
5. NITRO COMPOUNDS

SCHÖNBEIN'S WIFE'S exploding apron was not the first example of a man-made explosive molecule, nor would it be the last. When chemical reactions are very rapid, they can have an awesome power. Cellulose is only one of the many molecules we have altered to take advantage of the capacity for explosive reaction. Some of these compounds have been of enormous benefit; others have caused widespread destruction. Through their very explosive properties, these molecules have had a marked effect on the world.

Although the structures of explosive molecules vary widely, most often they contain a nitro group. This small combination of atoms, one nitrogen and two oxygens, NO_2 , attached at the right position, has vastly increased our ability to wage war, changed the fate of nations, and literally allowed us to move mountains.

GUNPOWDER—THE FIRST EXPLOSIVE

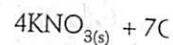
Gunpowder (or black powder), the first explosive mixture ever invented, was used in ancient times in China, Arabia, and India. Early Chinese texts refer to "fire-chemical" or "fire-drug." Its ingredients were not recorded until early in A.D. 1000, and even then the actual proportions required of the component nitrate salt, sulfur, and carbon were not given. Nitrate salt (called saltpeter or "Chinese snow") is potassium nitrate, chemical formula KNO_3 . The carbon in gunpowder was in the form of wood charcoal and gives the powder its black color.

Gunpowder was initially used for firecrackers and fireworks, but by the middle of the eleventh century flaming objects—used as weapons and known as fire arrows—were launched by gunpowder. In 1067 the Chinese placed the production of sulfur and saltpeter under government control.

We have no certainty as to when gunpowder arrived in Europe. The Franciscan monk Roger Bacon, born in England and educated at Oxford University and the University of Paris, wrote of gunpowder around 1260, a number of years before Marco Polo's return to Venice with stories of gunpowder in China. Bacon was also a physician and an experimentalist, knowledgeable in the sciences that we would now call astronomy, chemistry, and physics. He was also fluent in Arabic, and it is likely that he learned about gunpowder from a nomadic tribe, the Saracens, who acted as middlemen between the Orient and the West. Bacon must have been aware of the destructive potential of gunpowder, as his description of its composition was in the form of an anagram that had to be deciphered to reveal the ratio: seven parts saltpeter, five parts charcoal, and five parts sulfur. His puzzle remained unsolved for 650 years before finally being decoded by a British army colonel. By then gunpowder had, of course, been in use for centuries.

Present-day gunpowder varies somewhat in composition but con-

tains a large
chemical rea



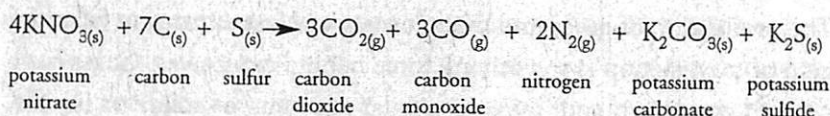
potassium carb
nitrate

This chemical
ratios of the p
is a solid, and
all the reactar
three carbon c
the hot, expan
der that prope
and sulfide fo
dense smoke c

Thought to
the first firearm
which was ign
cated firearms
need for differ
Sidearms neede
and cannons an
water was used
and screened to
powder, the fast
der that was app
manufacture wa
powder mill; th
particularly pote
bishop, was also

NITRO COMPOUNDS

tains a larger proportion of saltpeter than Bacon's formulation. The chemical reaction for the explosion of gunpowder can be written as



This chemical equation tells us the ratios of substances reacting and the ratios of the products obtained. The subscript (s) means the substance is a solid, and (g) means it is a gas. You can see from the equation that all the reactants are solids, but eight molecules of gases are formed: three carbon dioxide, three carbon monoxide, and two nitrogens. It is the hot, expanding gases produced from the rapid burning of gunpowder that propel a cannonball or bullet. The solid potassium carbonate and sulfide formed are dispersed as tiny particles, the characteristic dense smoke of exploding gunpowder.

