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

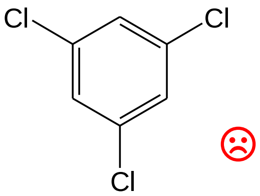
- ✓ safety tests

Conclusion and Prospects

Low-cost TATB - Evaluation of known methods

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

Benziger (1977)

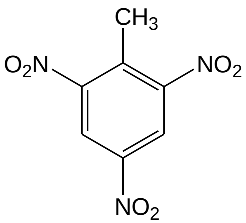


TCB

☺ industrial process (France)

☹ harsh reaction conditions → high cost

Atkins (1981)

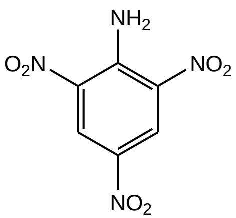


TNT

☺ cheap starting material

☹ sensitive intermediate (pentanitroaniline)

Mitchell (VNS chemistry) (1996)

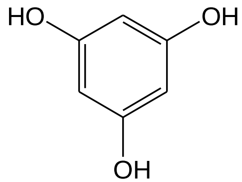


Picramide

☺ high yield

☹ environmentally non friendly, expensive reactant

Bellamy (2001)

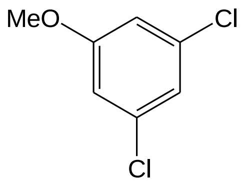


Phloroglucinol

☺ high yield
No Chlorine product

☹ expensive starting material

Ott (1990)



DCA

☺ 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:

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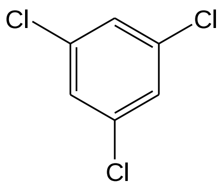

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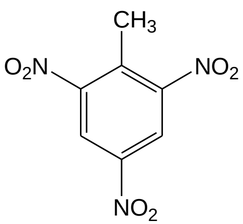

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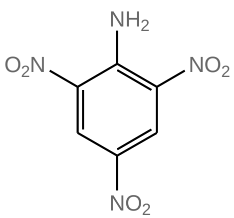

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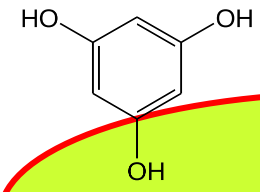


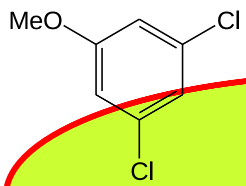
Phloroglucinol

☺ high yield
No Chlorine product

☹ expensive starting material

PHL cost = 18% TATB cost

Ott (1990)



DCA

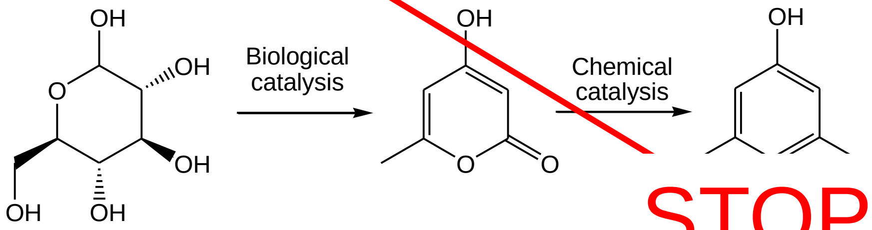
☺ high yield and soft reaction conditions

☹ 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:

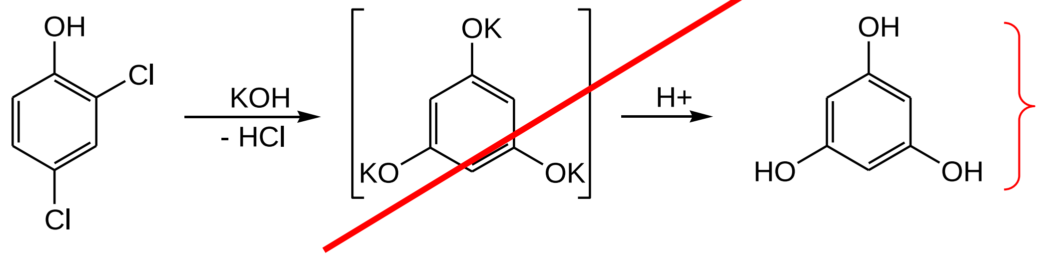


D-Glucose

Specific technology not available

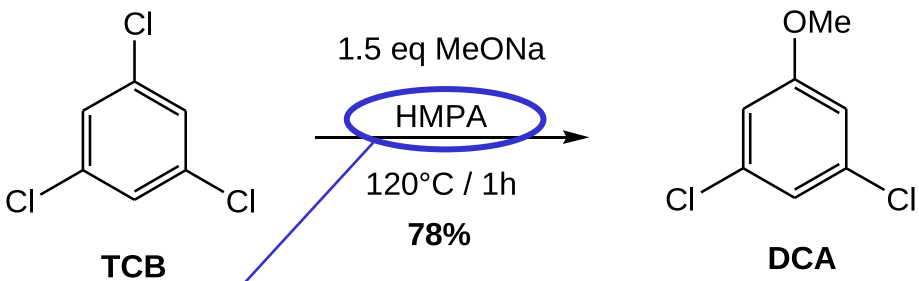
STOP

  - Chinese patent 2006 (from 2,4-dichlorophenol)



