Chemistry of High Energy Materials

**History of Explosives**
- 7th century A.D. - "Greek Fire" petroleum distillate used by Byzantines of Constantinopole
- 13th century - black powder (aka gunpowder) Chinese alchemists
- 18th century - black powder composition became standardized: KNO₃-charcoal/sulfur (75/15/10 w/w)
- 19th century - NH₄NO₃ replacement for KNO₃ in black powder
- 1846 - Italian Chemist Ascanio Sobrero invented nitroglycerin (NG)
- 1863 - German chemist Julius Wilbrand invented 2,4,6-trinitrotoluene (TNT) originally used as a yellow dye. Potential as an explosive not appreciated due to difficulty to detonate (insensitive).
- 1866 - Mixing of NG with silica (PBX) to make malleable paste (dynamite)
- Late 19th century - nitration chemistry on common materials (resins,cotton, etc.)
- 1910 - military use of TNT for artillery shells and armour-piercing shells
- 1939-1945 - World War II - Research on explosives intesified (nitration chemistry) Development of cyclotrimethylenetrimine (RDX) and cyclotetramethylenetetramine (HMX).

**Introduction to high energy materials terminology**
- **Brisance**: Shattering capability of explosive. Measure of rate an explosive develops its maximum pressure.
- **Relative effectiveness factor (R.E. factor)**: Measurement of an explosive's power for military purposes. It is used to compare an explosive's effectiveness relative to TNT by weight (TNT equivalent/kg or TNTe/kg).
- **Detonation velocity (VoD)**: The velocity at which the shock wave front travels through a detonated explosive. Difficult to measure in practice so use gas theory to make prediction.
- **Specific impulse (Isp)**: The force with respect to the amount of propellant used per unit time. Used to calculate propulsion performance.
- **Oxygen balance (OB%)**: Expression used to indicate degree to which explosive can be oxidized. If explosive contains just enough oxygen to form carbon dioxide from carbon, water from hydrogen molecules and all metal oxides from metals with no excess, the explosive is said to have zero oxygen balance.

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**Organic Chemistry of Explosives by J.P. Agrawal and R.D. Hodgson**

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**What makes an explosion?**
- Exothermic chemical reaction comprised of an oxidant and fuel, which releases energy (gas and heat) in a given time interval.

**What is the difference between explosive, propellants and pyrotechnics?**
- Rate at which it burns (Flaming gummy bear vs. rocket booster vs. TNT)
- Speed of reaction will determine subsonic vs. supersonic blast pressure waves
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Chemical types/class of organic explosives

**Aliphatic C-nitro compounds**

- **1° nitroalkane**
- **2° nitroalkane**

**Terminal gem-dinitroalkane**

- acidic protons (condensation chemistry)

**3° nitroalkane**

**Trinitromethyl**

**Internal gem-dinitroalkane**

- high explosive with high thermal and chemical stability

**heterocycles**

- Nitro derivatives of pyroles, thiophenes, and furans are not practical explosives:
  1. heat of formation offers no benefits over standard arylene hydrocarbons
  2. during nitration, these heterocycles are much more prone to oxidation and acid cat. ring opening compared to arenes

- H-bonding reduction in sensativity

- 4-amino-3,5-dinitropyrazole (LLM-116)
- 2,4-dinitroimidazole (2,4-DNI)
- furazans/benzofurazans
- furoxans/benzofuroxans

- pyridine N-oxide
- pyrazine N-oxide
- tetrazine N-oxide

**Aromatic C-nitro compounds**

- **MeNO2**
- **O2N**
- **TNT**
- 1,3,5-trinitrobenzene (TNB)
- 2,4,6-trinitrophenol (picric acid)

- **x ≥ 4**
- Poor chemical stability

**Aliphatic O-nitro compounds**

- **Nitroglycerin** (VOD=7750 m/s)
- **Pentaerythritol tetranitrate** (PETN) (VOD=8310 m/s)
- **3,3-bis(difluoroamino) octahydro-1,5,7,7-tetranitro-1,5-diazocine** (TNFX)
- **3,4-oxadiazoles**
- **1,2,4 triazoles**
- **1,3,4-oxadiazoles**

