The Explosive Chemistry of Nitrogen*

A Fascinating Journey From 9th Century to the Present

Dheeraj Kumar and Anil J Elias

The chemistry behind explosives is marked with the omnipresence of the element nitrogen. The discovery of the explosive properties of nitrogen-based compounds comprises many interesting and serendipitous observations made by inquisitive scientists. In this article, we unravel the fascinating history behind the development of explosives from the 9th century to the present. Every country with an army keeps on upgrading the sharpness and power of their arsenal, and in this regard, the role played by the chemists in developing new explosives, and the chemistry behind these explosives are explained in this article. The basic chemical properties of explosives, their classification, comparison and methods of evaluation are explained. The current status of research in making new explosives and the challenges involved in making explosive polynitrogen compounds such as pentazolates and pentazenium are also illustrated.

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1. Introduction

An interesting observation if one tries to analyse explosions from a chemist’s perspective is that the molecule, N_2 is one of the major products in almost all explosions except in a few cases involving peroxides. This remarkable property of the element nitrogen which otherwise is considered pretty inert is well known to chemists involved with the development of explosives and high energy density materials. The story of the development of the explosive chemistry of nitrogen which began in the 9th century and continues till date is one of interesting serendipities, challenges,

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and difficulties, overcome by fearless and daring chemists, often risking their lives and those of their co-workers.

The atmosphere of our Earth is 78% nitrogen, and the very poor reactivity of nitrogen has been well utilized as an inert and blanket gas in many industrial processes. Compounds of nitrogen have three major applications namely: fertilizers (ammonia, urea and related compounds), explosives (organic nitro and polynitrogen compounds) and as an inhalation anesthetic (nitrous oxide). The chemistry of fertilizers began when Justus von Liebig, considered as the founder of organic chemistry and the greatest chemistry teacher of all times, in 1840 identified nitrogen along with phosphorus and potassium as essential for plant growth. He also predicted the importance of ammonia in making synthetic fertilizers which became a reality soon. Since 1844, nitrous oxide, known also as laughing gas has been used in dentistry and surgery as an anesthetic and analgesic although British upper class were having laughing gas parties even in 1799. However, the origins of the explosive chemistry of nitrogen date even further back [1,2].

Keywords
Nitrogen, explosives, nitration, azide, pentazenium, pentazolate.

2. History of Explosives

In the 9th century, Chinese alchemists discovered gunpowder (also called black powder) which is a combination of sulfur, charcoal and potassium nitrate. Europeans brought this technology to mainland Europe in the 13th century. The demand for potassium nitrate for making gunpowder resulted in Europeans sailing all the way down to South America, mainly Atacama Desert of Chile where sodium nitrate was available in plenty (known by the name 'Chile saltpetre' as part of a mineral called *Caliche*). Sodium nitrate, although is not suitable for gunpowder due to its deliquescent nature was easily converted to potassium nitrate by a displacement reaction. By 1859, the British were importing as much as 47,000 metric tonnes of Chile saltpetre for use of the Royal army.

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A serendipitous observation in 1845 by Christian Schoenbein, who is also the discoverer of ozone gas led to another path-breaking discovery in the chemistry of explosives. Although his wife had not permitted him, Schoenbein used to do some chemistry on his wife's kitchen table whenever she was away. After one such messy chemistry session involving several acids, Schoenbein wiped off the acid mess with his wife's kitchen apron which was lying around, washed it and hung the wet apron on the hot oven to dry. After a few minutes, to his utter surprise, he saw the apron (which incidentally was made of cotton) disappear into thin air with a flash and with no smoke. Further investigation by him led to the finding that cellulose of cotton can be made to undergo nitration using a mixture of Con. HNO_3 and Con. H_2SO_4, now well known as the 'nitrating mixture', and what he accidentally made was 'nitrocellulose'. One can replicate this reaction easily in the laboratory if a swab of cotton wool is carefully nitrated using the nitrating mixture. A piece of nitrocellulose if kept on the palm of your hand and lighted with a matchstick will disappear with a flash in less than a second without burning your hand. Nitro groups are ready sources for oxygen which results in very fast oxidation. Nitrocellulose is also known as guncotton as by this time, gun enthusiasts observed that if you replace black powder with cellulose nitrate, it works better with hardly any smoke being produced, and this led to what is now known as the smokeless guns.