Thought to have been produced somewhere around 1300 to 1325, the first firearm, the firelock, was a tube of iron loaded with gunpowder, which was ignited by the insertion of a heated wire. As more sophisticated firearms developed (the musket, the flintlock, the wheellock), the need for different rates of burning of gunpowder became apparent. Sidearms needed faster-burning powder, rifles a slower-burning powder, and cannons and rockets an even slower burn. A mixture of alcohol and water was used to produce a powder that caked and could be crushed and screened to give fine, medium, and coarse fractions. The finer the powder, the faster the burn, so it was possible to manufacture gunpowder that was appropriate for the various applications. The water used for manufacture was frequently supplied as urine from workers in the gunpowder mill; the urine of a heavy wine drinker was believed to create particularly potent gunpowder. Urine from a clergyman, or better yet a bishop, was also considered to give a superior product.

NAPOLEON'S BUTTONS

EXPLOSIVE CHEMISTRY

The production of gases and their consequent fast expansion from the heat of the reaction is the driving force behind explosives. Gases have a much greater volume than do similar amounts of solids or liquids. The destructive power of an explosion is due to the shock wave caused by the very rapid increase in volume as gases form. The shock wave for gunpowder travels around a hundred meters per second, but for "high" explosives (TNT or nitroglycerin, for example) it can be up to six thousand meters per second.

All explosive reactions give off large amounts of heat. Such reactions are said to be highly exothermic. The large amounts of heat act dramatically to increase the volume of the gases—the higher the temperature the larger the volume of gas. Heat comes from the energy difference between the molecules on each side of the explosive reaction equation. The molecules produced (on the right of the equation) have less energy tied up in their chemical bonds than the starting molecules (on the left). The compounds that form are more stable. In explosive reactions of nitro compounds, the extremely stable nitrogen molecule, N_2 , is formed. The stability of the N_2 molecule is due to the strength of the triple bond that holds the two nitrogen atoms together.



Structure of the N_2 molecule

That this triple bond is very strong means that a lot of energy is needed to break it. Conversely, when the N_2 triple bond is made, a lot of energy is released, which is exactly what is wanted in an explosive reaction.

Besides production of heat and of gases, a third important property

of explosive reactions is the rapidity of the explosive reaction. The reaction must be so rapid that the pressure of the gases produced can build up before the gases have time to escape. The violent pressure of the explosion is characteristic of an explosion. The explosion has to come from the reaction of the explosive with the air, because oxygen is not enough. Thus nitroglycerin is bonded together, and the explosion is due to the breaking of both nitrogen and oxygen bonds.

This can be seen in the reaction of nitro compounds that have the same structure. *Para*-nitrotoluene and nitrobenzene have the same atoms, seven hydrogen atoms, seven carbon atoms for identical molecules, but the atoms are arranged differently.



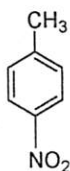
p-nitrotoluene

Para- or *p*-nitrotoluene and nitrobenzene groups are at opposite ends of the benzene ring. *p*-aminobenzoic acid is rubbed over your skin to protect it from ultraviolet light at the same time as it is damaging to skin cells.

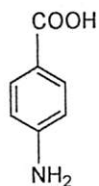
NITRO COMPOUNDS

of explosive reactions is that they must be extremely rapid. If the explosive reaction were to occur slowly, the resulting heat would dissipate and the gases would diffuse into the surroundings without the violent pressure surge, damaging shock wave, and high temperatures characteristic of an explosion. The oxygen required for such a reaction has to come from the molecule that is exploding. It cannot come from the air, because oxygen from the atmosphere is not available quickly enough. Thus nitro compounds, in which nitrogen and oxygen are bonded together, are often explosive, while other compounds containing both nitrogen and oxygen, but not bonded together, are not.

This can be seen using isomers as an example, isomers being compounds that have the same chemical formula but different structures. *Para*-nitrotoluene and *para*-aminobenzoic acid both have seven carbon atoms, seven hydrogen atoms, one nitrogen atom, and two oxygen atoms for identical chemical formulae of $C_7H_7NO_2$, but these atoms are arranged differently in each molecule.



