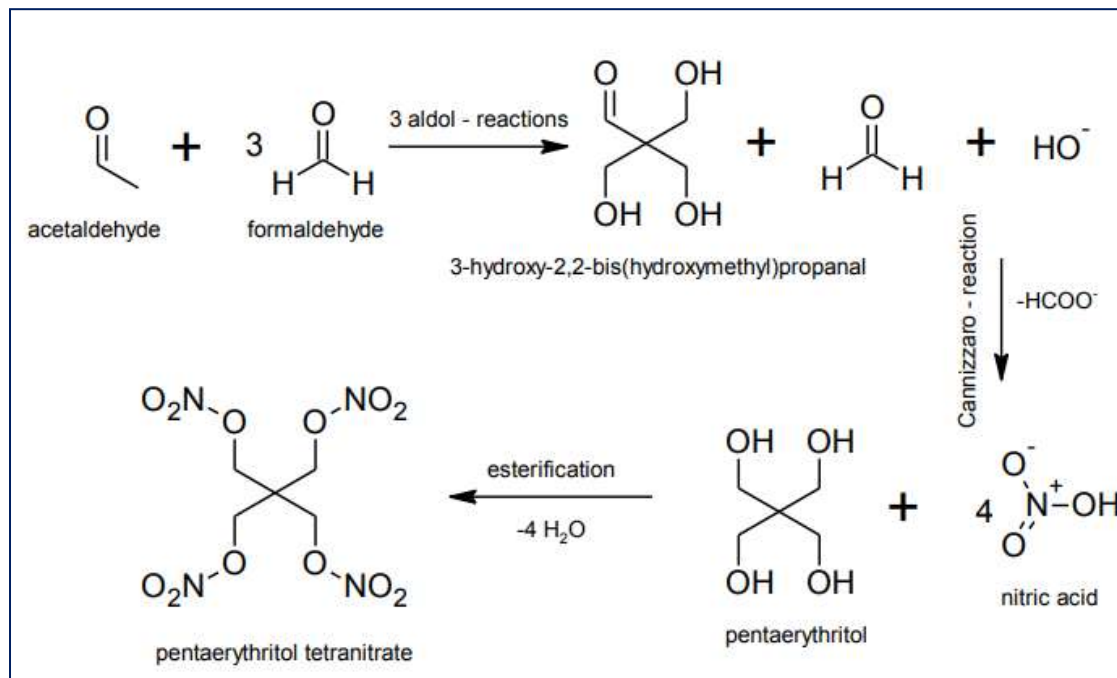
PETN is a secondary explosive and is not as sensitive as primary explosives such as lead azide. In various degrees of granulation it is used as a priming composition in detonators, a base charge in blasting caps, a core load for detonating cord, and in the manufacture of pentolite.

The hydrolysis of PETN can be accelerated with 0.1% nitric acid. As well as other nitrate esters, PETN degrades by losing  $NO_2$  autocatalytically.

It can also be degraded by iron metal to pentaerythritol.

PETN shows in the environment a biodegradation. Bacteria use PETN to gain energy by denitrating into trinitrate and dinitrate. But because of the insolubility in water PETN is not available for organisms. It is also not very toxic.

**Preparation** - In the first step the starting material pentaerythritol is produced by the reaction of formaldehyde and acetaldehyde. There are three aldol reactions which form three new carbon-carbon bonds. After these reactions a Cannizzaro reaction leads to the intermediate pentaerythritol. Here is the aldehyde reduced to an alcohol and formaldehyde is oxidized to formic acid. Now pentaerythritol tetranitrate is formed by the reaction of pentaerythritol with concentrated nitric acid. This step is an esterification of an alcohol (pentaerythritol) and an acid (nitric acid), four hydroxyl groups are transformed into four nitrate ester groups



PETN is a strong but chemical insensible Explosive. Compared to TNT it has 70% more power considering the explosion heat (The Explosion heat gives the amount of energy which is set free during the detonation.)

The PETN is used as Explosive in combination with TNT or Hexogen for Grenades or for detonating cords to start bigger Explosion from the distance. But it's also used in combination with plasticizers like wax for plastic explosives.

The most popular explosive in this class is Semtex.

PETN, a nitro preparation, is used in case of Coronary artery disease to relieve the symptoms. CAD is caused by deposits accumulating in the inner walls of the arteries of the heart. This leads to constriction of the heart arteries, so the heart muscles are undersupplied with blood, which causes an oxygen deficiency in the heart muscles.

