CHEMISTRY

Explosive Chemistry
The History and Chemistry of Explosives

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For many, it is easy to associate explosives with images of the outlandish use of TNT or dynamite, popularized by cartoons (perhaps Wile E. Coyote comes to mind). Yet, while most are familiar with explosives' role in American pop culture, an understanding of the science behind explosive chemistry is not as common. Several intriguing questions may be posed: What constitutes an explosion? What causes an explosion? How do explosions actually work? Perhaps by the end of this paper, we might just find ourselves a little more impressed by the remarkable chemical processes behind the explosive wonders of exothermic, gas-producing reactions.

Basic Thermodynamics

There are some important properties common among all chemical explosives. Explosive reactions are exothermic and spontaneous, giving off a significant amount of heat and is self-sustaining once initiated.

Explosions also release a considerable amount of gas very rapidly (1). Gay Lussac's Law states that the pressure of any gas is proportional to its temperature. As the gas produced by the reaction heats up from the reaction's exothermic nature, Gay Lussac's Law dictates a proportional temperature-pressure increase that is ultimately relieved in the form of an explosion (2).

Basic History and Chemistry

Black powder was one of the first explosives to be actively analyzed from a chemical perspective. A mixture of potassium nitrate, charcoal, and sulfur, black powder undergoes a highly reactive combustion which produces large quantities of heat and gas in the process (3). The use of the charcoal, however, produces copious amounts of smoke in the process, making black power an inherently messy explosive.

Smokeless powder quickly proved a safer, less messy alternative to black powder as an explosive. By the 1840s, two particularly promising smokeless chemicals were discovered: nitroglycerine, and nitrocellulose. Colloquially called "guncotton," nitrocellulose was first produced when Henry Broconnot treated cotton with nitric acid in 1833 (4). However, it was not until 1846 that two chemists, Christian Friedrich Schonbein and F. J. Otto, independently optimized the creation of nitrocellulose by placing the cotton into a mixture of nitric acid and sulfuric acid (4, 5). Nitrocellulose is simple in structure and aptly named; the compound consists only of cellulose with nitro-groups ($-NO_2$) attached via the oxygen in cellulose. The simplicity of its synthesis reflects its chemical make up: one need only add the appropriate amounts of nitric acid, sulfuric acid, and cellulose in the right solvents to yield the explosive substance. The addition of sulfuric acid initiates nitration to the compound of interest. As a strong Brønsted–Lowry acid, sulfuric acid forces an additional proton upon nitric acid, causing nitric acid's -OH group to become an $-OH_2$ group. The $-OH_2$ group is simply a water molecule, which is relatively low-energy and therefore inclined to leave the protonated nitric acid. The resulting NO_2^+ molecule is called a nitronium ion. Flanked by two highly electronegative oxygen atoms, the nitrogen loses most of its electron density and gains a partial positive charge. This nitronium ion now falls prey to one of cellulose's oxygen atoms, whose negatively charged lone pairs attack the highly positively charged nitrogen center of the nitronium ion. After this process of nitration occurs three times on each glucose monomer of cellulose, the highly flammable nitrocellulose is produced (6,7). Since the nitration results in an oxygen-nitrogen bond, the process is called O-Nitration (6). Unlike high-order explosives, however, the combustion of nitrocellulose is not fast enough to be considered detonation. An explosion involving nitrocellulose requires its combustion in the presence of oxygen, resulting in only subsonic pressure waves. Nitrocellulose is therefore considered to deflagrate rather than detonate. (8, 9).
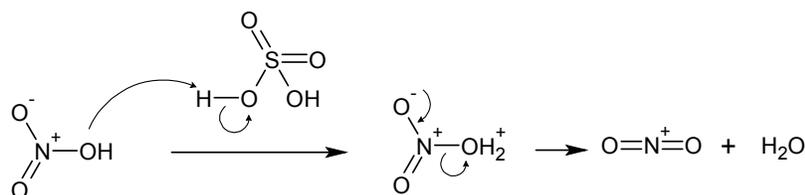

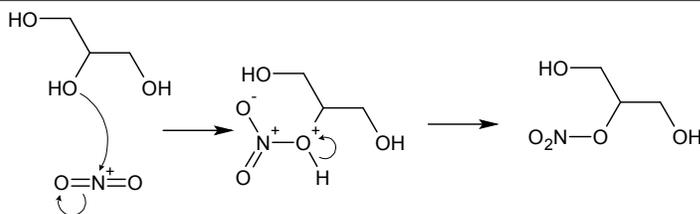*Image courtesy of Rui Shu*

Figure 1: Creation of nitronium ion.