**Aliphatic N-nitro compounds**

- **RDX** (VOD=8440 m/s)
- **HMX** (VOD=9110 m/s)
- **N,N'-dinitrourea** (DNU)
- **Si-PETN**
- **3-nitro-1,2,4-triazol-5-one** (NTO)
- **Hexanitrohexaazaisowurtzitane** (HNIW or CL-20) (VOD=9380 m/s)

- **Ar**

**H-bonding reduction in sensativity**
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Nitration chemistry

The nitro group, whether attached to aromatic or aliphatic carbon, is probably the most widely studied of the functional groups and this is in part attributed to its use as an 'explosophore' in many energetic materials.

Borgardt et al. Chem Rev 1964, 64, 19 (polymer functionality)

Routes to C-Nitro functionality

Direct nitration of aliphatic and alicyclic hydrocarbons possible in the vapor phase using HNO₃ or NO₂ (toxic redish-brown gas) at elevated temperatures.

HNO₃ reaction:

- colorless liquid

Radical methods

Ph

1 atm NO
DCE/ rt

\[
\text{Ph} + \text{NO}_2 \rightarrow \text{Ph-NO}_2 + \text{Ph-NO}_2
\]

76%  
23%


Taniguchi et al. JOC 2010. 75, 8126

alkaline nitration

\[
\begin{align*}
\text{O}_2\text{N} & \rightarrow \text{O}_2\text{N} \\
\text{O}_2\text{N} & \rightarrow \text{O}_2\text{N} \\
\text{O}_2\text{N} & \rightarrow \text{O}_2\text{N}
\end{align*}
\]

77%

Nitration selectivity on arene/heteroarene
Kakiuchi, et al. Synlett 1999. 901

H₂SO₄

KNO₃

traditional

[NO₂]²

44%

TBAN

TFAA

76%

* No rxn in presence of TEMPO

\[
\begin{align*}
\text{F}_3\text{C} & \rightarrow \text{F}_3\text{C} \\
\text{F}_3\text{C} & \rightarrow \text{F}_3\text{C}
\end{align*}
\]

84%

80 - 90%
1° and 2° nitro compounds

Victor Meyer rxn
- alkyl chlorides too slow
- only good for 1° (2° alkyl halide gives nitrate ester)
- nitrate ester arises from disproportionation of silver nitrate acc. by heat/light

\[ R - X + N\text{O}_2^- \overset{\text{ether}}{\rightarrow} R - \text{ONO}_2^- + \text{AgX} \]

modified VM (alkali metal nitriles e.g. NaNO2) time and solubility is VIMP

\[ R - X + \text{NaNNO}_2 \overset{\text{fast}}{\rightarrow} R - \text{NO}_2^- + \text{N} = \text{O} \]

\[ \text{phloroglucinol} \rightarrow \text{Kornblum et al. JACS 1956. 78, 1497} \]

Fluorotrinitromethane

\[ \text{O}_2\text{N-NO}_2^- (\text{or}) \text{F-NO}_2^- \]

gem-dinitros from acids

\[ R - \text{CO}_2\overset{20 \text{-} 30\%}{\rightarrow} R - \text{NO}_2 \]

oxidation of amines

\[ \text{NH}_3\text{+Cl}^- \overset{\text{DMDO}}{\rightarrow} \text{Acetone 91\%} \]

oxidation of isocyanates

\[ \text{NCO} \overset{\text{DMDO}}{\rightarrow} \text{Acetone/H}_2\text{O 85\%} \]

via amine thus H2O essential

Eaton et al. JOC 1988. 5353

Synthesis of an energetic nitrate ester

Chavez, D.E. et al. Angew. 2008, 47, 8307

Original Target/Route via modified Kaplan Shechter Rxn

[Fe]

activation

[O]
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Initial Results: homocoupled product

![Chemical reaction diagram]

