The development of an alternative route to triaminotrinitrobenzene

J. Hanks, T. Highsmith, A. Sanderson, and S. Velarde

ATK ALLIANT TECHSYSTEMS
Thiokol Propulsion

Acknowledgements

- The funding for this work was provided to Thiokol by the US Navy ManTech office

- Special thanks to Rob Schmitt, Alex Mitchell, Al Stern, Lori Nock, John Brough, Tim Mahony and Mike Coburn in US
- Anthony Bellamy, RMCS and Peter Golding, AWE

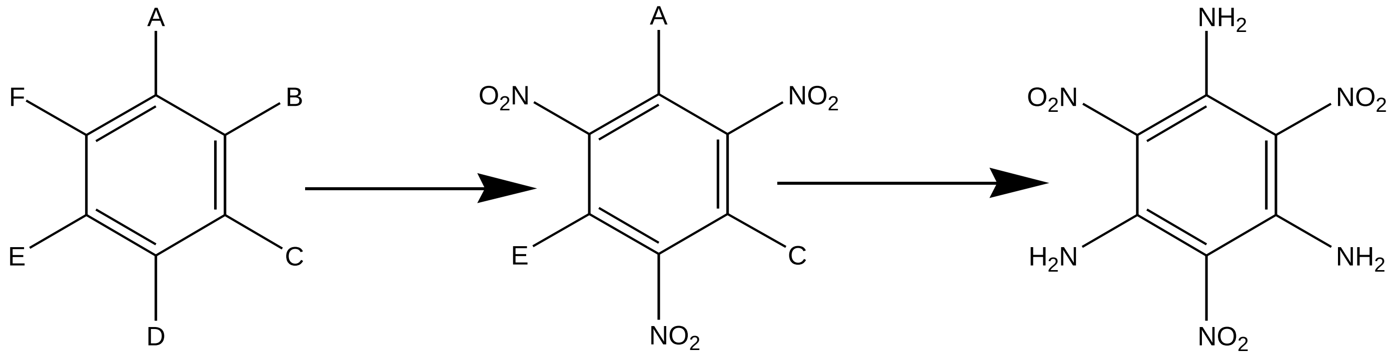
Why TATB Synthesis?

- Current production method produces undesirable waste
- TCB is no longer readily available
- Presence of ammonium chloride is a concern in TATB from traditional process

New TATB Synthesis objectives

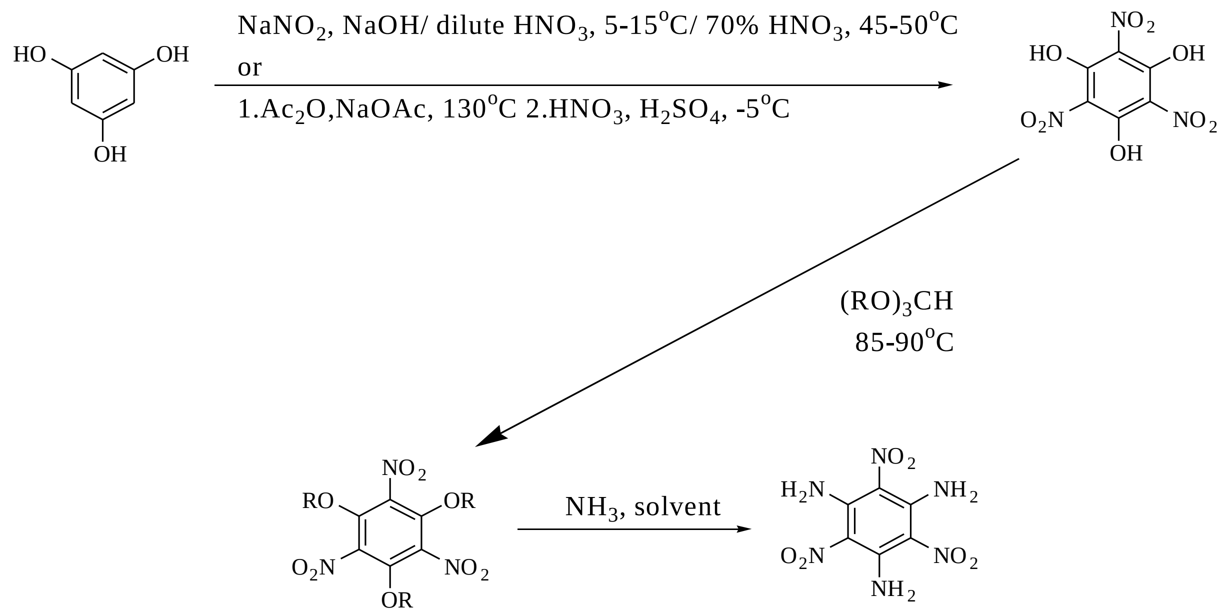
- **Develop a viable sustainable route to TATB**
  - Reasonable cost
  - Acceptable waste streams
  - TATB meets current specifications
  - Scaleable
  - Avoids chlorides