p-nitrotoluene



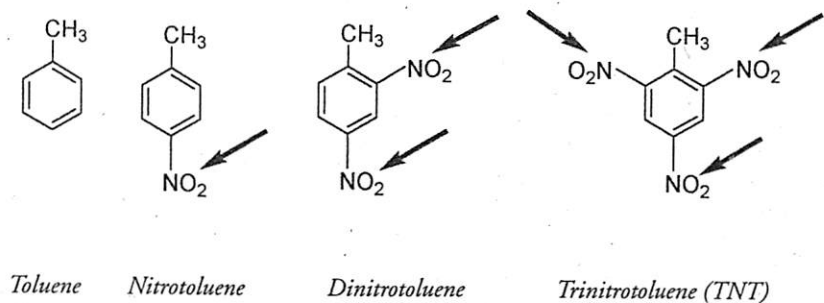
p-aminobenzoic acid

Para- or *p*-nitrotoluene (the *para* just tells you that the CH_3 and NO_2 groups are at opposite ends of the molecule) can be explosive, whereas *p*-aminobenzoic acid is not at all explosive. In fact you have probably rubbed it over your skin in the summer; it is PABA, the active ingredient in many sunscreen products. Compounds such as PABA absorb ultraviolet light at the very wavelengths that have been found to be most damaging to skin cells. Absorption of ultraviolet light at particular

NAPOLEON'S BUTTONS

wavelengths depends on the presence in the compound of alternating double and single bonds, possibly also with oxygen and nitrogen atoms attached. Variation in the number of bonds or atoms of this alternating pattern changes the wavelength of absorption. Other compounds that absorb at the required wavelengths can be used as sunscreens provided they also do not wash off easily in water, have no toxic or allergic effects, no unpleasant smell or taste, and do not decompose in the sun.

The explosiveness of a nitrated molecule depends on the number of nitro groups attached. Nitrotoluene has only one nitro group. Further nitration can add two or three more nitro groups, resulting in di- or trinitrotoluenes respectively. While nitrotoluene and dinitrotoluene can explode, they do not pack the same power as the high-explosive trinitrotoluene (TNT) molecule.

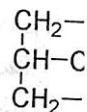


The nitro groups are indicated by arrows.

Advances in explosives came about in the nineteenth century when chemists began studying the effects of nitric acid on organic compounds. Only a few years after Friedrich Schönbein destroyed his wife's apron with his experiments, an Italian chemist, Ascanio Sobrero, of Turin, prepared another highly explosive nitro molecule. Sobrero had been studying the effects of nitric acid on other organic compounds. He dripped glycerol, also known as glycerin and readily obtained from animal fat, into a cooled mixture of sulfuric and nitric acids and poured the resulting mixture into water. An oily layer of what is

now known as ni
normal in Sobrer
compound and re
but not swallowed
accompanied by gre.

Later investigation in the explosives industry showed that the dilation of blood vessels and the covering resulted in heart disease and angina.



Glycerol (g)

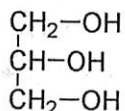
For angina sufferer supplying the heart lieves the pain of ar releases the simple 1 the dilation effect. F velopment of the a the blood-vessel-dil

Other physiologi pressure, acting as a establishing long-ter ing high blood pres have been develop for medicine was aw Murad for the discov Yet in one of chem nitroglycerin-derived prizes, personally rel

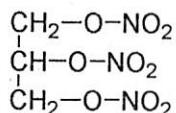
NITRO COMPOUNDS

now known as nitroglycerin separated out. Using a procedure that was normal in Sobrero's time but unthinkable today, he tasted the new compound and recorded his comments: "a trace placed on the tongue but not swallowed gives rise to a most pulsating, violent headache, accompanied by great weakness of the limbs."

Later investigations into the severe headaches suffered by workers in the explosives industry showed that these headaches were due to the dilation of blood vessels caused by handling nitroglycerin. This discovery resulted in the prescription of nitroglycerin for treatment of the heart disease angina pectoris.



Glycerol (glycerin)



Nitroglycerin

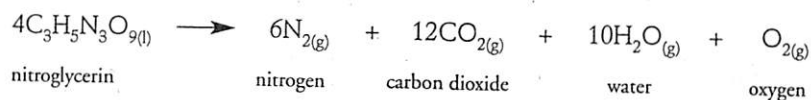
For angina sufferers, dilation of previously constricted blood vessels supplying the heart muscle allows an adequate flow of blood and relieves the pain of angina. We now know that in the body nitroglycerin releases the simple molecule nitric oxide (NO), which is responsible for the dilation effect. Research on this aspect of nitric oxide led to the development of the anti-impotence drug Viagra, which also depends on the blood-vessel-dilating effect of nitric oxide.