The possibility of nitrating other compounds similar to cellulose was tried out by many during this period, and two years later in 1847, Ascanio Sobrero, an Italian chemist made nitroglycerin by nitrating glycerine. Later the Swedish family of Nobel headed by Immanuel Nobel and his two sons Emil and Alfred began experimenting with nitroglycerin and started an armament factory in Heleneborg, Sweden. In an accidental explosion involving nitroglycerin in 1864, the youngest of the brothers, Emil Nobel lost his life. Alfred Nobel then moved to an isolated place near Hamburg in Germany called Krümmel hills and started another factory with the name '*Alfred Nobel and Company*'. Nitroglycerin was in great demand in America those days for blasting purposes especially by the railways which were making tunnels in the Sierra

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Nevada Mountains for the American transcontinental railroad. Nitroglycerin which was shipped from Germany often ended up exploding while in transit. One such explosion killed 15 people and this lead to a ban on the transport of nitroglycerin in California state. Alfred Nobel then discovered that nitroglycerin can be tamed and can be transported without fear of explosion if *kieselguhr*, a naturally occurring, soft, siliceous powder[1] is mixed with it. This mixture was called *dynamite* which was much safer to handle than nitroglycerine or nitrocellulose. He obtained a patent for this discovery in 1867. Dynamite rapidly gained wide-scale use as a safe, portable explosive instead of black powder and nitroglycerin. Alfred Nobel made a considerable profit from the sale of dynamite, and when he died in 1896 he left in his will, nine million dollars to establish what is now famous as the Nobel Prizes.

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We all hear the phrase '*necessity is the mother of invention*'. It was one such necessity which led to the path-breaking discovery of ammonia by the Haber Bosch process. During the first World War (1914–18), Chile saltpetre was in very high demand for making ammunition. Europeans and Americans were in the Atacama Desert trying to mine the mineral Caliche which contained $NaNO_3$ and ship it out to their countries. The enemies of Germany especially the British blocked the German ships from getting access to Chile saltpetre. Germans in the meantime discovered that ammonia can be oxidized to nitric oxide and further converted to nitric acid which can be used for making explosive nitrates. So, Germans focused on finding ways to make ammonia from atmospheric nitrogen, and a very smart chemist by the name Fritz Haber succeeded in making ammonia by mixing hydrogen and nitrogen and passing the mixture over a heated osmium catalyst at high pressure. This process was scaled up to industrial scale by Carl Bosch of BASF, a German chemical company using an iron catalyst. Thus, the demand for Chile saltpetre drastically reduced. So historically, it is correct to say that the necessity of making explosives lead to ammonia synthesis rather than the need of making fertilizers, although now 85% of all the ammonia made

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[1] A fossilized form of algae, also known a diatomaceous earth.

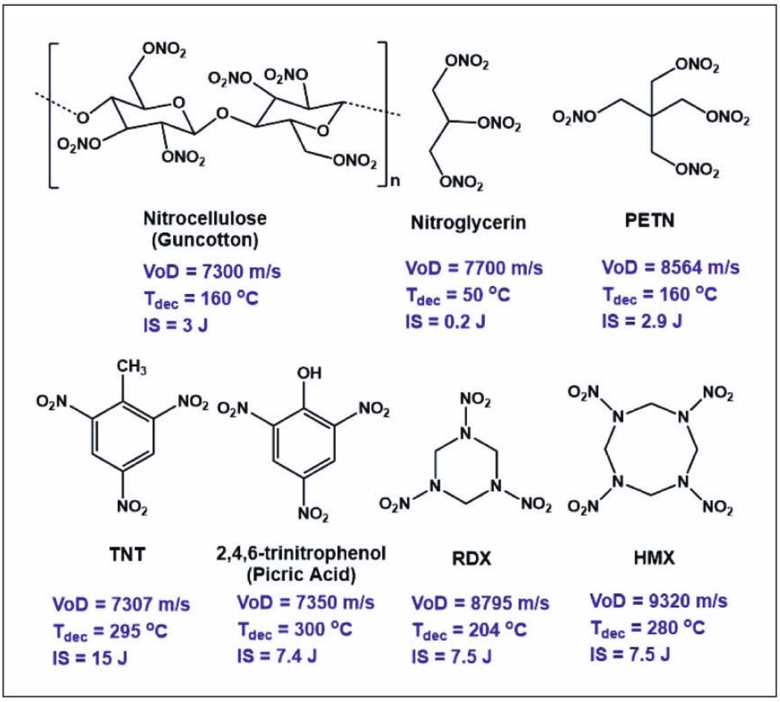

Figure 1. Examples of common explosives and their properties.

in the world is used for making fertilizers.