Possible TATB routes



- **Need to cleanly have 1,3,5 nitration**
  - Mild conditions
  - High yield
  - Acceptable waste
  - Intermediate that can be undergo aminolysis/amination
- **Aminolysis/amination should be simple**
  - High yield
  - Mild conditions
  - Available aminating agent
  - Acceptable waste

Phloroglucinol Route

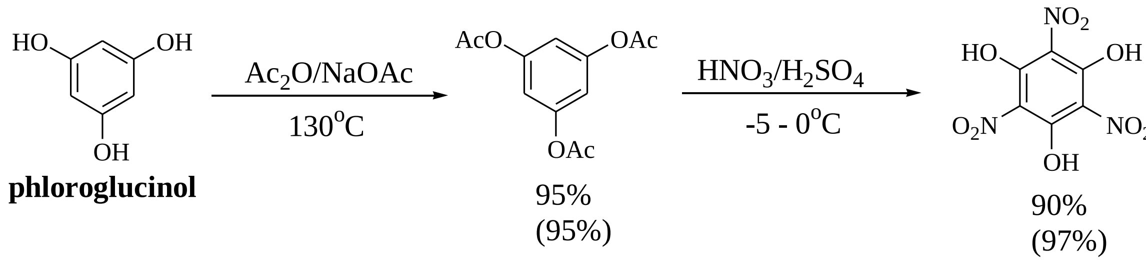


- **Phloroglucinol is ubiquitous**
  - **In bark of fruit trees as glycoside derivative**
  - **Free form in the acacia tree and the kino gum of the eucalyptus tree**
  - **Worldwide, approximately 140-200 metric tons of phloroglucinol are produced each year**
  - Numerous synthetic industrial routes (including demil of TNT)
- **Route developed by Bellamy, Golding and Ward**

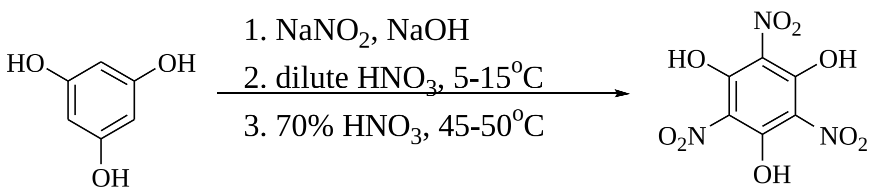
Phloroglucinol route assessment

- **What is the best route and optimum conditions?**
- **Is route scaleable?**
  - Safety
  - Processing
  - Product quality
  - Reproducibility
  - Waste
  - Cost (Materials, labour and waste disposal at production scale)

Synthesis of TNPG



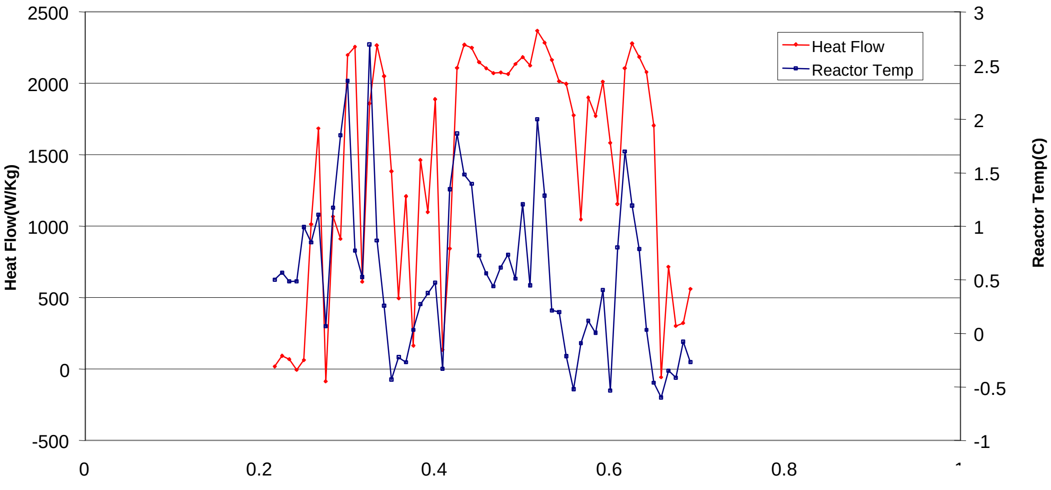
- **Acetylation hard to scale**
  - Lower yield as scale increased
- **Extra step over nitrosation**