Other physiological roles of nitric oxide include maintaining blood pressure, acting as a messenger molecule carrying signals between cells, establishing long-term memory, and aiding digestion. Drugs for treating high blood pressure in newborns and for treating shock victims have been developed from these investigations. The 1998 Nobel Prize for medicine was awarded to Robert Furchgott, Louis Ignarro, and Ferid Murad for the discovery of the role played by nitric oxide in the body. Yet in one of chemistry's many ironic twists, Alfred Nobel, whose nitroglycerin-derived fortune would be used to establish the Nobel prizes, personally refused nitroglycerin treatment for the chest pains

NAPOLEON'S BUTTONS

from his heart disease. He did not believe it would work—only that it would cause headaches.

Nitroglycerin is a highly unstable molecule, exploding when heated or struck with a hammer. The explosive reaction



produces clouds of rapidly expanding gases and vast amounts of heat. In contrast to gunpowder, which produces six thousand atmospheres of pressure in thousandths of a second, an equal amount of nitroglycerin produces 270,000 atmospheres of pressure in millionths of a second. Gunpowder is relatively safe to handle, but nitroglycerin is very unpredictable and can spontaneously explode due to shock or heating. A safe and reliable way to handle and set off or "detonate" this explosive was needed.

NOBEL'S DYNAMITE IDEA

Alfred Bernard Nobel, born in 1833 in Stockholm, had the idea of employing—instead of a fuse, which just caused nitroglycerin to burn slowly—an explosion of a very small amount of gunpowder to detonate a larger explosion of nitroglycerin. It was a great idea; it worked, and the concept is still used today in the many controlled explosions that are routine in the mining and construction industries. Having solved the problem of producing a desired explosion, however, Nobel still faced the problem of preventing an undesired explosion.

Nobel's family had a factory that manufactured and sold explosives, which by 1864 had begun to manufacture nitroglycerin for commercial applications such as blasting tunnels and mines. In September of that year one of their laboratories in Stockholm blew up, killing five people, including Alfred Nobel's younger brother, Emil. Though the cause

of the accident
banned the pro
built a new lat
just beyond the
creased rapidly
powder becam
plants in eleve
United States v

Nitroglycerin
facturing proce
duced by this d
which the expl
pure nitroglyce
Packing materia
to absorb any le
and did little to
quently led to te
nitroglycerin oil
cart transporting
1866 a shipment
in San Francisco,
thousand-ton ste
troglycerin on th
and causing mor
plosions leveled
ities around the v
nitroglycerin, and
spite an increase
powerful explosiv

Nobel began to
ing its power. Sol
mented by mixing
as sawdust, ceme

NITRO COMPOUNDS

of the accident was never precisely determined, Stockholm officials banned the production of nitroglycerin. Not one to be deterred, Nobel built a new laboratory on pontoons and anchored it in Lake Mälaren, just beyond the Stockholm city limits. The demand for nitroglycerin increased rapidly as its advantages over the much less powerful gunpowder became known. By 1868, Nobel had opened manufacturing plants in eleven countries in Europe and had even expanded to the United States with a company in San Francisco.

Nitroglycerin was often contaminated by the acid used in the manufacturing process and tended to slowly decompose. The gases produced by this decomposition would pop the corks of the zinc cans in which the explosive was packed for shipping. As well, acid in the impure nitroglycerin would corrode the zinc, causing the cans to leak. Packing materials such as sawdust were used to insulate the cans and to absorb any leakages or spills, but such precautions were inadequate and did little to improve safety. Ignorance and misinformation frequently led to terrible accidents. Mishandling was common. In one case, nitroglycerin oil had even been used as a lubricant on the wheels of a cart transporting the explosive, obviously with disastrous results. In 1866 a shipment of nitroglycerin detonated in a Wells Fargo warehouse in San Francisco, killing fourteen people. In the same year a seventeen-thousand-ton steamship, the S.S. *European*, blew up while unloading nitroglycerin on the Atlantic coast of Panama, killing forty-seven people and causing more than a million dollars in damages. Also in 1866 explosions leveled nitroglycerin plants in Germany and Norway. Authorities around the world became concerned. France and Belgium banned nitroglycerin, and similar action was proposed in other countries, despite an increased worldwide demand for the use of the incredibly powerful explosive.