2,4,6-trinitrotoluene (TNT), the most commonly used high explosive was first synthesized in 1863 by a German chemist Julius Wilbrand by the nitration of toluene. Another German chemist, Carl Häussermann discovered its explosive properties in 1891. TNT is an example of melt-casting explosive as it melts at 80 °C, way below its decomposition temperature (300 °C), allowing it to be melted with steam and safely cast into shells. Therefore, TNT, in addition to being an explosive, acts as an energetic binder and is usually used in combination with other high explosives. Energetic binders are important part of explosives as in addition to imparting integrity to the main explosive charge, they also improve safety in handling, transportation and storage. Some of the most commonly used explosive blends containing TNT includes (a) Composition B (59.5% RDX[2] + 39.4% TNT + 1% Paraffin wax), (b) Amatex (51% NH_4NO_3 + 40% TNT + 9% RDX).

[2] Research Department Explosive.

2,4,6-trinitrophenol (TNP), more commonly known as picric acid, was initially synthesized by nitration of substances like silk, animal horns, indigo and natural resins. Its synthesis by nitration of phenol and correct structural determination was accomplished in 1841. In 1885, French chemist Eugéne Turpin patented the use of pressed and cast picric acid in blasting charges and artillery shells. During the next few years, France and Britain adopted a mixture of picric acid and guncotton under different names; *Melinite* and *Lyddite*, respectively. In 1889, the Japanese came up with another improved formulation known as *Shimose powder*, which played a vital role in the Japanese victory in the Russo–Japanese war of 1904–1905. However, picric acid is one of the most acidic phenols, and shells filled with picric acid become highly unstable if picric acid reacts with the metal shells to form metal picrates, which are primary explosives. Ammonium picrate, also known as Dunnite, is an explosive developed by US Army during World War I. Importance of picric acid in World War I was demonstrated by efforts to control the availability of phenol. During that time, phenol was obtained from coal as co-product of coke ovens and the manufacture of gas for gaslighting. Germans bought US supplies of phenol and converted it to aspirin (acetylsalicylic acid), to keep it away from the allies.

Nitration of organic compounds continued and many examples of C-nitrated, O-nitrated and N- nitrated explosives were discovered. Classic examples such as RDX and HMX (Her Majesty's Explosive) were used during the second World War. Methods were established to compare the blasting capability of explosives. Designer explosives such as CL-20, DDF, and octanitrocubane were prepared using multistep synthesis where the ratio of carbon, hydrogen, oxygen and nitrogen were balanced so that all constituent elements got converted to stable products such as CO_2, N_2 and H_2O. Determining the velocity of detonation is one way to compare the power of explosion of different explosives. Compounds such as CL-20 and octanitrocubane have some of the highest velocities of detonation (*Figure* 2).

Nowadays, the use of explosives is no longer limited to military

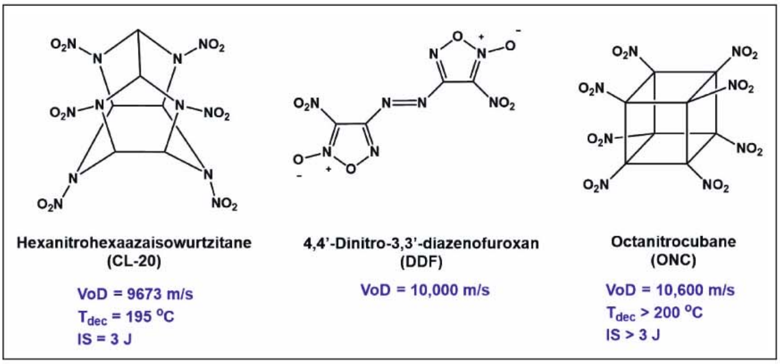

Figure 2. Examples of designer explosives and their properties.

applications. They are extensively used for space exploration and various civilian applications such as, in the construction industry, in forecasting earthquakes, for exploration and mining of minerals, for correction of weather phenomena, in extinguishing fires, for processing metals, for the synthesis of nano-materials, etc [3]. Therefore, growth and development of chemistry of explosives is an essential field of chemistry and material science.

3. Basic Chemistry and Properties of Explosives

The most common property of explosives is their ability to release a large amount of energy in the form of heat and pressure under specific conditions of heat, shock, friction, electrostatic discharge, etc. Once initiated, the reaction is self-sustaining and is accompanied by the generation of very high temperature (3000–5000 $^{\circ}$C), humongous expansion of released gases in a few microseconds, shock and loud noise. As per Gay Lussac's pressure-temperature law, a proportional temperature-pressure increase is ultimately relieved in the form of an explosion. It is worthwhile to note that release of heat without sufficient rapidity can't be considered as an explosion. For example, although burning of coal releases approximately five times as much heat as an equivalent amount of nitroglycerin, the rate at which coal releases heat is very slow and, therefore, coal cannot be described as an explosive [4].

