Towards low-cost TATB-based formulations

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Context of the study

- TATB is an attractive insensitive explosive:
  - it satisfies safety requirements at high temperatures
  - it resists to accidental initiation and explosion

- The current cost of TATB makes it unusable in conventional weapons

Development of low cost TATB-based formulations by acting on:
- cost of the TATB synthesis
- TATB ratio in formulations, without damaging the energetic characteristics (safety, performances, ...)

Low-cost TATB

✓ evaluation of known methods
✓ development of the DCA route

New TATB-based formulations

✓ safety tests

Conclusion and Prospects
Low-cost TATB - Evaluation of known methods

- New synthesis: a first evaluation gave poor results
- Five significant synthetic routes:

Benziger (1977)

- ☺ industrial process (France)
- ☹ high yield and soft reaction conditions → high cost

Atkins (1981)

- ☺ cheap starting material
- ☹ sensitive intermediate (pentanitroaniline)

Mitchell (VNS chemistry) (1996)

- ☺ high yield
- ☹ environment friendly, expensive reactant

Bellamy (2001)

- ☺ high yield
- No Chlorine product
- ☹ expensive starting material

Ott (1990)

- ☺ high yield and soft reaction conditions
- ☹ expensive starting material
Low-cost TATB – Evaluation of known methods

- New synthesis: a first evaluation gave poor results
- Five significant synthetic routes:

Benziger (1977)

\[ \text{Cl} \begin{array}{c} \text{Cl} \\ \text{Cl} \\ \text{TCB} \end{array} \]

- ☺ industrial process (France)
- ☹ harsh reaction conditions → high cost

Atkins (1981)

\[ \begin{array}{c} \text{O}_2 \text{N} \\ \text{CH}_3 \\ \text{NO}_2 \\ \text{NO}_2 \\ \text{TNT} \end{array} \]

- ☺ cheap starting material
- ☹ sensitive intermediate (pentanitroaniline)

Bellamy (2001)

\[ \begin{array}{c} \text{OH} \\ \text{OH} \\ \text{OH} \end{array} \]

- ☺ high yield
- No Chlorine product
- ☹ expensive starting material

PHL cost = 18% TATB cost

Mitchell (VNS chemistry) (1996)

\[ \begin{array}{c} \text{O}_2 \text{N} \\ \text{NH}_2 \\ \text{NO}_2 \\ \text{NO}_2 \\ \text{Picramide} \end{array} \]

- ☺ high yield
- ☹ environmentally non friendly, expensive reactant

Ott (1990)

\[ \begin{array}{c} \text{MeO} \\ \text{Cl} \end{array} \]

- ☺ high yield and soft reaction conditions
- ☹ expensive starting material

DCA cost = 43% TATB cost
Low-cost TATB – Evaluation of known methods

- **Phloroglucinol synthesis**: few methods are attractive for cost studies:
  - **Biochemical route**:
    - Specific technology not available
  - **Chinese patent 2006** (from 2,4-dichlorophenol)
    - Different attempts = no good result

  - Improvements (cost):
    - solvent
    - treatment of RM
    - improvement of reaction parameters (concentration, duration, temperature, ...)
  - Carcinogenic
  - TCB
  - Treatment = extraction + purification by column chromatography

1.5 eq MeONa

HMPA

120°C / 1h

78%
Low-cost TATB - Development of the DCA route

- Improvement on the laboratory scale
- Solvent:
  - Low conversion: MeOH, THF, CH₃CN
  - Good yield: tetramethylurea, NMP, DMSO

Solvent comparison

![Solvent comparison graph]

- DMSO
- NMP
- TMU

Legend:
- DMSO
- NMP
- TMU

Graph showing the DCA yield over time for different solvents.
Low-cost TATB - Development of the DCA route

- Improvement on the laboratory scale
  - Treatment / product isolation:
    - DCA precipitates upon dilution with water
    - Crude product is pure enough (96% by NMR)
    - Yield = 91% (20g scale)

- Development of a GC/MS method: to follow conversion during reaction
Low-cost TATB - Development of the DCA route

- Improvement on the laboratory scale
- RM concentration and reaction duration:

**Variation of DMSO volume (mTCB = 5g)**

- Reaction duration: 3h00

**Reaction exothermicity**

- Ratio $m_{TCB}/V_{DMSO} = 0.5$
  (yield, selectivity, exotherm, cost)

**Reaction duration: 3h00**
Low-cost TATB - Development of the DCA route

- Improvement on the laboratory scale
  - Temperature control (precursors addition order): best control was obtained by addition of $\text{TCB}_\text{(s)}$ in a suspension of $\text{MeONa}_\text{(s)}$ in DMSO at 62°C

- Water volume for DCA precipitation

<table>
<thead>
<tr>
<th>Water volume</th>
<th>Yield (%)</th>
<th>Purity by GC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 x $V_{\text{DMSO}}$</td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td>5 x $V_{\text{DMSO}}$</td>
<td>97</td>
<td>95</td>
</tr>
<tr>
<td>3 x $V_{\text{DMSO}}$</td>
<td>97</td>
<td>95</td>
</tr>
</tbody>
</table>