Nobel began to look for ways to stabilize nitroglycerin without losing its power. Solidification seemed an obvious method, so he experimented by mixing the oily liquid nitroglycerin with such neutral solids as sawdust, cement, and powdered charcoal. There has always been

speculation as to whether the product we now know as "dynamite" was the result of a systematic investigation, as claimed by Nobel, or was more a fortuitous discovery. Even if the discovery was serendipitous, Nobel was astute enough to recognize that kieselguhr, a natural, fine, siliceous material that was occasionally substituted for sawdust packing material, could soak up spilled liquid nitroglycerin but remain porous. Kieselguhr, also known as diatomaceous earth, is the remains of tiny marine animals and has a number of other uses: as a filter in sugar refineries, as insulation, and as a metal polish. Further testing showed that mixing liquid nitroglycerin with about one-third of its weight of kieselguhr formed a plastic mass with the consistency of putty. The kieselguhr diluted the nitroglycerin; separation of the nitroglycerin particles slowed down the rate of their decomposition. The explosive effect could now be controlled.

Nobel named the nitroglycerin/kieselguhr mixture dynamite, from the Greek *dynamis* or power. Dynamite could be molded into any desired shape or size, was not readily subject to decomposition, and did not explode accidentally. By 1867, Nobel and Company, as the family firm was now called, began shipping dynamite, newly patented as Nobel's Safety Powder. Soon there were Nobel dynamite factories in countries around the world, and the Nobel family fortune was assured.

That Alfred Nobel, a munitions manufacturer, was also a pacifist may seem a contradiction, but then Nobel's whole life was full of contradictions. As a child he was sickly and was not expected to live to adulthood, but he outlasted his parents and brothers. He has been described in somewhat paradoxical terms as shy, extremely considerate, obsessed by his work, highly suspicious, lonely, and very charitable. Nobel firmly believed that the invention of a truly terrible weapon might act as a deterrent that could bring lasting peace to the world, a hope that over a century later and with a number of truly terrible weapons now available has still not been realized. He died in 1896, working alone at his desk in his home in San Remo, Italy. His enormously wealthy estate was left to provide yearly prizes for research in chemistry, physics, medicine, liter-

ature, and peace. Nobel, established the Nobel Prize, it

WAR AND I

Nobel's invention of dynamite could not be used in war. Military leaders, one that could be used, and allowed formulations of nitroglycerin based on the basis of fire. It was not as restricted as dynamite. It contained many yellow solid fire. It was a special dye for silk. It was very easy to

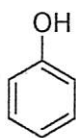
In 1871 it was sufficiently powerful by the French 1899-1902. It was to misfiring u

NITRO COMPOUNDS

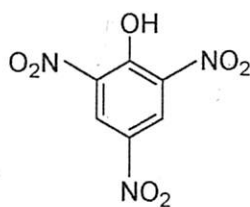
ature, and peace. In 1968 the Bank of Sweden, in memory of Alfred Nobel, established a prize in the field of economics. Although now called a Nobel Prize, it was not part of the original endowment.

WAR AND EXPLOSIVES

Nobel's invention could not be used as a propellant for projectiles, as guns cannot withstand the tremendous explosive force of dynamite. Military leaders still wanted a more powerful explosive than gunpowder, one that did not produce clouds of black smoke, was safe to handle, and allowed for quick loading. From the early 1880s various formulations of nitrocellulose (guncotton), or nitrocellulose mixed with nitroglycerin had been used as "smokeless powder" and are still today the basis of firearm explosives. Cannons and other heavy artillery are not as restricted in the choice of propellant. By World War I, munitions contained mainly picric acid and trinitrotoluene. Picric acid, a bright yellow solid first synthesized in 1771, was used originally as an artificial dye for silk and wool. It is a triple-nitrated phenol molecule and relatively easy to make.



Phenol



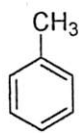
Trinitrophenol or picric acid

In 1871 it was found that picric acid could be made to explode if a sufficiently powerful detonator was used. It was first employed in shells by the French in 1885, then by the British during the Boer War of 1899–1902. Wet picric acid was difficult to detonate, however, leading to misfiring under rainy or humid conditions. It was also acidic and

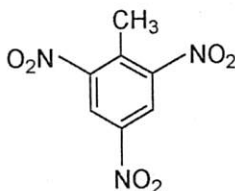
NAPOLEON'S BUTTONS

would react with metals to form shock-sensitive "picrates." This shock sensitivity caused shells to explode on contact, preventing them from penetrating thick armor plate.