Image courtesy of Rui Shu

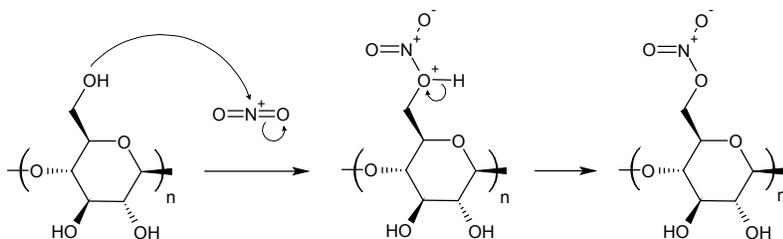**Figure 2:** First nitration step of nitroglycerin synthesis.

Image courtesy of Rui Shu

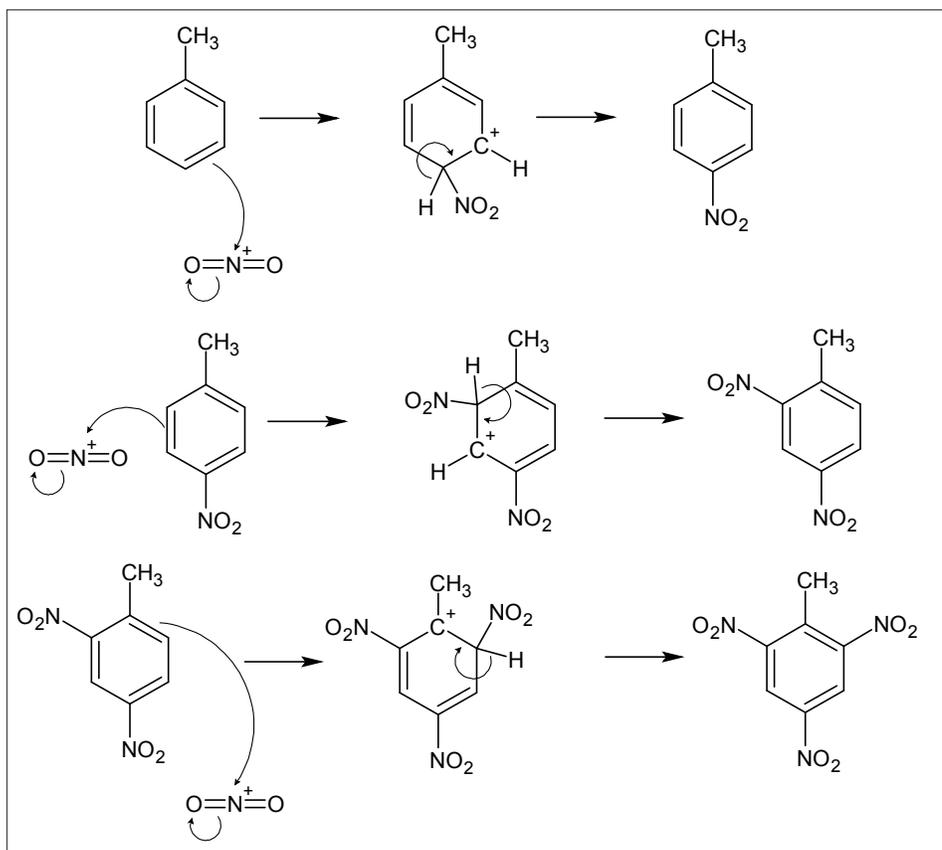**Figure 3:** First nitration step of nitrocellulose synthesis.

Figure 4: Synthesis of 2,4,6-trinitrotoluene.

Nitroglycerine was first synthesized by Ascanio Sobrero, an Italian chemist at the University of Turin (10). Like nitrocellulose, nitroglycerine can be thought of as a glycerol-derivative with nitro-groups. The addition of sulfuric acid and nitric acid to glycerol leads to the O-nitration of glycerol, whereby the nitro-group replaces the protons of glycerol's hydroxyl groups. However, unlike nitrocellulose nitroglycerin's molecular make up allows it to exothermically decompose into gases without an external oxygen source; rather than deflagrating, nitroglycerin detonates. Unfortunately, the combustion of nitroglycerine has a very low activation energy barrier; which makes nitoglycerine susceptible to explosion upon physical contact, and thus impractical for use in most contexts (11). By 1867, however, Alfred Nobel was able to calm the shock sensitivity of nitroglycerin to produce dynamite (12).

While nitroglycerine may have been the first practical explosive stronger than black powder, dynamite was the first explosive that was also safe and manageable. The chemical marvel of dynamite lies not in its reaction (it is still nitroglycerine), but in its successful use of absorbents to stabilize nitroglycerine. Alfred Nobel found that liquid nitroglycerin is effectively absorbed by diatomaceous earth, a highly porous fossil product of diatoms. The absorption of the explosive into this new medium successfully diffused the sensitivity of nitroglycerine and made the production and transportation of dynamite much more practical than that of nitroglycerine (13). Due to dynamite's relative stability, it came to replace the use of pure nitroglycerine in high-order explosives.