Different attempts = no good result

- **DCA synthesis**: Testaferri L., Tetrahedron, 1983, 39(1),193-197



Improvements (cost)

- solvent
- treatment of RM
- improvement of reaction parameters (concentration, duration, temperature, …)

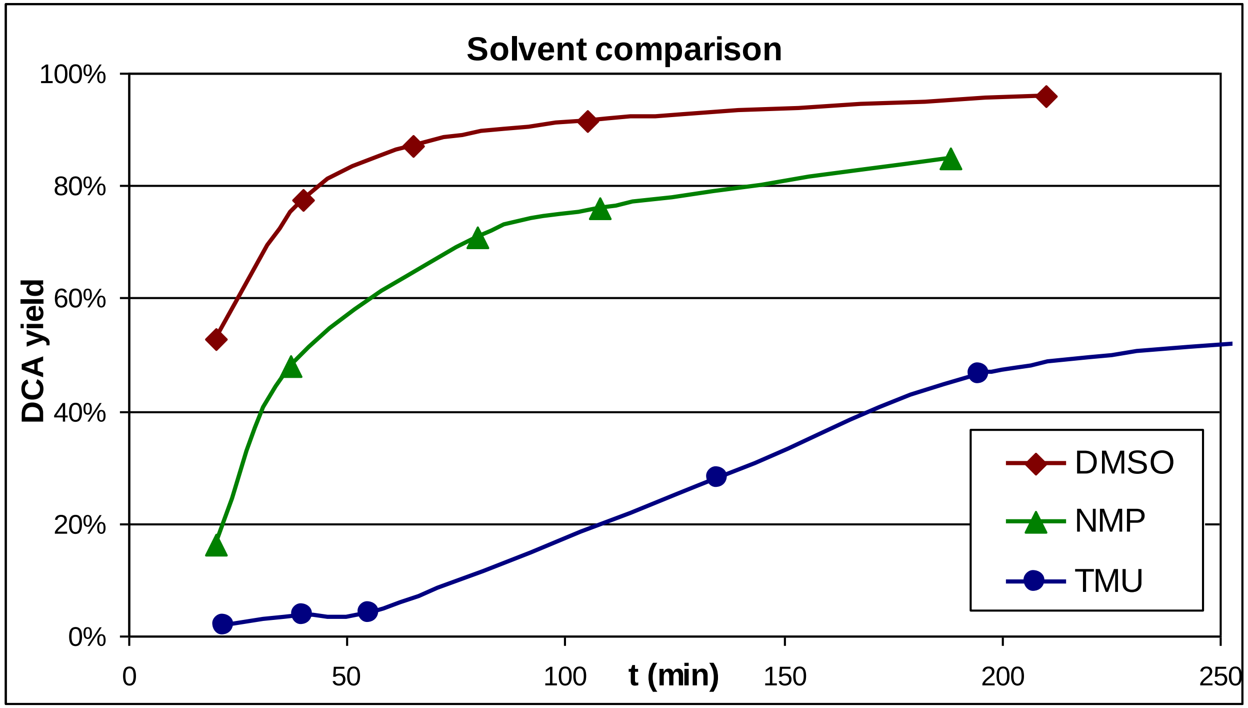
Carcinogenic

Treatment= extraction + purification by column chromatography

Low-cost TATB – Development of the DCA route

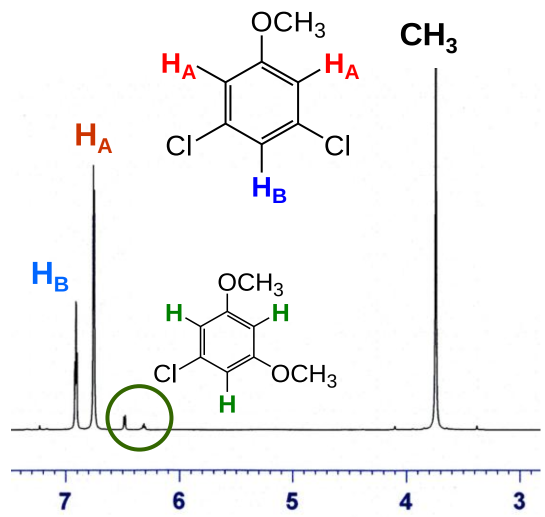
- Improvement on the laboratory scale
  - Solvent:
    - ✓ Low conversion: MeOH, THF, CH_3CN
    - ✓ Good yield: tetramethylurea, NMP, DMSO