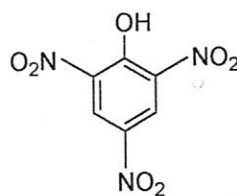
Chemically similar to picric acid, trinitrotoluene, known as TNT from the initials of *tri*, *nitro*, and *toluene*, was better suited for munitions.



Toluene

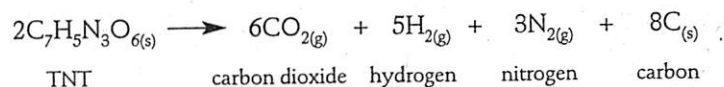


Trinitrotoluene or TNT



Picric acid

It was not acidic, was not affected by the damp, and had a relatively low melting point so it could be readily melted and poured into bombs and shells. Being harder to detonate than picric acid, it could take a greater impact and thus had better armor-penetrating ability. TNT has a lower ratio of oxygen to carbon than nitroglycerin, so its carbon is not converted completely to carbon dioxide nor its hydrogen to water. The reaction can be represented as



Carbon produced in this reaction causes the large amount of smoke that is associated with the explosions of TNT compared to those of nitroglycerin and guncotton.

At the beginning of World War I, Germany, using TNT-based munitions, had a definite advantage over the French and British, who were still using picric acid. A crash program to start producing TNT, aided by large quantities shipped from manufacturing plants in the United

States, allowed bombs containing

Another molecule used during World War I was picric acid, a material for making explosives. Nitric acid, known as Hayyan, the Greeks have known about (potassium nitrate) because of its green color (nitrogen dioxide (NO₂), and nitric acid.

Nitrates are found in water and the deserts of north Chile (saltpeter) because of nitrate for dirt with sulfuric acid it has a lower boiling point collected in cool

$\text{NaNO}_3(\text{s})$
sodium nitrate

During World War I by a British navy for manufacturing source.

While nitrates contain oxygen, that makes our atmosphere and 80 percent of the oxygen combining readily with

NITRO COMPOUNDS

States, allowed Britain to rapidly develop similar quality shells and bombs containing this pivotal molecule.

Another molecule, ammonia (NH_3), became even more crucial during World War I. While not a nitro compound, ammonia is the starting material for making the nitric acid, HNO_3 , which is needed to make explosives. Nitric acid has probably been known for a long time. Jabir ibn Hayyan, the great Islamic alchemist who lived around A.D. 800, would have known about nitric acid and probably made it by heating saltpeter (potassium nitrate) with ferrous sulfate (then called green vitriol because of its green crystals). The gas produced by this reaction, nitrogen dioxide (NO_2), was bubbled into water to form a dilute solution of nitric acid.

Nitrates are not commonly found in nature, as they are very soluble in water and tend to be dissolved away, but in the extremely arid deserts of northern Chile huge deposits of sodium nitrate (so-called Chile saltpeter) have been mined for the past two centuries as a source of nitrate for direct preparation of nitric acid. Sodium nitrate is heated with sulfuric acid. The nitric acid that is produced is driven off because it has a lower boiling point than sulfuric acid. It is then condensed and collected in cooling vessels.



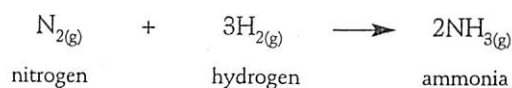
During World War I supplies of Chile saltpeter to Germany were cut off by a British naval blockade. Nitrates were strategic chemicals, necessary for manufacture of explosives, so Germany needed to find another source.

While nitrates may not be plentiful, the two elements, nitrogen and oxygen, that make up nitrates exist in the world in a generous supply. Our atmosphere is composed of approximately 20 percent oxygen gas and 80 percent nitrogen gas. Oxygen (O_2) is chemically reactive, combining readily with many other elements, but the nitrogen molecule

NAPOLEON'S BUTTONS

(N₂) is relatively inert. At the beginning of the twentieth century, methods of "fixing" nitrogen—that is, removing it from the atmosphere by chemical combination with other elements—were known but not very advanced.

For some time Fritz Haber, a German chemist, had been working on a process to combine nitrogen from the air with hydrogen gas to form ammonia.