Routes to O-Nitro functionality

- Use of mixed acids (esterification) and nitrogen oxides described for C-Nitraion
- Key points:
  1. Fuming (anhydrous) HNO₃ prep: dry air bubbled through anhydrous HNO₃ to remove any oxides of nitrogen present, followed by addition of trace urea to remove any nitrous acid present. AKA "white nitric acid"
  2. Urea destruction of nitrous acid important to avoid violent fume-off
  3. O-nitrations with mixed acids of "white nitric acid" above ambient temperatures is dangerous and has increase risk of explosion
  4. Anhydrous HNO₃/Ac₂O: Acetyl nitrate is generally a weak nitrating agent but in the presence of a strong acid like HNO₃, ionization to nitronium ion occurs

Transfer nitration (neutral conditions - good for acid sensitive alcohols)

- In situ halide displacement with AgNO₃
  - Low yields for 2° HGNO₃ can be used for 2° and 3° alkyl halide displacements
  - Decomposition of nitrocarbonates (very mild, rt or reflux MeCN)

Table 1: Sensitivity properties of 1.

<table>
<thead>
<tr>
<th></th>
<th>Impact (J)</th>
<th>Spark (J)</th>
<th>Friction (N)</th>
<th>DSC (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.7</td>
<td>0.625</td>
<td>74.5</td>
<td>140°</td>
</tr>
<tr>
<td>PETN</td>
<td>2.9</td>
<td>0.625</td>
<td>56.8</td>
<td>160°</td>
</tr>
</tbody>
</table>

- LANL type 12, 50% drop height, 2.5 kg. [b] ABL spark threshold initiation level (TIL). [c] 50% load Brueton up/down method. [d] 10°C

Table 2: Predicted performance properties of 1.

<table>
<thead>
<tr>
<th></th>
<th>Vₖₐₜ [km s⁻¹]</th>
<th>P₀ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1⁴</td>
<td>9.1</td>
<td>40</td>
</tr>
<tr>
<td>HMX⁵</td>
<td>9.1</td>
<td>39</td>
</tr>
</tbody>
</table>

- [a] Cheetah 5.0 calculation. [b] Livermore Explosives Handbook.

CHEETAH calculates as powerful as HMX
selective O-nitrations

- Compounds resulting from nitration of nitrogen are of far less use for mainstream organic synthesis. However the N-NO₂ group is an important 'explosophile' and is present in many energetic materials.
- Direct nitration of a 1° amine to a nitramine using HNO₃/mixed acids is not possible due to instability of the tautomeric isonitramine in strongly acidic conditions. 2° amines are more stable and can undergo electrophilic nitration using HNO₃/Ag₂O.

analines - must contain one or more nitro groups on the aromatic ring

How to get around this problem??
- synthesis via condensation chemistry (Mannich, 1,4 addition, etc)

What about if need more direct method??
- non-acidic nitrating reagents (nucleophilic nitrination)

 Routes to N-Nitro functionality

- Nitrolysis of fully substituted nitrogen

rupture of C-N bond leading to formation on N-NO₂

 Ease of alkyl nitrolysis depends on stability of the resulting cation: benzyl, tertiary (t-Bu), etc...
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**Synthesis of Hexanitrohexaazaisowurtzitane (HNIW)**

- Many nitramines are more powerful than aromatic C-nitro compounds and have high brisance and high chemical stability and low sensitivity to impact and friction compared to nitrate ester explosives. This is why they are of interest to military applications.

\[
\begin{align*}
\text{NH}_2 + \text{H}_2\text{C} = \text{O} & \xrightarrow{\text{MeCN/H}_2\text{O}} \text{HNIW} \\
\text{Ph} + \text{H}_2\text{C} = \text{O} & \xrightarrow{\text{cat. } \text{H}^+} \text{HNIW} \\
\text{O}_2 & \xrightarrow{[\text{Pd}]} \text{HNIW} \\
\text{H}_2\text{, Pd(OAc)}_2 & \xrightarrow{\text{Ac}_2\text{O}, \text{PhBr cat.}} \text{HNIW} \\
\text{H}_2\text{, Pd} & \xrightarrow{[\text{Pd}]} \text{HNIW} \\
\end{align*}
\]