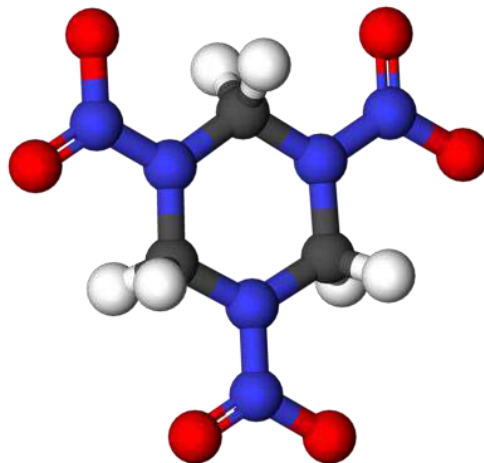
PETN retains its properties in storage for longer periods than do nitroglycerin and nitrocellulose. Nevertheless, it is a sensitive compound and is easily detonated by an appropriate mechanical shock. PETN was first synthesized in 1894 and was introduced as a commercial explosive after World War I. It has been valued in both military and civilian applications for its shattering force and efficiency. It is used by itself in detonators, blasting caps, and a detonating fuse known as Primacord, which is used to propagate a series of detonations from one explosive charge to another. A mixture of roughly equal amounts of PETN and trinitrotoluene (TNT) creates a military high explosive called pentolite, which is used in grenades, artillery projectiles, and shaped-charge warheads such as the ones launched by the old bazooka-type antitank weapons of World War II and their modern descendants. Mixed with the extremely powerful compound RDX in an appropriate solvent, PETN forms a plastic explosive mixture known as Semtex.

# RDX

**Research Department eXplosive**

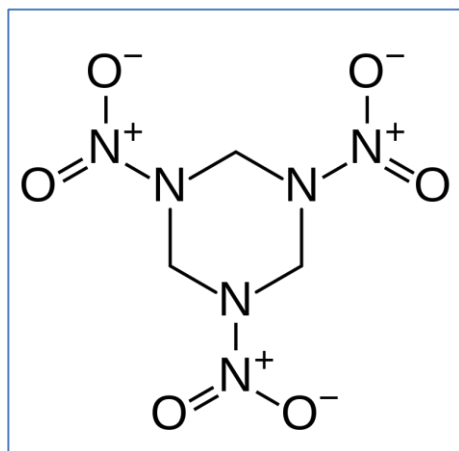
or

**Royal Demolition eXplosive**





- **RDX**, formally **cyclotrimethylenetrinitramine**, also called **cyclonite**, **hexogen**, or **T<sub>4</sub>**, powerful explosive, discovered by Georg Friedrich Henning of Germany and patented in 1898 but not used until World War II, when most of the warring powers introduced it.
- Relatively safe and inexpensive to manufacture, RDX was produced on a large scale in the United States by a secret process developed in the United States and Canada.



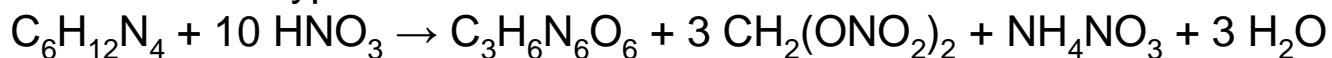
## Properties -

- RDX is a hard, white crystalline solid, insoluble in water and only slightly soluble in some other solvents.
- Its principal nonmilitary use is in blasting caps. It is often mixed with other substances to decrease its sensitivity.
- Explosion may be prompted by sudden shock, high temperature, or combination of both

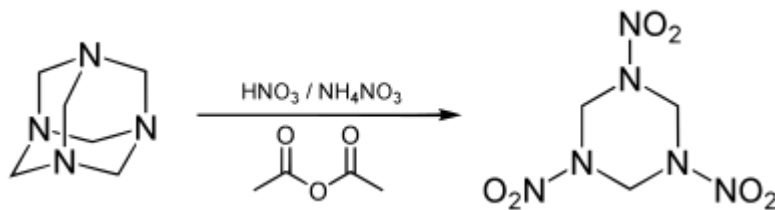
## Synthesis –

RDX is classified by chemists as a hexahydro-1,3,5-triazine derivative. It is obtained by treating hexamine with white fuming nitric acid.