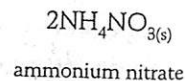
Haber was able to solve the problem of using inert atmospheric nitrogen by working with reaction conditions that produced the highest yield of ammonia for the lowest possible cost: high pressure, temperatures of around 400 to 500°C, and removal of the ammonia as soon as it formed. Much of Haber's work involved finding a catalyst to increase the rate of this particularly slow reaction. His experiments were aimed at producing ammonia for the fertilizer industry. Two-thirds of the world's fertilizer needs were at that time being supplied from the saltpeter deposits in Chile; as these deposits became depleted, a synthetic route to ammonia was needed. By 1913 the world's first synthetic ammonia plant had been established in Germany, and when the British blockade later cut nitrate supply from Chile, the Haber process, as it is still known, was quickly expanded to other plants to supply ammonia not only for fertilizers but also for ammunition and explosives. The ammonia thus produced is reacted with oxygen to form nitrogen dioxide, the precursor of nitric acid. For Germany, with ammonia for fertilizers and nitric acid to make explosive nitro compounds, the British blockade was irrelevant. Nitrogen fixation had become a vital factor in waging war.

The 1918 Nobel Prize for chemistry was awarded to Fritz Haber for his role in the synthesis of ammonia, which ultimately led to increased fertilizer production and the consequent greater ability of agriculture to

feed the world's population. A storm of protest against many's gas warfare, chlorine gas had been used. Five thousand died. Haber's leadership in these circumstances, including the use of gas. Ultimately gas came of the war, but a great innovation—synthesis—for the appalling results. Many scientists under these circumstances.

Haber saw little of it and was greatly upset. In prestigious Kaiser Wilhelm Institute for Physical Chemistry, he was dismissed. All Jewish workers were dismissed. Those times, Haber more than forty years of their intelligence and mothers, and I am not a method that I have found.

Today, worldwide Haber's process, is abundant. Nitrate (NH₄NO₃), prismatic nitrate is also used. Ammonium nitrate and

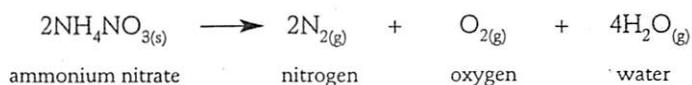


NITRO COMPOUNDS

feed the world's population. The announcement of this award aroused a storm of protest because of the role Fritz Haber had played in Germany's gas warfare program in World War I. In April 1915 cylinders of chlorine gas had been released over a three-mile front near Ypres, Belgium. Five thousand men had been killed and another ten thousand suffered devastating effects on their lungs from chlorine exposure. Under Haber's leadership of the gas warfare program, a number of new substances, including mustard gas and phosgene, were also tested and used. Ultimately gas warfare was not the deciding factor in the outcome of the war, but in the eyes of many of his peers Haber's earlier great innovation—so crucial to world agriculture—did not compensate for the appalling result of the exposure of thousands to poisonous gases. Many scientists considered awarding the Nobel Prize to Haber under these circumstances to be a travesty.

Haber saw little difference between conventional and gas warfare and was greatly upset by the controversy. In 1933, as director of the prestigious Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry, he was ordered by the Nazi government of Germany to dismiss all Jewish workers on his staff. In an unusual act of courage for those times, Haber refused, citing in his letter of resignation that "for more than forty years I have selected my collaborators on the basis of their intelligence and their character and not on the basis of their grandmothers, and I am not willing for the rest of my life to change this method that I have found so good."

Today, worldwide annual production of ammonia, still made by Haber's process, is about 140 million tons, much of it used for ammonium nitrate (NH_4NO_3), probably the world's most important fertilizer. Ammonium nitrate is also used for blasting in mines, as a mixture of 95 percent ammonium nitrate and 5 percent fuel oil. The explosive reaction

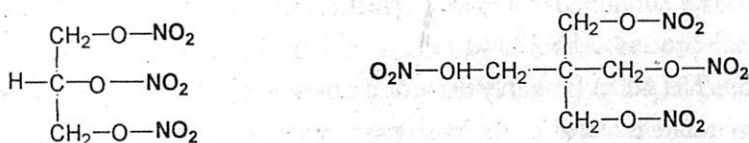


NAPOLEON'S BUTTONS

produces oxygen gas as well as nitrogen and steam. The oxygen gas oxidizes the fuel oil in the mixture, increasing the energy released by the blast.