75%
(70%)

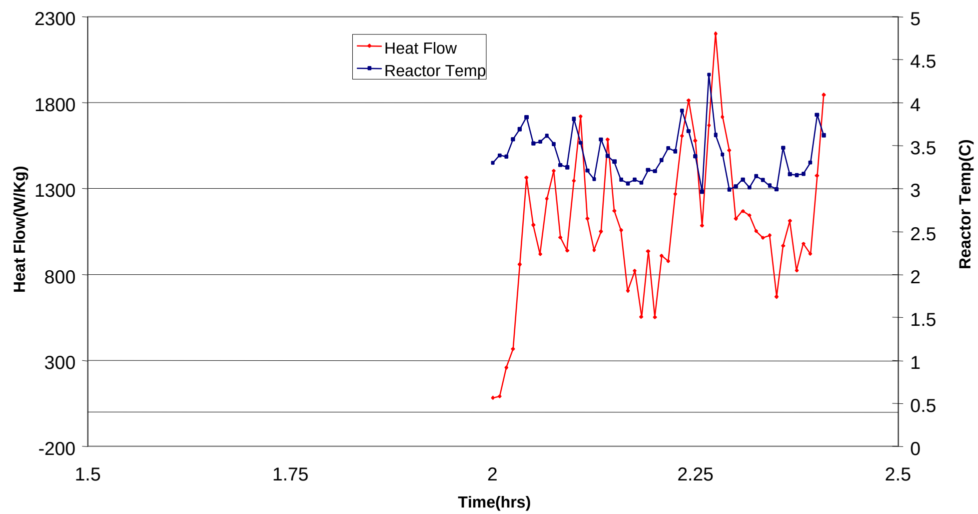
- **Higher temperatures**
- **Easy to scale**
  - Higher yields at bigger scales
- **Moderate yield**

Reaction Calorimetry Data



Nitrosation of phloroglucinol

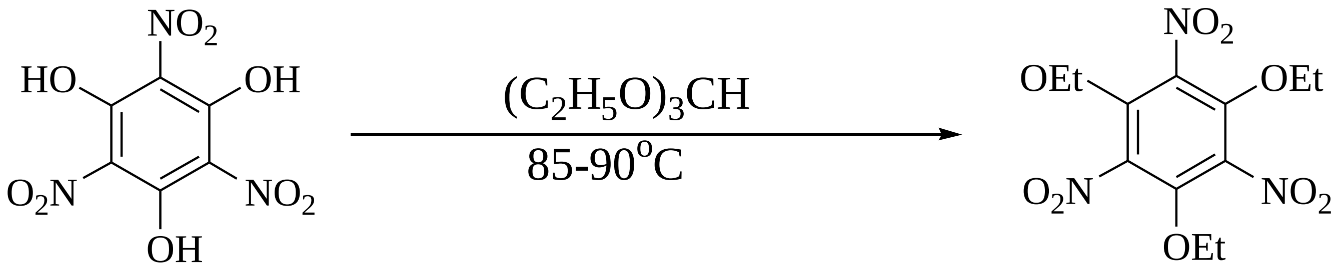
- **Reasonable exotherms**
- **Addition rate controls heat evolution**
- **Easily controllable in 1700l reactor**