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The basic design of all explosives has various energetic functionalized groups (called explosophores) attached to the carbon-rich backbones. These carbon-rich backbones act as the fuel, whereas, the oxygen-rich functionalized groups act as oxidizers. Although many advanced explosions use external oxidizers (like ammonium perchlorate) to assist oxidation and detonation of the main fuel, the best approach to design 'green explosives' is to incorporate both fuel and oxidizer moieties into the same structure. Traditional explosives like TNT and picric acid has benzene ring, and RDX has 1,3,5-triazacyclohexane ring as fuel, whereas various other advanced explosives use more complex carbon-based frameworks as their backbone. In contrast, modern-day green explosives have nitrogen and oxygen-rich backbones based on azoles, tetrazines, oxadiazoles, etc. Common explosophores include nitro ($-NO_2$), nitramine ($-NHNO_2$), azido ($-N_3$), amino ($-NH_2$), nitrito ($-ONO_2$), azo bridge (-N=N-), azoxy [-N=N(O)], dinitromethane [$-CH(NO_2)_2$] and trinitromethane [$-C(NO_2)_3$.

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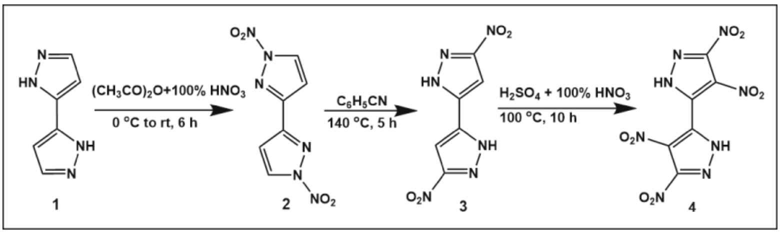
The most common explosives have multiple nitro groups attached to the different carbon and nitrogen-rich backbones. So, the question arises, why is nitro group so important in explosive chemistry? The significance of $-NO_2$ groups is two-fold. First, nitro group is a source of nitrogen, which is in a significantly higher energy level (nitrogen has a significantly higher energy level in its oxidized state within the nitro group), which reduces to the highly-stable inert nitrogen gas (in significantly lower energy level) during an explosion, releasing high amount of energy in the form of heat and making the enthalpy of overall reaction very large and negative. Secondly, nitro group is also a source of oxygen, which is required for the oxidation of the hydrocarbon part of the explosive molecule. This allows the combustion of the hydrocarbon backbone (carbon to carbon dioxide and hydrogen to water) without the need for an external source of oxygen.

The most common method of introducing nitro groups in organic compounds is by carrying out nitration using 100% nitric acid or a mixture of 100% nitric acid with various other acids like acetic acid, sulphuric acid, trifluoroacetic acid, etc. Scheme 1 represents



Scheme 1. Synthesis of tetranitrobipyrazole (TNBP) using different nitration conditions.

the synthesis of one of the most recent nitro explosives, tetranitrobipyrazole (TNBP, 4), synthesized by Shreeve and co-workers. Its synthesis starts with di-N-nitration of bipyrazole (1) using a mixture of acetic anhydride and 100% nitric acid to give (2), followed by thermal rearrangement in benzonitrile at high temperature to give (3). Finally, nitration of (3) with nitrating mixture (H_2SO_4 + 100% HNO_3) at 100 °C results in tetranitrobipyrazole, TNBP (4) [5].

4. Classification of Explosives

Explosives are classified according to the chart shown (*Figure* 3). Deflagration and detonation are two terms often used in association with explosives. Deflagration involves subsonic[3] flame propagation velocity, typically below 100 m/s, and relatively modest overpressures, below 0.5 bar. Although all combustion (fires) can be defined as a deflagration, these are often associated with natural gas or propane releases and gasoline burning. A detonation, on the other hand, is branded by supersonic flame propagation velocities, often up to 2000 m/s, and high overpressures of gases released – up to 20 bars. Being very fast reactions, these explosions create a high-pressure shock wave that causes significant damage at large distances from the site of the blast. Detonations usually are associated with blasting agents or munitions (high explosives). Examples of a classic compound which undergoes both deflagration and detonation is ammonium nitrate.

High explosives are also classified as primary and secondary ex-

[3] Less than the speed of sound.