In 1863, several years before Nobel's invention of dynamite, a less appreciated molecule was prepared by the German chemist Julius Wilbrand (14). This solid had a yellow hue and was originally intended as a dye (15). The material was prepared in three nitration steps (a recurring theme in explosive chemistry); each time, a nitro-group would attach to the benzene ring with a single methyl group attached (6). When introduced to sulfuric acid in conjunction with nitric acid, the benzene temporarily destroys its own stable, aromatic system so that one of its pi electron pairs can attack the positive-nitrogen center of the nitronium ion. As soon as this happens, the benzene ring steals the two electrons that it shares in a covalent bond with the less electronegative hydrogen atom. Relieved of this bond , the methylated benzene

ring replaces the two pi electrons which it expended in the electrophilic attack and returns to its calmer, aromatic self – now with a nitro-group attached (7). Because this process effectively substitutes the proton on the aromatic ring with an electron-deficient group (in this case, a nitro-group), this reaction is called electrophilic aromatic substitution.

In the first nitration step, the nitro-group selectively attaches to the carbon directly opposite that which attaches the methyl group despite the presence of four other possible binding sites on the methylbenzene (toluene) ring. The regional specificity of the nitration is due to the presence of the methyl group, which does in fact have a directing effect (7). The same direct influence of the methyl group determines the placement of the remaining two nitro-groups, thus positioning the three nitro-groups on every other carbon, creating the molecule 2,4,6-trinitrotoluene, or TNT. TNT exhibits several important differences from the nitroglycerin in dynamite. Unlike nitroglycerin, the detonation of TNT has an unusually high activation energy barrier (16). Its stability makes the transportation of TNT safe, with little chance of accidental detonation. This stability, however, also means that TNT is much more difficult to detonate. In fact, its insensitivity prevented it from being seriously considered for use as an explosive until the early twentieth century.

Making an Explosive Explosive

As shown, the most famous, and often the most destructive, explosives frequently exhibit nitro-groups embedded within their molecular structures. The significance of the nitro-groups is two-fold. First, the nitro-groups provide a source of nitrogen, which reduces to the inert (highly-stable) nitrogen gas during the course of the reaction. Compared to its incredible stability as N_2 gas, nitrogen has a significantly higher energy level in its oxidized state within the nitro-group. The transition of nitrogen from a high energy state to a significantly lower energy state produces a significant amount of heat, making the enthalpy of reaction very large and very negative. Nitro-groups also provide a source of oxygen with which the hydrocarbon parts of the molecule may interact. This allows for the combustion of the hydrocarbon, creating carbon dioxide and water without the need for contact
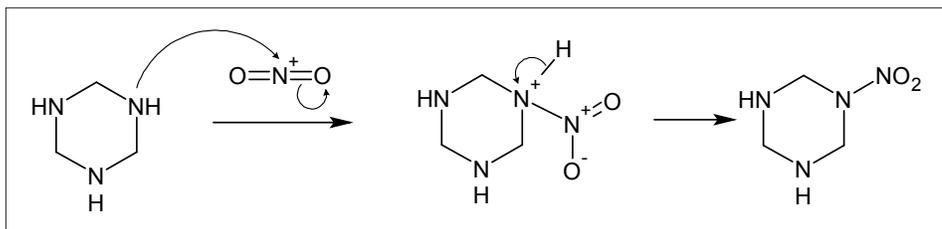
Figure 5: First N-nitration step of RDX synthesis.

Image courtesy of Rui Shu

with an external source of oxygen gas. The fact that combustion can happen as a result of an intramolecular rearrangement rather than an intermolecular reaction makes the combustion significantly more likely and, therefore, faster.

By exploiting these concepts, people have managed to make ever stronger explosives in the twentieth century. By the 1900's, RDX, HMX, and HNIW had emerged as parts of a new batch of explosives that made use of nitroamines. These compounds were far more powerful than other explosives of their time, capable of incredibly fast detonations. The synthesis of nitroamines involves the N-nitration of an already nitrogenous molecule, placing the nitro-groups on the nitrogen atoms. HNIW is the strongest of the three, followed by HMX, and RDX. The trend is readily understood through the principles of the explosives' densities and the molar ratio of C, H, O, and N. HMX has the same empirical formula as RDX, but differs in that it contains an additional nitroamine group in its ring. This increased density allows a greater amount of HMX to be used per unit volume, creating a larger reaction. The fact that HMX is an eight ring molecule (as opposed to RDX's six ring molecule) introduces slightly more angle strain, making HMX a higher-energy molecule. HNIW, however, differs in the molar ratio of each element present. The molar ratio of oxygen within HNIW allows complete combustion without need of an external oxygen source, making HNIW even more energetic (17).