expensive teratogenic

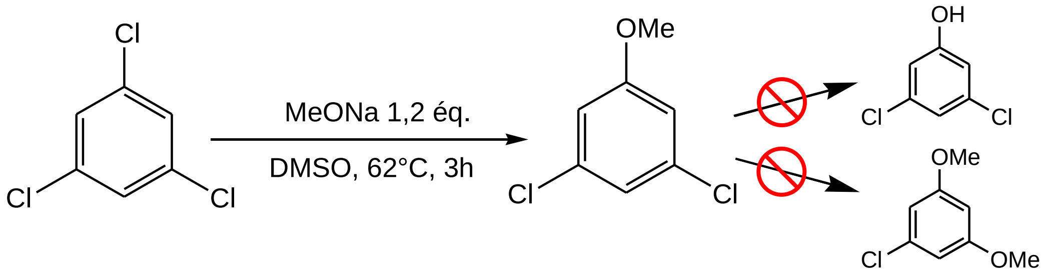


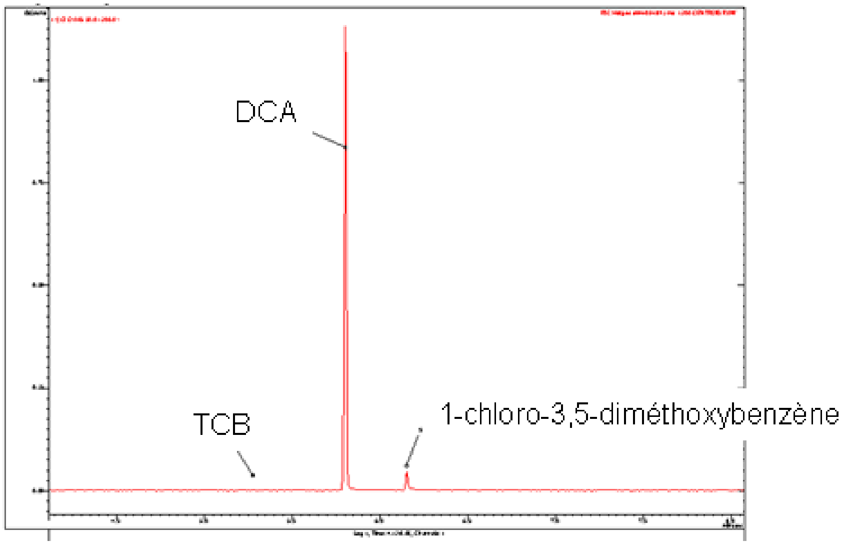
Low-cost TATB – Development of the DCA route

- <u>Improvement on the laboratory scale</u>
  - 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