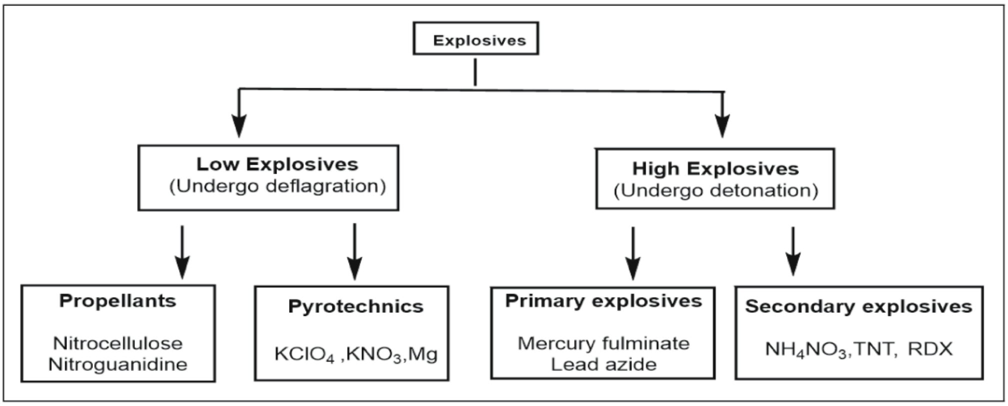


Figure 3. Classification of explosives.

plosives. Primary explosives usually explode or detonate when they are heated or subjected to shock. They do not burn and may not have elements needed for combustion. These are extremely sensitive to friction, impact, heat, etc. Primary explosives are often used as detonators to initiate the explosion of larger charges of less sensitive secondary explosives. Secondary explosives, on the other hand, detonate only under the influence of the shock of the explosion of a primary explosive. Not all of them are combustible, and most of them can even be ignited by a flame and generally burn without vigor and can be extinguished also easily. They differ from primary explosives in not getting exploded by a simple heat or shock and requires substantially more energy to make them explode and the explosions are much more powerful. Consider the case of the most commonly used secondary explosive ammonium nitrate (sometimes as a mixture with fuel oil called ANFO). If it is simply heated, it will get converted to N_2O and H_2O and this is the laboratory method for preparation of N_2O. When sufficient initial energy is given by detonation using a primary explosive, ammonium nitrate will explode releasing the highly stable molecules N_2, H_2O and O_2 [2].

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There had been many strong explosions reported in history which involved ammonium nitrate and some of them happened when this compound, also a common fertilizer was being loaded on to ships. The most devastating among these explosions was the Texas City disaster which happened on April 16, 1947. A cargo ship called *Grandcamp* was being loaded on that fateful day at the port of Texas City, when a fire was detected in the hold of the ship. At that point of time, 2300 tons of ammonium nitrate in sacks were already stacked aboard. The captain attempted to douse the fire by closing the hold and pumping in pressurized steam. An hour later, the ship exploded, killing hundreds of people and setting fire to another vessel, the *High Flyer*, which was moored 250 metres away from the *Grandcamp* and which contained 1050 tonnes of sulfur and 960 tons of ammonium nitrate. The *Grandcamp* explosion was so powerful that it created a powerful shockwave which broke the glass windows of houses as far as 40 miles away and even knocked down two small aeroplanes flying at 1,500 feet (460 m) in the sky. After burning for sixteen hours, the *High Flyer* also exploded the next day. All but one member of the Texas City fire department died. Close to 600 people died, and 5,000 people were injured [6].

5. Evaluation of Explosives

There are various parameters which are used to judge the stability and energy content of an explosive. Energetic properties of an explosive are determined by measuring its density, heat of formation, detonation velocity and detonation pressure. Detonation velocity or velocity of detonation (VoD) is the velocity at which the shock wave front travels through a detonated explosive, whereas detonation pressure (DP) is the peak dynamic pressure in the shock front. Both of these important parameters depend on the molecular formula of explosive, values of heat of formation (ΔH_f) and density. The density of an explosive is a highly important parameter as both VoD and DP are directly proportional to the value of density and (density)^2, respectively. The typical detonation velocity of explosives ranges from 2700 to 10,000 m/s. Stability of explosive is determined by measuring its decomposition temperature (T_d) and sensitivity towards impact, friction and electrostatic discharge. Impact sensitivity (IS) indicates the ease with which an explosive material can be set off by a blow impact, and it is expressed in terms of the minimum distance through

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which a standard weight is allowed to drop to cause an explosive to explode. Generally, compounds with an impact sensitivity value less than 10 J are considered sensitive, compounds having impact sensitivity values in the range 10–40 J are less sensitive, whereas compounds with impact sensitivity values more than 40 J are insensitive. *Figures* 1, 2 and 7 lists these properties measured for some explosives.