Pushing the limits of explosives further still are the molecules heptanitrocubane and octanitrocubane. These two molecules currently rank highest in terms of chemical explosive power, but involve impressively complex pathways of synthesis. Heptanitrocubane and octanitrocubane are derivatives of cubane, which is difficult to produce in and of itself. While insensitive to shock, these molecules take advantage of the huge carbon-ring strain to rapidly collapse and combust the entire structure.

Octanitrocubane is especially unique in that it does not contain any hydrogen at all – its combustion produces only carbon dioxide and nitrogen gas. With eight nitro-groups crowded around the small carbon cube, it is no wonder that it is one of the most powerful explosives to date. However, while octanitrocubane outperforms heptanitrocubane in terms of enthalpy, heptanitrocubane compensates with higher density. Its physical structure has made it empirically easier to pack heptanitrocubane than octanitrocubane, making heptanitrocubane slightly more powerful as an explosive (18).

The Offshoots of Explosive Chemistry

Despite their initial designation as explosives, many of these molecules have carried on to fulfill much greater and more diverse roles. Nitroglycerin proved to be an effective vasodilator and has since been incorporated in several heart-related medications (13). Nitrocellulose exhibits a high affinity to proteins and nucleic acids. This property greatly aids the field of biotechnology, which now uses nitrocellulose membranes in techniques such as western blotting to assay proteins (19). The invention of dynamite also prompted Alfred Nobel to establish the Nobel Price in an effort to contribute more positively to the world of science (20).

A Reflection on Chemical Explosives

Once we look past the "explosives" label, we may come to appreciate that these substances are no less intimidating than any other chemical. "Explosive" molecules obey the same chemical rules and physical rules as any other molecule or compound, and many have the potential to create positive effects beyond the realm of explosive chemistry.

References

1. Office for Domestic Preparedness, Explosive Devices. Available at http://cryptome.org/ieds.pdf (1 April 2012)
2. D. W. Oxtoby, H. P. Gillis, A. Campion, *Principles of Modern Chemistry* (Saunders College Pub., Philadelphia, ed. 6, 2008).
3. V. Summers, Gunpowder – The Chemistry Behind the Bang (30 September 2010). Available at http://voices.yahoo.com/gunpowder-chemistry-behind-6884202.html?cat=15 (3 April 2012)
4. D. Williams, Materials Compatability. Available at http://www.shsu.edu/~chm_dlw/index.html (28 March 2012)
5. Encyclopaedia Britannica, *Nitrocellulose* (2012). Available at http://www.britannica.com/EBchecked/topic/416152/nitrocellulose (1 April 2012)
6. T. Urbanski, *Chemistry and Technology of Explosives* (Pergamon Press, New York, Vol 1, 1964)
7. K. P. Vollhardt, N. E. Schore, *Organic Chemistry: Stucture and Function* (W. H. Freeman and Co., New York, 2003)
8. G. Berwick, *The Executives Guide to Insurance and Risk Management* (QR Consulting, Haberfield, 2001).
9. Exponent Engineering and Scientific Consulting, *Explosions, Detonations, & Detonations* (2012). Available at http://brochures.exponent.com/PDF.aspx?capability=explosions (1 April 2012)
10. L. J. Ignarro, Proc. *Natl. Acad. Sci. U.S.A.*, **99** (12), 7816-7817 (2002).
11. H. Henkin, R. McGill, *Industrial and Engineering Chemistry*, **44** (6), 1391-1395 (1952).
12. K. Fant, *Alfred Nobel: a Biography* (Arcade Pub., New York, 1993).
13. L. C. Holmes and F. J. DiCarlo, *Journal of Chemical Education*, **48** (9), 573-576 (1971).
14. B. Stenuit, L. Eyers, S. E. Fantroussi, S. N. Agathos, *Environmental Science and Bio/Technology*, **4**, 39-60 (2005).
15. International Chemical Safety Cards, *2,4,6,-Trinitrotoluene* (1993). Available at http://hazard.com/msds/mf/cards/file/0967.html (1 April 2012)
16. G. Hill and J. Holman, *Chemistry in Context* (Nelson Thornes Ltd, UK, 2000).
17. U.S. Army Materials Command, *Elements of Armament Engineering* (1964). Available at http://www.dtic.mil/dtic/tr/fulltext/u2/830272.pdf (1 April 2012)
18. P. E. Eaton and M. Zhang, *Propellants, Explosives, Pyrotechnics*, **27**, 1-6 (2002).
19. R. Jahn, W. Schiebler, P. Greencard, Proc. *Natl. Acad. Sci. USA*, **81**, 1684-1687 (1984).
20. Nobelprize.org, Alfred Nobel. Available at http://www.nobelprize.org/alfred_nobel/ (1 April 2012)