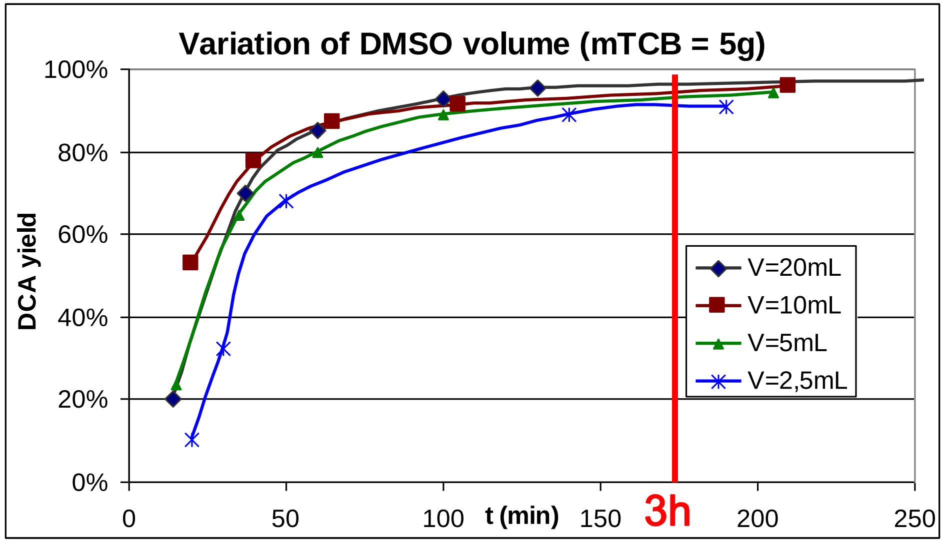


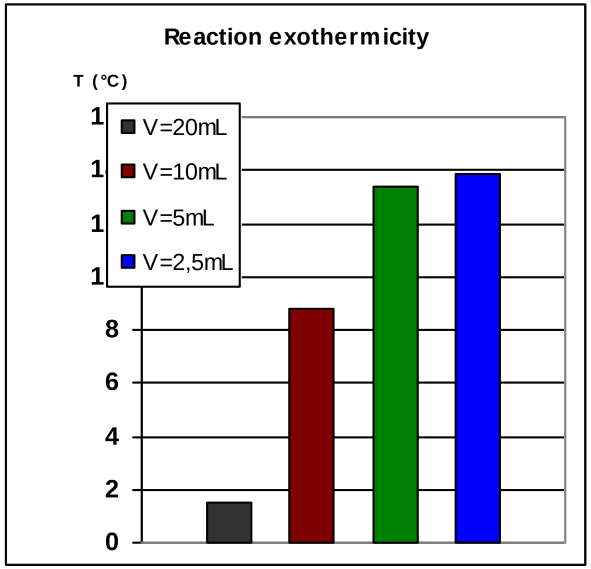


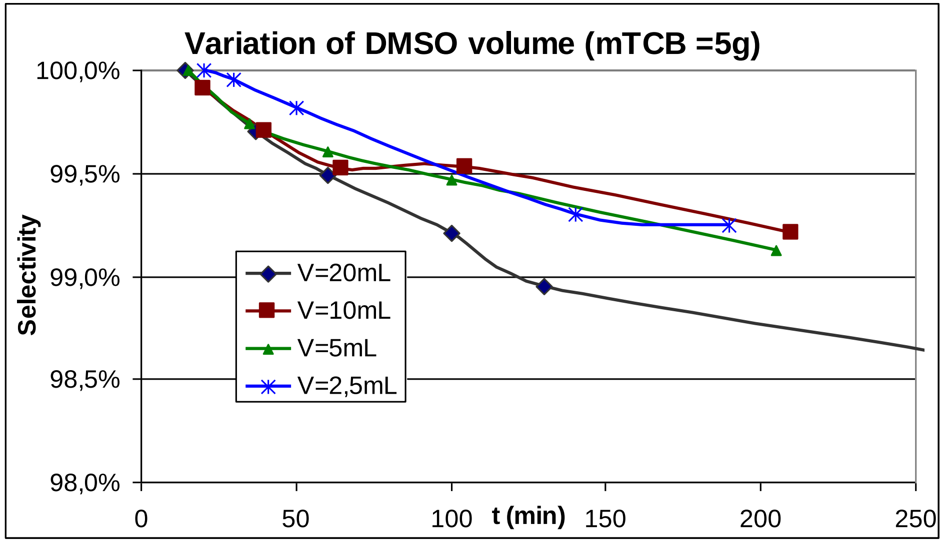
Low-cost TATB – Development of the DCA route

➢ Improvement on the laboratory scale

➢ RM concentration and reaction duration:







Ratio m_{TCB}/V_{DMSO} = 0,5
(yield, selectivity, exotherm, cost)

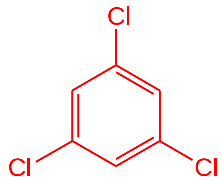
Reaction duration: 3h00

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 $TCB_{(s)}$ in a suspension of $MeONa_{(s)}$ in DMSO at 62° C
  - Water volume for DCA precipitation

Water volume	Yield (%)	Purity by GC (%)
10 x V_{DMSO}	*96*	*95*
5 x V_{DMSO}	97	95
3 x V_{DMSO}	**97**	**95**