Oxygen balance (OB% or Ω%) is another very important parameter of explosives and it indicates the degree to which an explosive can be oxidized. An explosive molecule is said to have a zero oxygen balance if it contains just enough oxygen to convert all carbons to carbon dioxide, hydrogens to water, and all metals to metal oxides. The results of oxygen balance show good correlation with both energetic performance and sensitivity of the energetic compounds, and it is often observed that explosive molecules with an oxygen balance closer to zero are more powerful and sensitive. Apart from having high detonation velocity and detonation pressure, explosives are also expected to have high decomposition temperature ($T_d > 200\,^{\circ}C$), good oxygen balance (close to zero), and lesser sensitivity towards external stimuli. In addition, explosives should be free from any elements that can cause harm to the environment.

6. Primary Explosives

Primary explosives are very sensitive materials and can easily detonate by application of impact, friction, spark, fire, etc. They are used in fewer quantities (compared to secondary explosives) in detonators, primers, and percussion caps. Lead azide, $Pb(N_3)_2$, synthesized for the first time by Curtius in 1891, is the most commonly used primary explosive. In fact, so much of it along with another lead compound – lead styphnate – has been used by armies over decades during training that military training grounds have been highly contaminated with lead with harmful effects on the environment. According to the US Army, some 10 million lead azide-containing devices, everything from cartridges to det-

According to the US Army, some 10 million lead azide-containing devices, everything from cartridges to detonators, are produced in the US every year.

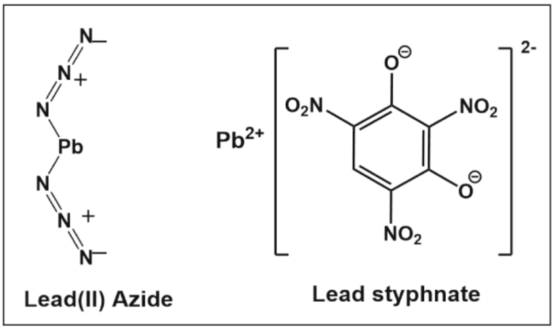

Figure 4. Examples of traditional lead-based primary explosives.

onators, are produced in the US every year (*Figure* 4) [7].

Potassium metal is a green species with excellent coordination ability to energetic ligands. There are few potassium metal-based primary explosives like potassium 1,1'-di-nitramino-5,5'-bis-(tetrazolate) (K_2DNABT), potassium 1,5-di(nitramino)-tetrazole (K_2DNAT) and potassium 4,5-bis(dinitromethyl)-furoxanate (K_2BDNMF) synthesized by Klapotke and Shreeve's group (*Figure* 5) [8]. However, it was found that potassium-based primary explosives are relatively weaker in terms of their priming and initiating ability. Therefore, scientists are now looking for the development of metal-free, high-performance primary explosives. In 2016, Prof. Klapotke's group at Munich synthesized a metal-free primary explosive, based on methylene bridged pyrazole, bis (4-diazo-5-nitro-3-oxopyrazolyl)methane. Recently, in 2018, Guangbin Cheng group from China reported another metal-free primary explosive based on tetrazene bridged azidotriazine, 3,6-bis-(2-(4,6-diazido-1,3,5-triazin-2-yl)-hydrazinyl)-1,2,4,5-tetrazine (*Figure* 6). They also showed that their compound can generate an intense shockwave to transfer to initiate larger masses of RDX and initiation capacity is comparable to lead azide [9].

7. Current Status of Secondary Explosives

Modern-day explosives not only concentrate on high denotation properties, but also give equal importance to safety and environmental concerns. Traditional explosives like RDX, HMX and CL-

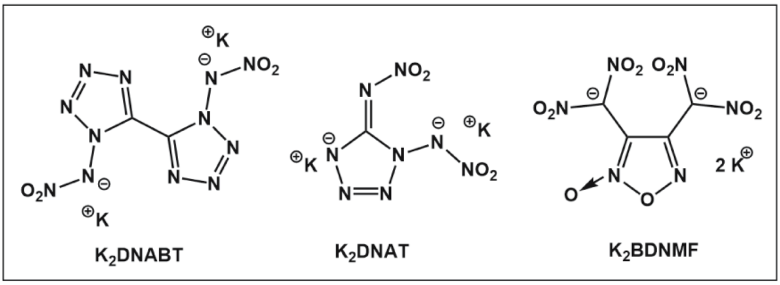

Figure 5. Potassium-based primary explosives.

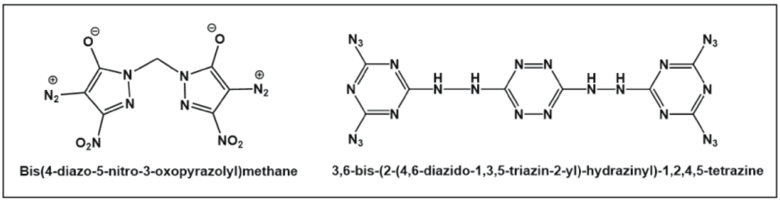

Figure 6. Metal-free primary explosives.