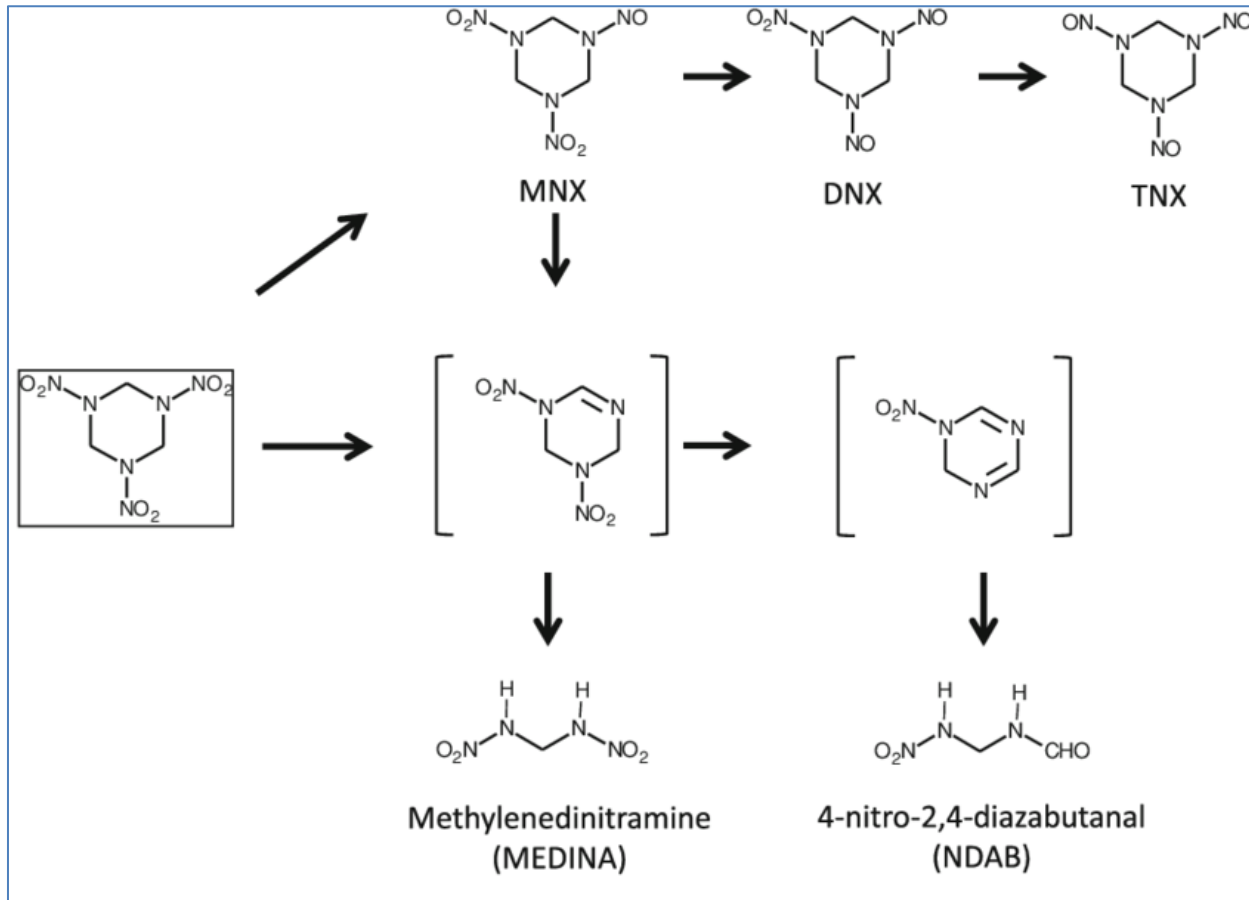
This [nitrolysis](#) reaction also produces [methylene dinitrate](#), ammonium nitrate, and water as byproducts . The overall reaction is:



Modern syntheses employ hexahydro triacyl triazine as it avoids formation of HMX.



# Decomposition product of RDX -



## Stability –

- RDX has a high nitrogen content and a high O:C ratio, both of which indicate its explosive potential for formation of  $N_2$  and  $CO_2$ .
- RDX undergoes a deflagration to detonation transition (DDT) in confinement and certain circumstances.
- The velocity of detonation of RDX at a density of  $1.76 \text{ g/cm}^3$  is  $8750 \text{ m/s}$ .
- It starts to decompose at approximately  $170 \text{ }^\circ\text{C}$  and melts at  $204 \text{ }^\circ\text{C}$ . At room temperature, it is very stable. It burns rather than explodes.
- It detonates only with a detonator, being unaffected even by small arms fire. This property makes it a useful military explosive. It is less sensitive than pentaerythritol tetranitrate (PETN).
- RDX sublimes in vacuum, which restricts or prevents its use in some applications.
- RDX, when exploded in air, has about 1.5 times the explosive energy of TNT per unit weight and about 2.0 times per unit volume
- RDX is insoluble in water, with solubility  $0.05975 \text{ g/L}$  at temperature of  $25^\circ\text{C}$ .