Productivity and cost improvement

$\text{Cl} \quad \text{Cl} \quad \text{Cl}$

$\text{TCA}$

$\text{<<1\%}$

$\text{OMe}$

$\text{CDMB}$

$\text{~ 4\%}$
Low-cost TATB – Development of the DCA route

Scale up and summary

- Use of a non-carcinogenic solvent
- Simple isolation of the product (dilution + filtration)
- No further purification
- High yield and purity (1kg scale)

Validation laboratory-made DCA in TATB synthesis

Laboratory-made DCA

\[ \text{Laboratory-made DCA} \rightarrow \approx 60\% \text{ cost saved} \]

TATB

\[ \text{TATB} \rightarrow \approx 30\% \text{ cost saved} \]
New TATB-based formulations

➢ **Approach:**

➢ Decrease TATB ratio in TATB/HMX/binder formulations

➢ Preserve as much as possible the overall performances (safety, energetic and mechanical properties)

**Influent parameters:**

- nature and ratio of binder
- HMX ratio

![Bar chart showing estimated cost (based on raw materials) for different TATB/HMX/binder formulations.](image-url)
New TATB-based formulations – Safety tests

- Influence of binder nature and ratio on impact sensitivity:
  - Apparatus: Pendular fallhammer Sorgues (5kg)
  - Formulations prepared (200g scale):

<table>
<thead>
<tr>
<th>No</th>
<th>HMX wt%</th>
<th>TATB wt%</th>
<th>Binder wt%</th>
<th>H&lt;sub&gt;50&lt;/sub&gt; (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
<td>49</td>
<td>PKHJ* 6%</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>52</td>
<td>Cariflex** 3%</td>
<td>54</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>45</td>
<td>Cariflex** 10%</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>52</td>
<td>Technoflon*** 3%</td>
<td>46</td>
</tr>
</tbody>
</table>

* PKHJ: phenoxy binder (d = 1.18)
** Cariflex: copoly(styrene/diene) (d = 0.94)
*** Technoflon (fluoropolymer) (d = 1.8)

- Only weak influence of the binder nature and ratio on the impact sensitivity
- Slightly lower sensitivity with 10% Cariflex but energetic performances may be affected at this level (low density)
New TATB-based formulations - Safety tests

- Influence of HMX ratio on impact sensitivity:
  - Apparatus: Pendular fallhammer Sorgues (5kg)
  - Formulations prepared (wt% binder = 3) (200g scale):

2 compositions were selected for first energetic characterizations:
- HMX/TATB/technoflon 65/30/5
- HMX/TATB/PKHJ 66,3/30,5/3,2
New TATB-based formulations - Safety tests

- Closed-chamber experiments:
  - Combustion behavior:
    5 samples of 9g
    \( P = f(t) \) was measured
    \[ P_{\text{max}} \text{(bar)} \]
    \[ (dP/dt)_{\text{max}} \text{ (bar/ms)} \]
    Evaluation of the Combustion Deflagration Detonation Transition (CoDDT) danger

- Closed-chamber experiments:
  - Combustion behavior:
    - \( P_{\text{max}} \): increase of HMX wt\% \( \rightarrow \) increase of the burning rate
    - \( (dP/dt)_{\text{max}} \): if HMX< 65wt\% linear relation between HMX wt\% and \( (dP/dt)_{\text{max}} \)
      if HMX> 65wt\% high risk of CoD(D)T
    - The two formulations have a good combustion behavior
New TATB-based formulations - Safety tests

- Closed-chamber experiments:
  - Friability test:
    - 1 sample of 9g thrown (150m/s) towards a steel surface
    - Fragments combustion in 130 cm³ vessel
    - $P = f(t)$ was measured

  - UNO threshold for Extremely Insensitive Detonating Substances (EIDS): $(dP/dt)_{max} = 150$ bar/ms

  - $P_{max}$: increase of HMX wt% → increase of the burning rate (linear relation)
  - $(dP/dt)_{max}$: if HMX > 65wt% high risk of DDT
  - The two formulations studied succeed the friability test
New TATB-based formulations - Safety tests

- **Small-scale gap test:**
  - Donor: ADFP 12 EAB M702
  - Barrier: Au4G
  - Sample to be tested
  - Witness plate

  - 30 to 50 tests (Up-and-down method)
  - Determination of the barrier thickness ($e_{50}$) driving to the sample initiation probability of 50%

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Reference (45wt% HMX)</th>
<th>F1: HMX/TATB/PKHJ (66,3/30,5/3,2)</th>
<th>F2: HMX/TATB/technoflon (65/30/5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{50}$ (mm)</td>
<td>&lt; 1</td>
<td>1,482</td>
<td>1,880</td>
</tr>
</tbody>
</table>

- ✓ When HMX wt% increases, initiation is easier ($e_{50}$ higher)
- ✓ F2 is easier to initiate than F1 → influence of the binder nature
Conclusion and Prospects

- A cost-effective DCA synthesis (TATB precursor following Ott route) was optimized and developed on the kilogram scale. A first estimation of TATB cost reduction was about -30%.

- New TATB/HMX formulations using different kind of binder and up to 65wt% HMX (30wt% TATB) were processed.

- The behavior of the formulations towards impact, combustion, friability and small-scale gap test is acceptable.

- Scale-up of nitration (to TNDCA) and amination (to TATB) will be performed as future work.

- 20kg of the two studied formulations will be processed and fully characterized (mechanical properties and energetic performances).