Unlike traditional explosives, which generate most of their strength from the oxidation of the carbon backbone, modern day explosives are based on nitrogen-rich heterocycles e.g., azoles, oxadiazoles, tetrazenes, etc. These explosives have high nitrogen/carbon ratio and are considered as green explosives, as they mainly generate nitrogen gas after decomposition.

20, in addition to being sensitive to physical stimuli, are toxic and carcinogenic because of the nitramine (N-NO$_2$) moiety. Other high explosives like ONC and DDF also suffers from their tedious and expensive synthesis. Unlike traditional explosives, which generate most of their strength from the oxidation of the carbon backbone, modern-day explosives are based on nitrogen-rich heterocycles e.g., azoles, oxadiazoles, tetrazenes, etc. These explosives have high nitrogen/carbon ratio and are considered as green explosives, as they mainly generate nitrogen gas after decomposition. TKX-50, TATOT, and TNDPT are the best examples of modern-day explosives with excellent energetic performance along with good thermal and physical stability (*Figure* 7). Dihydroxylammonium 5,5'-bistetrazole-1,10-diolate (TKX-50) is one of the most promising nitrogen-rich explosives developed by Klapötke and co-workers. TKX-50 is not only extremely powerful and easy to synthesize but also has low sensitivity (thermal and mechanical) and lower toxicity compared to nitramine explosives (RDX, HMX, and CL-20). Another excellent molecule, 3,6,7-triamino-[1,2,4]triazolo[4,3-b][1,2,4]triazole (TATOT), first reported in 1966, was explored as neutral as well

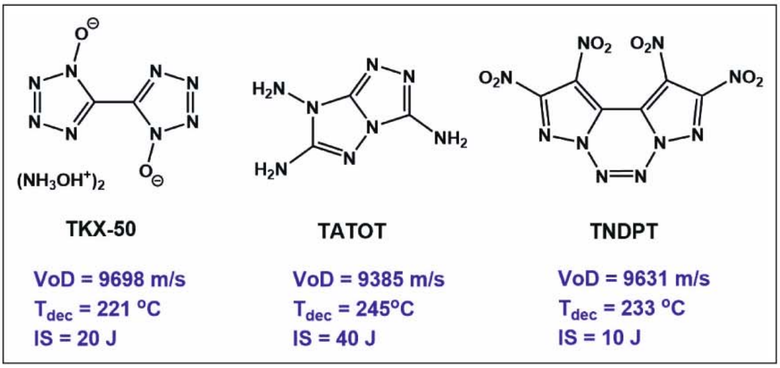

Figure 7. Examples of most promising modern-day explosives and their properties.

as energetic cation by Shreeve and Klapötke in 2015. TATOT is a non-toxic, highly energetic building block with excellent stability. Most recently, in 2017, Shreeve and coworkers have synthesized a dinitropyrazole fused 1,2,3,4-tetrazine (TNDPT), which is much more powerful than CL-20 and also show better thermal stability and sensitivity [10].

8. Azides, Pentazenium and Pentazolates

Another class of nitrogen-based explosives are poly-nitrogen compounds and the most well-known among them are the azides. The water solution of the parent compound hydrazoic acid, HN_3, was first prepared in 1890 by Theodore Curtius by oxidation of hydrazine with nitrous acid. At room temperature and pressure, hydrazoic acid is a toxic, volatile and explosive liquid (b.p. 37 °C) and is, therefore, more easily handled as a salt such as sodium azide, NaN_3. There are two major synthetic routes for sodium azide namely the Curtius method and the Wislicenus methods. The Wislicenus method involves the reaction of sodamide with nitrous oxide while in the Curtius method a nitrite ester (R-ONO) is made first and reacted with hydrazine hydrate and sodium hydroxide to make NaN_3. Allen K. Breed, in 1967, demonstrated that using sodium azide, along with a collision sensor in automobile airbags, one can achieve inflation of the airbag under 30 milliseconds required for collision safety. Widespread use of sodium

Allen K. Breed, in 1967, demonstrated that using sodium azide, along with a collision sensor in automobile airbags, one can achieve inflation of the airbag under 30 milliseconds required for collision safety.

azide in airbags have since then saved thousands of lives in automobile accidents [11].