# Rocket\_propellant



*Propellant* is the chemical mixture burned to produce thrust in rockets and consists of a fuel and an oxidizer.

A *fuel* is a substance that burns when combined with oxygen producing gas for propulsion.

An *oxidizer* is an agent that releases oxygen for combination with a fuel.

The ratio of oxidizer to fuel is called the *mixture ratio*.

Propellants are classified according to their state - liquid, solid, or hybrid.

## Liquid Propellants

In a liquid propellant rocket, the fuel and oxidizer are stored in separate tanks, and are fed through a system of pipes, valves, and turbopumps to a combustion chamber where they are combined and burned to produce thrust. Liquid propellant engines are more complex than their solid propellant counterparts, however, they offer several advantages. By controlling the flow of propellant to the combustion chamber, the engine can be throttled, stopped, or restarted.

N.B - A good liquid propellant is one with a high specific impulse or, stated another way, one with a high speed of exhaust gas ejection. This implies a high combustion temperature and exhaust gases with small molecular weights.



Liquid propellants used in rocketry can be classified into three types: petroleum, cryogenics, and hypergols.

**Petroleum** fuels are those refined from crude oil and are a mixture of complex hydrocarbons, i.e. organic compounds containing only carbon and hydrogen. The petroleum used as rocket fuel is a type of highly refined kerosene, called RP-1 in the United States. Petroleum fuels are usually used in combination with liquid oxygen as the oxidizer. Kerosene delivers a specific impulse considerably less than cryogenic fuels, but it is generally better than hypergolic propellants.

**Cryogenic** propellants are liquefied gases stored at very low temperatures, most frequently liquid hydrogen (LH<sub>2</sub>) as the fuel and liquid oxygen (LO<sub>2</sub> or LOX) as the oxidizer. Hydrogen remains liquid at temperatures of -253 °C (-423 °F) and oxygen remains in a liquid state at temperatures of -183 °C (-297 °F). Another cryogenic fuel with desirable properties for space propulsion systems is liquid methane (-162 °C).

#### **Drawbacks of Cryogenic Propellants –**

Because of the low temperatures of cryogenic propellants, they are difficult to store over long periods of time. For this reason, they are less desirable for use in military rockets that must be kept launch ready for months at a time. Furthermore, liquid hydrogen has a very low density (0.071 g/ml) and, therefore, requires a storage volume many times greater than other fuels. Despite these drawbacks, the high efficiency of liquid oxygen/liquid hydrogen makes these problems worth coping with when reaction time and storability are not too critical. Liquid hydrogen delivers a specific impulse about 30%-40% higher than most other rocket fuels.

***Hypergolic*** propellants are fuels and oxidizers that ignite spontaneously on contact with each other and require no ignition source. The easy start and restart capability of hypergols make them ideal for spacecraft systems.

Hypergolic fuels commonly include hydrazine, monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH)

## **Solid Propellants –**

Solid propellant motors are the simplest of all rocket designs. They consist of a casing, usually steel, filled with a mixture of solid compounds (fuel and oxidizer) that burn at a rapid rate, expelling hot gases from a nozzle to produce thrust. When ignited, a solid propellant burns from the center out towards the sides of the casing. The shape of the center channel determines the rate and pattern of the burn, thus providing a means to control thrust. Unlike liquid propellant engines, solid propellant motors cannot be shut down. Once ignited, they will burn until all the propellant is exhausted.

**There are two families of solids propellants: i) homogeneous and ii) composite.**

Both types are dense, stable at ordinary temperatures, and easily storable.

Homogeneous propellants are either simple base or double base. A simple base propellant consists of a single compound, usually nitrocellulose, which has both an oxidation capacity and a reduction capacity. Double base propellants usually consist of nitrocellulose and nitroglycerine, to which a plasticiser is added.

## Hybrid Propellants

Hybrid propellant engines represent an intermediate group between solid and liquid propellant engines. One of the substances is solid, usually the fuel, while the other, usually the oxidizer, is liquid. The liquid is injected into the solid, whose fuel reservoir also serves as the combustion chamber. The main advantage of such engines is that they have high performance, similar to that of solid propellants, but the combustion can be moderated, stopped, or even restarted. It is difficult to make use of this concept for very large thrusts, and thus, hybrid propellant engines are rarely built.

A hybrid engine burning nitrous oxide as the liquid oxidizer and HTPB rubber as the solid fuel powered the vehicle *SpaceShipOne*, which won the Ansari X-Prize.

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