HNIW aka CL-20

- explosive/propellant (low smoke-emission)
- most powerful to date (better oxidizer-to-fuel than RDX/HMX)
- first prep by Nielsen 1987 Naval Air Warefare
- pilot plant in 1990 for 200 kg in China Lake facility
- unmatched performance in specific impulse, burn rate, detonation velocity (9.38 km/s = 21,000 MPH!!!)
- highest density than any other explosive (d = 2.044 g/cm³)
- thermally stable (250 -260 °C) but sensitive to mechanical stress still greater stability than nitrocellulose, PETN and others.
- 4 different polymorphs with different densities/properties

**Syntheses of some nitramine explosives**

1. CrO₃, AcOH
2. HOCH₂CH₂OH TsOH
3. NH₃OH/NaOAc
4. HNO₃/Na₂SO₄, CFCl₃
5. HNO₃/SbF₅
6. HNO₃/TFAA

(TNFX: 3,3 bis(difluoroaminooctahydro 1,5,7,7 tetranitro 1,5 diazocine)
Chemistry of High Energy Materials

No single nitration agent is as diverse and versatile. It is considered as the future for energetic materials synthesis.

**non-acidic nitrating reagents (neutral)**

- $^1$-amines/nitramines leads to deamination and formation of nitrate ester by-product but alamines is successful.

$$\text{N}_2\text{O}_5\quad \xrightarrow{\text{sublime slightly above rt}} \quad \text{nitronium nitrate salt}$$

- adopts two structures depending on condition
- clean and selective
- non-oxidizing & non-acidic

1. prepared over 150 years ago but due to difficult prep and low thermal stability (require $-60^\circ\text{C}$ long term storage) received little attention.
2. Environmental restrictions and push for green chemistry sparked interest

**Advantage: Rxns are very clean**
- faster and less exothermic (due to absence of oxidation byproducts)
- high yields
- simple isolation

$$\text{N}_2\text{O}_5 \quad \xrightarrow{\text{rt}} \quad 2\text{N}_2\text{O}_4 + \text{O}_2$$

- Stable for 2 weeks at $-20^\circ\text{C}$
- Stable for up to 1 yr at $-60^\circ\text{C}$

- synthesis of TNT under mild conditions

- **NO explosion hazard**

- N-nitration of urea

- O-nitration of polyols

**Preparation of $\text{N}_2\text{O}_5$ [Deville 1849]**

$$\text{AgNO}_3 + \text{Cl}_2 \quad \xrightarrow{\Delta} \quad \text{N}_2\text{O}_5$$

**Dehydration of nitric acid**

$$\text{HNO}_3 + \text{P}_2\text{O}_5 \quad \xrightarrow{\Delta} \quad \text{N}_2\text{O}_5 + \text{H}_3\text{PO}_4$$

- isolation by sublimation and collection trap at $-78^\circ\text{C}$
- stream of ozone needed to avoid collection on $\text{N}_2\text{O}_4$
- if don’t care about acidity, can use $\text{HNO}_3/\text{P}_2\text{O}_5$ mixture directly (no ozone stream)

Process chemist at Defense and Evaluation Research Agency (DERA) in the UK Development of a flow process: Using commercial ozonizer to generate 5 - 10% mix of ozone in oxygen and mixed in flow with $\text{N}_2\text{O}_4$ $\text{N}_2\text{O}_5$ is trapped in solid condenser tubes (cooled by dry ice/acetone).

**Explosives in JACS: Sila explosives**

- Used in WW I
- One of most high energy explosives known
- more shock sensitive than TNT. used as booster mix
- Europe marketed as lentonitrat (vasodilator) like NG

- **Det. Velocity 8,400 m/s**
- $d = 1.7$ g/cm$^3$

**“The crystalline compound exploded on every occasion upon contact with Teflon spatula... Solutions in diethyl ether exploded upon the slightest evaporation of the solvent.”**

**Silicon analogue of PETN**

- **Very high e’ dens**
- **Very low e’ dens**

Why does Si-PETN have drastically increased sensitiveness?

Theoretical: electrostatic potential:
1. Surface electrostatic potential, in general, is related to the sensitivity of the bulk
2. The more evenly distribued the electrostatic potential is over the surface of a molecule, the more stable it is to impact.