Why poly-nitrogen compound show explosive character can be understood from the comparison of bond energies. A unique feature of poly-nitrogen compounds is the fact that their decomposition is accompanied by the release of a large amount of heat and voluminous amount of N_2. This is because these compounds have N-N single or double bonds, which are much weaker than the triple bond of N_2. The N≡N bond energy is 945 kJ/mol, whereas the N=N bond energy is 419 kJ/mol, and the N-N bond energy is only 159 kJ/mol. These significant differences in bond dissociation energies between single, double, and triple bonds make the polynitrogens highly endothermic and thermodynamically unstable. In general, sensitivity to decomposition increases with endothermicity.

In 1999, 109 years after the discovery of the azide, K. O. Christe and co-workers made the pentanitrogen cation N_5^+ which was trapped as a salt with AsF_6^-. The novel cation was marginally stable at room temperature and was characterized by spectroscopy. The N_5^+ ion was found to be a powerful oxidizer and reacted explosively with water and organic materials, thus becoming the third stable member of the polynitrogen family. It was reported that explosion of a few milligrams of the shock-sensitive salt actually destroyed a sample chamber of a Raman spectrometer and Teflon reactors! Subsequently, the same researchers were able to make (N_5^+ SbF_6^-) and (N_5^+ $Sb_2F_{11}^-$) salts which were stable and the latter was found to have a V-shaped structure for N_5^+ from X-ray diffraction studies. The cation is highly energetic with calculated enthalpy of formation (ΔH_f) of 1471.8 kJ/mol (*Figure* 8) [12].

While theoretically it was predicted that the polynitrogen anion, N_5^- should be a relatively stable cyclic compound, attempts to make it were not quite successful. Substituted arylpentazole ring compounds of the type Ar–N_5 have been known for quite some time, and many examples with varying substituents on the aryl ring were made and well characterized. However, till 2017, selective cleavage of the C–N bond in arylpentazoles without destroy-

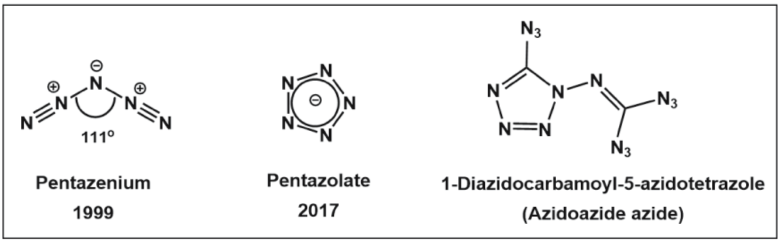

Figure 8. Pentazenium, pentazolate and azidoazide azide.

ing the N_5^- cyclic unit remained impossible. The breakthrough of isolating and structurally characterizing pentazolate anions was made possible by Zhang and coworkers of Nanjing University of Science and Technology, China in 2017. By using ferrous bisglycinate, $Fe(Gly)_2$ were able to selectively cleave the C–N bond of 3,5-dimethyl-4-hydroxyphenylpentazole and stabilize the resulting pentazolate anion. The N_5^- anion was isolated as an air-stable white solid, $(N_5)_6(H_3O)_3(NH_4)_4Cl$ in 19% yield (*Figure* 8) [13].

The pentagonal N_5^- ring was found to comprise five nitrogen atoms in a perfectly planar arrangement from X-ray diffraction studies. Due to the hydrogen bonding present, the salt was found to have remarkable thermal stability up to 117 °C. The cations in the salt apparently play a role in stabilizing the pentazolate anion as attempts to replace them resulted in the decomposition of the salt. However just like wet firecrackers, due to the presence of solvent units and non-energetic counterions, this pentazolate compound was not sensitive to explosion and was quite stable, unlike azides and pentazenium. To overcome these issues, a solvent-free N_5^- was prepared in 2018 by Christie, Zhang and coworkers by the reaction of $[Mg(H_2O)_6][(N_5)_2(H_2O)_4]$ with $AgNO_3$. The $Ag^+N_5^-$ formed has potential explosive properties. This is where this challenging and fascinating chemistry stands as of today [14].

The challenge for making even more powerful explosive nitrogen compounds still remain. Azidoazide azide, a compound containing 14 nitrogen and 2 carbon atoms made in 2011, shows that one can still bring more than 5 nitrogens together (*Figure* 8). Molecules such as N_8 (which in principle can be made by the reaction of N_3^- and N_5^+) or N_{10} (by the reaction of N_5^- and N_5^+) are immediate targets although attempts to make such compounds were disastrous so far. Let us hope that synthetic chemists will design novel methods to make such inaccessible compounds eventually and use them for peaceful civilian applications.

9. Summary

The development of the explosive chemistry of nitrogen-based compounds is presented giving historical landmarks and recent status of research in this area of chemistry as of 2018. The reason why nitrogen is an integral part of almost all explosives is also presented as well as how great chemists succeeded in taming the dangers involved in this chemistry.

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