Ammonium nitrate is considered a very safe explosive when properly handled, but it has been responsible for a number of disasters as a result of improper safety procedures or deliberate bombings by terrorist organizations. In 1947, in the port of Texas City, Texas, a fire broke out in the hold of a ship as it was being loaded with paper bags of ammonium nitrate fertilizer. In an attempt to stop the fire, the ship's crew closed the hatches, which had the unfortunate effect of creating the conditions of heat and compression needed to detonate ammonium nitrate. More than five hundred people were killed in the ensuing explosion. More recent disasters involving ammonium nitrate bombs planted by terrorists include the incidents at the World Trade Center in New York City in 1993 and at the Alfred P. Murrah Federal Building in Oklahoma City in 1995.

One of the more recently developed explosives, pentaerythritoltetranitrate (abbreviated to PETN), is regrettably also favored by terrorists because of the very same properties that have made it so useful for legitimate purposes. PETN can be mixed with rubber to make what is called a plastic explosive, which can be pressed into any shape. PETN may have a complicated chemical name, but its structure is not that complicated. It is chemically similar to nitroglycerin but has five carbons instead of three and one more nitro group.



*Nitroglycerin (left) and pentaerythritoltetranitrate (PETN) (right).
The nitro groups are bolded.*

Easily detonated, shock sensitive, very powerful, and with little odor so that even trained dogs find it difficult to detect, PETN may have be-

come the explosion
a component of the
Lockerbie, Scotland
2001 "Shoebomb"
Airlines flight from
of his sneakers. L
and passengers.

The role of explosives
and terrorism. The
and charcoal mix
early 1600s. The
the original canal
was just the first
gunpowder. The
way tunnel, thro
molecules of the
ing easy passage
was first used in c
at North Adams
accomplished wi
Canadian Pacific
Rockies; the eigh
1914; and the 19
the west coast
explosion.

In 218 B.C.,
through the Alps
sult on the heart
tremely slow ro
heated by bonfir
Had Hannibal po

NITRO COMPOUNDS

come the explosive of choice for airplane bombings. It gained fame as a component of the bomb that brought down Pan Am flight 103 over Lockerbie, Scotland, in 1988. Further notoriety has resulted from the 2001 "Shoebomber" incident, in which a passenger on an American Airlines flight from Paris attempted to set off PETN hidden in the soles of his sneakers. Disaster was averted only due to quick action by crew and passengers.

The role of explosive nitro molecules has not been confined to wars and terrorism. There is evidence that the power of the saltpeter, sulfur, and charcoal mixture was used in mining in northern Europe by the early 1600s. The Malpas Tunnel (1679) of the Canal du Midi in France, the original canal linking the Atlantic Ocean to the Mediterranean Sea, was just the first of many major canal tunnels built with the help of gunpowder. The 1857–1871 building of the Mont Cenis or Fréjus railway tunnel, through the French Alps, was the largest use of explosive molecules of the time, changing the face of travel in Europe by allowing easy passage from France to Italy. The new explosive nitroglycerin was first used in construction in the Hoosac railway tunnel (1855–1866) at North Adams in Massachusetts. Major engineering feats have been accomplished with the aid of dynamite: the 1885 completion of the Canadian Pacific Railway, allowing passage through the Canadian Rockies; the eighty-kilometer-long Panama Canal, which opened in 1914; and the 1958 removal of the navigational hazard Ripple Rock off the west coast of North America—still the largest-ever nonnuclear explosion.

In 218 B.C., the Carthaginian general Hannibal made his way through the Alps with his vast army and his forty elephants for an assault on the heart of the Roman Empire. He used the standard but extremely slow road-building method of the day: rock obstacles were heated by bonfires, then doused with cold water to crack them apart. Had Hannibal possessed explosives, a rapid passage through the Alps

NAPOLEON'S BUTTONS

might have allowed him an eventual victory at Rome, and the fate of the whole western Mediterranean would have been very different.

From Vasco da Gama's defeat of the rulers of Calicut, through the conquest of the Aztec empire by Hernán Cortés and a handful of Spanish conquistadors, to the British army's Light Cavalry Brigade charge of Russian field batteries in the 1854 Battle of Balaklava, explosive-propelled weapons have had the advantage over bows and arrows, spears, and swords. Imperialism and colonialism—systems that have molded our world—depended on the power of armaments. In war and in peace, from destroying to constructing, for worse or for better, explosive molecules have changed civilization.

6. S

seem very remote f
sheen conjured up
chemical connection
new textiles, and by

Silk has always b
wide choice of both
still considered irrep
it so desirable—its c
ness in hot weather,
so beautifully—are
chemical structure
routes between the