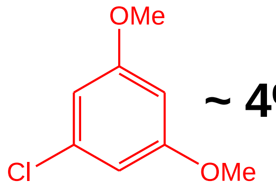
Productivity and cost improvement



TCB

<<1%

and



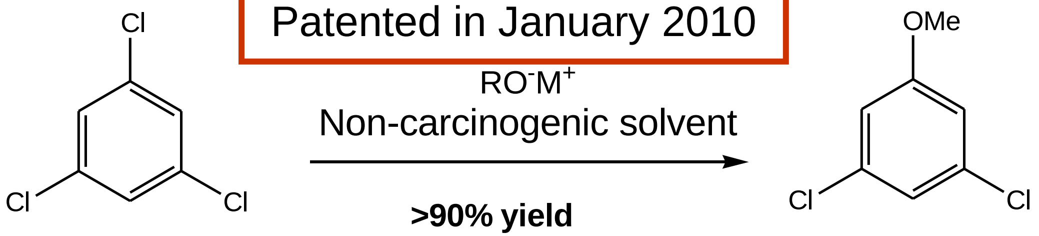
CDMB

~ 4%

Low-cost TATB – Development of the DCA route

➢ Scale up and summary

Patented in January 2010



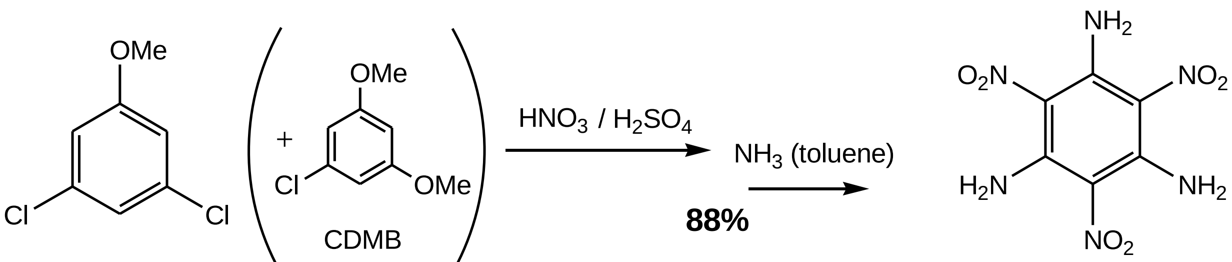
>90% yield
>90% purity

TCB
12€/kg

DCA
~~83€/kg~~ → ~ 35 €/kg
60% cost saved

- ✓ 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



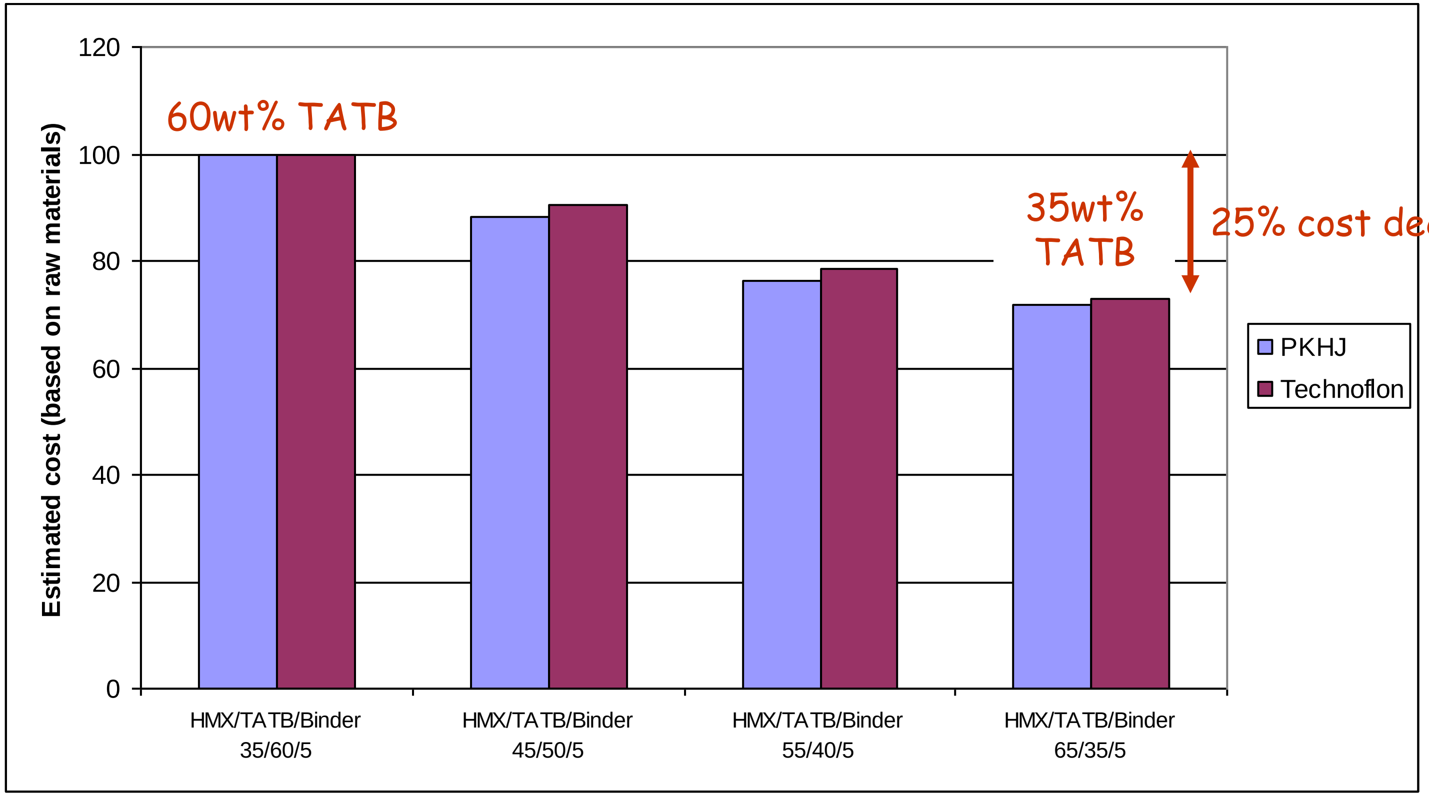
Laboratory-made DCA

TATB

~ 60% cost saved → ~30% 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

New TATB-based formulations – Safety tests

Influence of binder nature and ratio on impact sensitivity:

- ✓ Apparatus: Pendular fallhammer Sorgues (5kg)
- ✓ Formulations prepared (200g scale):

N°	HMX wt%	TATB wt%	Binder wt%	H_{50} (cm)
1	45	49	PKHJ* 6%	52
2	45	52	Cariflex** 3%	54
3	45	45	Cariflex** 10%	61
4	45	52	Technoflon*** 3%	46

* PKHJ: phenoxy binder (d = 1,18)
**Cariflex: copoly(styrene/diene) (d = 0,94)
***Technoflon (fluoropolymer) (d = 1,8)

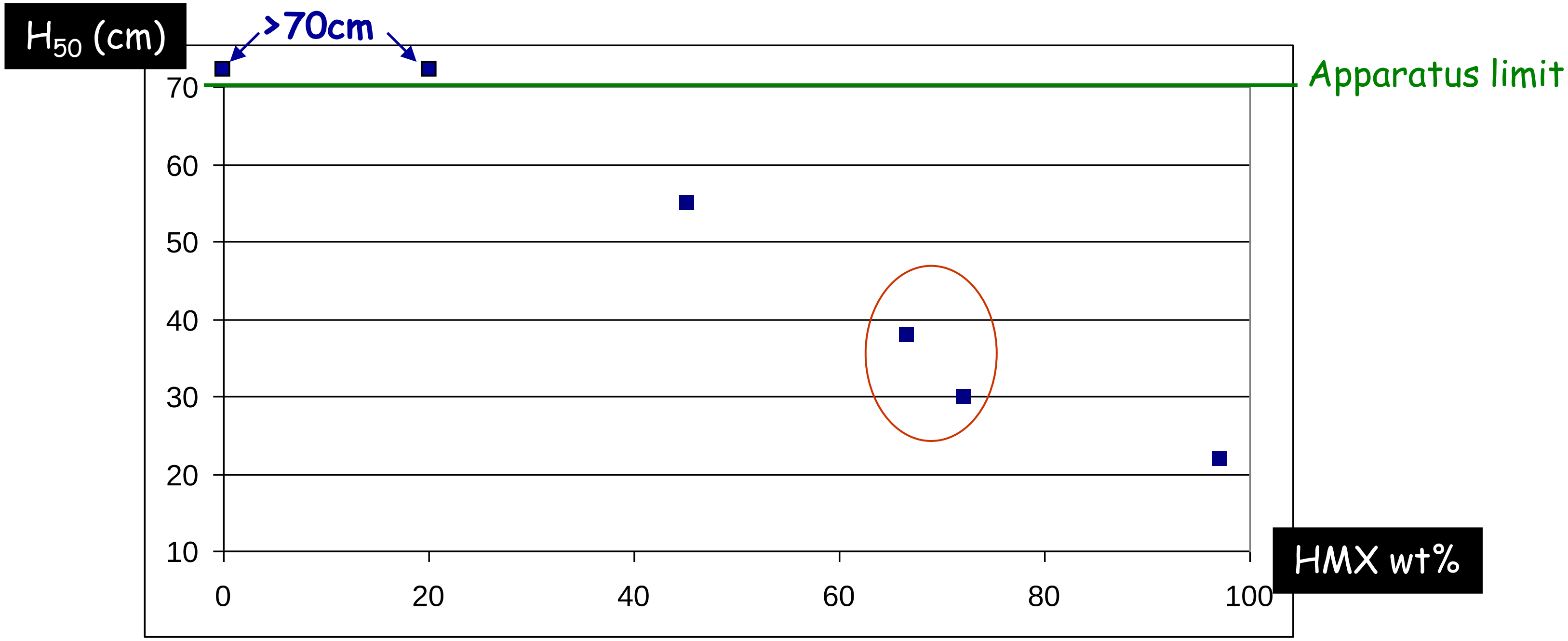
- Only weak influence of the binder nature and ratio on the impact sensitivity

- 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):



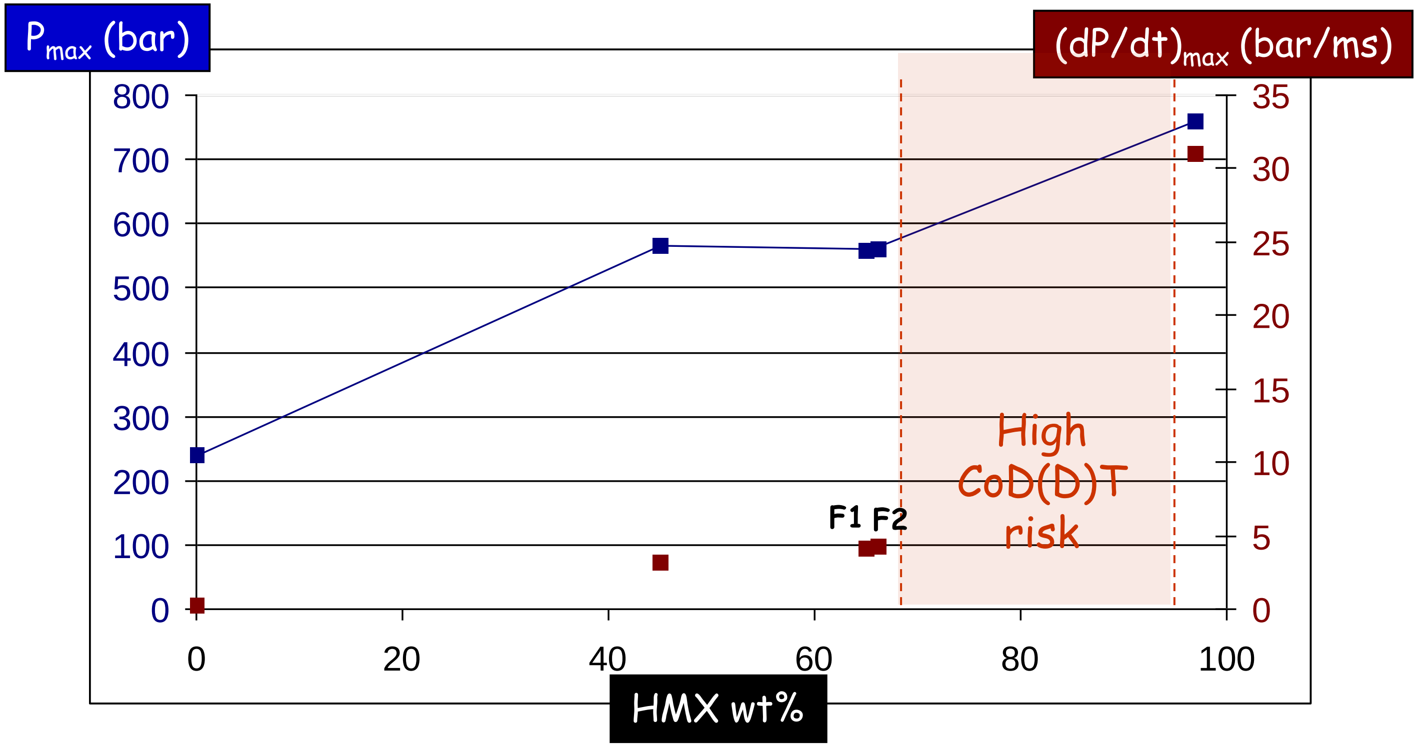
2 compositions were selected for first energetic characterizations:
- HMX/TATB/technoflon 65/30/5
- HMX/TATB/PKHJ 66,3/30,5/3,2

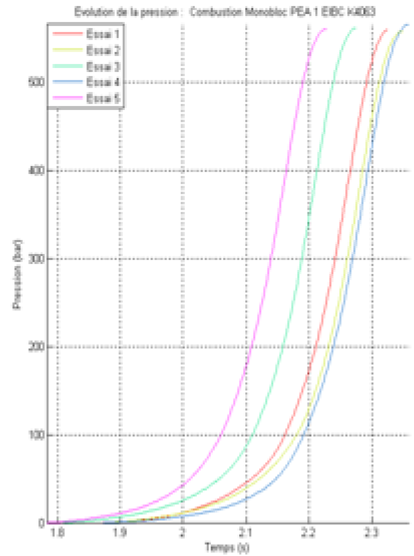
New TATB-based formulations – Safety tests

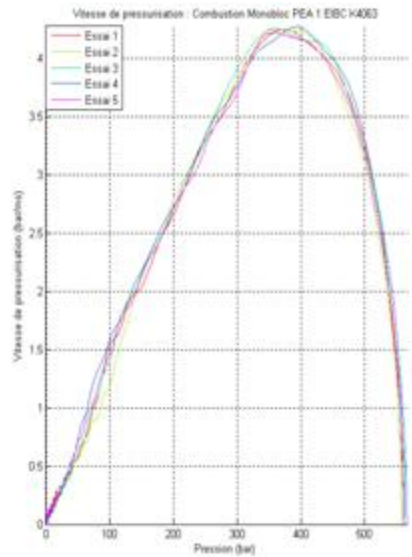
- <u>Closed-chamber experiments</u>:
  - Combustion behavior:

5 samples of 9g
P = f(t) was measured

Evaluation of the Combustion Deflagration Detonation Transition (CoDDT) danger







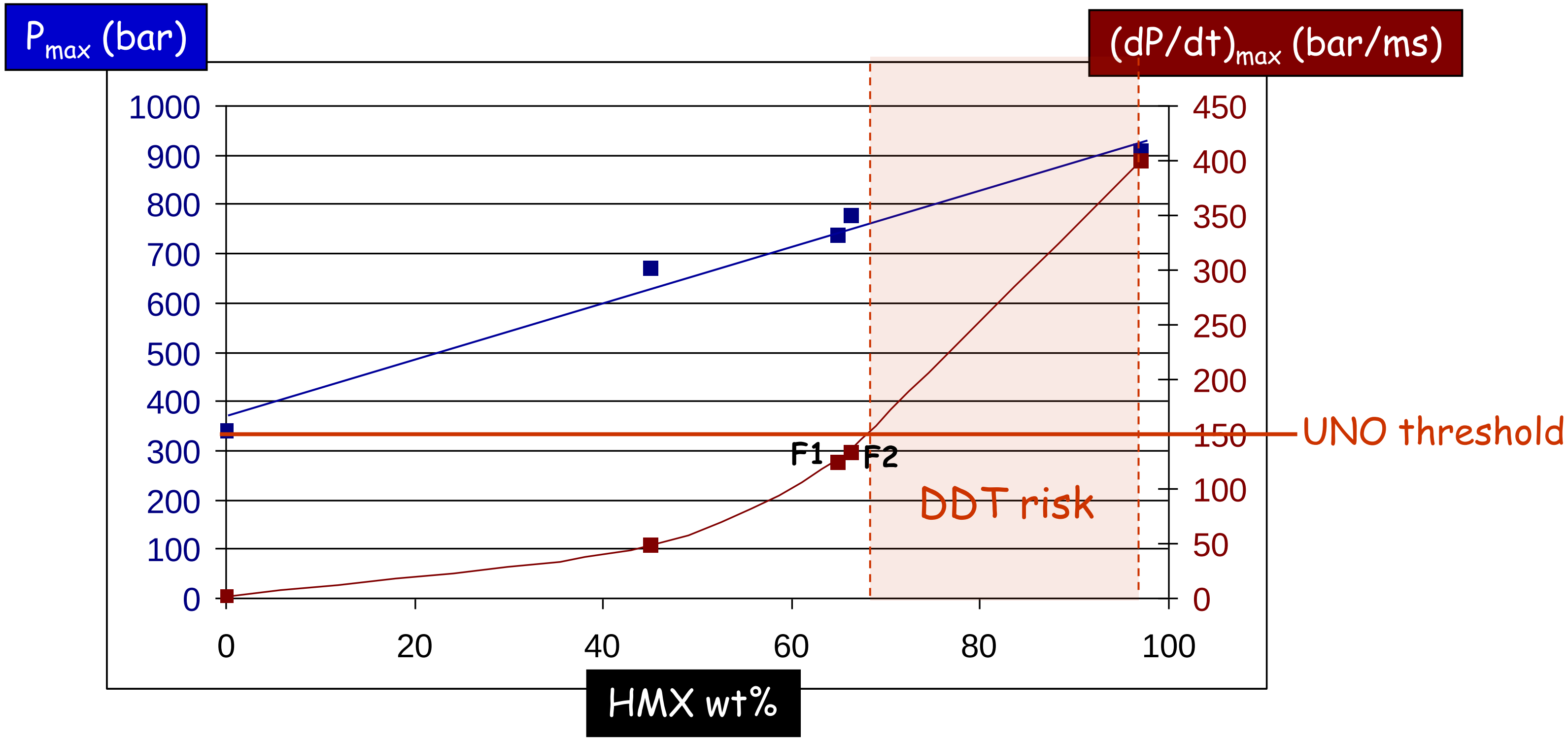
- ✓ P_{max} : increase of HMX wt% → increase of the burning rate
- ✓ $(dP/dt)_{max}$: if HMX< 65wt% linear relation between $HMX_{wt\%}$ and $(dP/dt)_{max}$
  if HMX> 65wt% high risk of CoD(D)T
- ✓ The two formulations have a good combustion behavior

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 cm^3 vessel
• P = f(t) was measured

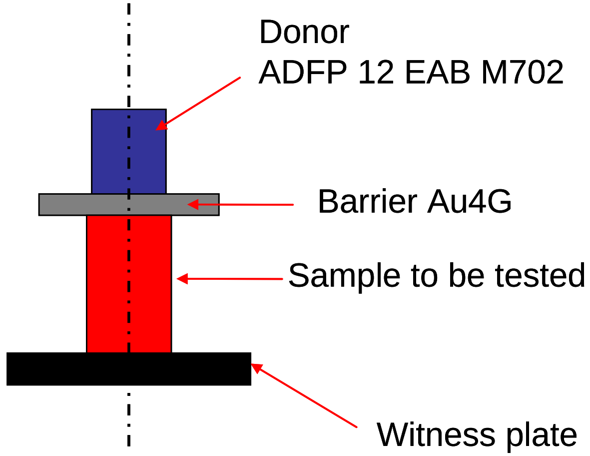
UNO threshold for Extremely Insensitive Detonating Substances (EIDS): $(dP/dt)_{max}$ = 150 bar/ms



✓ 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:



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

Formulation	Reference (45wt% HMX)	F1: HMX/TATB/PKHJ (66,3/30,5/3,2)	F2: HMX/TATB/technoflon (65/30/5)
e_{50} (mm)	< 1	1,482	1,880

✓ 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 developped 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 futur work

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

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