Nitration of trinitroso intermediate

Synthesis of TETNB

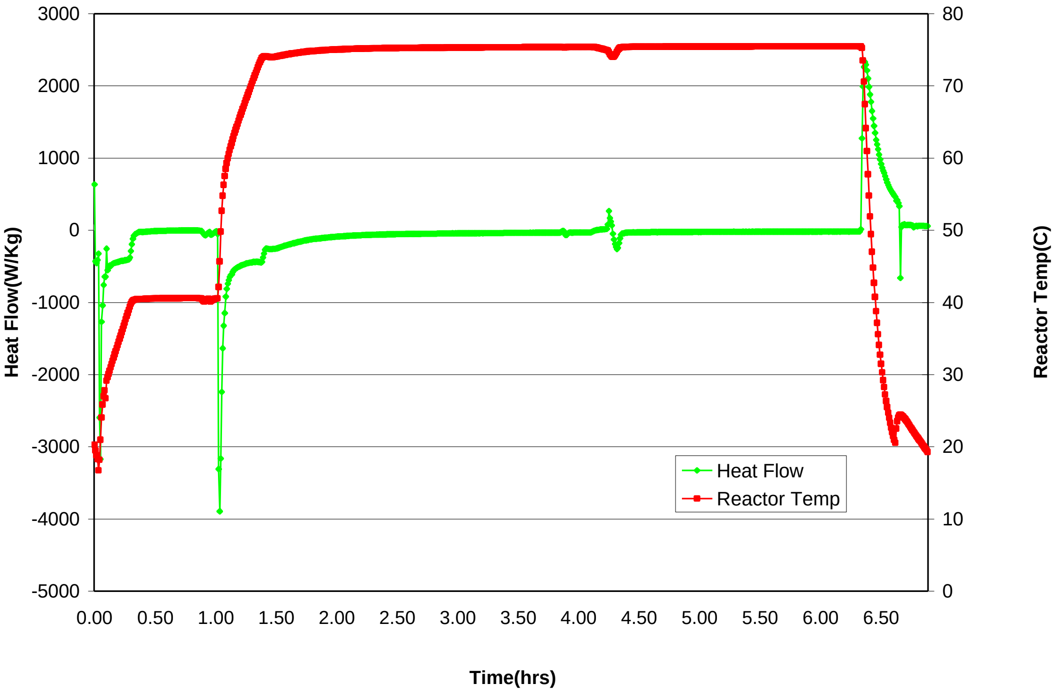
- Used triethylorthoformate due to cost
- Maximized reaction concentrations
- Increased isolated yield



95%
(90%)

Reaction Calorimetry Data for Alkylation

- **Not exothermic reaction**
- **Very exothermic crystallization**
  - Needs to be controlled for viable scale-up



Safety Data of Intermediates

- No special hazards
- TNPG is very acidic

	TNPG	TETNB	Acceptable limits
ABL impact (cm)	13	51	=3.5
ABL friction (lbs @ ft/s)	800 @ 8	800 @ 8	=50 @ 3
DSC onset/peak (°C)	219/223	307/318	--
VTS, 100°C, 48 h (ml gas/g substrate)	0.189	0.450	<2.0
TC ESD unconfined (J)	8, no mass ignition	0.6, no mass ignition	no mass ignition
TC impact (in)	27.7	45	>4
TC friction (lbs)	>64	>64	>10
SBAT onset (°F)	297	391	>225
Russian deflagration-to-detonation (500 psi)	GO	NO GO	NO GO
IHE mini-card gap (zero cards)	GO	NO GO	NO GO

Aminolysis Results

solvent system†	particle size-micron (10%,50%,90%)	temperature(ºC)	yield
MeOH	1.9, 5.5, 11.4	-5	97.8
EtOH	3.9, 8.2, 13.8	-5	98
DMF	1.8, 8.8, 20.0	-5	99.1
EtOH/DMSO (2/1)	4.5, 9.6, 15.8	0	99.4
i-PrOH	4.7, 15.6, 28.8	-5	99.1
dimethoxydiethylether	6.1, 12.0, 19.8	-5	97.5
acetonitrile	4.1, 14.6, 35.9	-5	97.8
pyridine	4.9, 13.7, 25.1	-7	99
dichloromethane	8.8, 22.9, 45.4	-5	99.8
toluene	16.6, 30.4, 53.0	-5	95.3
Navy TATB (included for comparison)	26.0, 62.6, 114.5	--	--

- **Bubbled ammonia into reaction solution**
- **Simple and reproducible**

TATB Analysis

- **Analysis (purity) is difficult due to TATB insolubility**
- **Quantitative HPLC method developed but needs standard**

	ATK Thiokol TATB	Navy TATB	Acceptable limits
ABL impact (cm)	80	80	=3.5
ABL friction (lbs @ ft/s)	800 @ 8	800 @ 8	=50 @ 3
DSC onset/peak (°C)	367/370	385/389	--
VTS, 100°C, 48 h (ml gas/g substrate)	0.252	0.166	<2
TC ESD unconfined (J)	0.8, no mass ignition	2.66, no mass ignition	no mass ignition (at 8 J)
TC impact (in)	>46	>46	>4
TC friction (lbs)	>64	>64	>10
SBAT onset (°F)	N/A (off scale)	N/A (off scale)	>225
Russian deflagration-to-detonation (500 psi)	NO GO	--	NO GO
IHE mini-card gap (zero cards)	NO GO	--	NO GO

TATB Processing

- Made moulding powder
- Processed and safety properties as standard TATB

Conclusions

- Synthesis of TATB from phloroglucinol as described by Bellamy et al has been found to be reproducible and scaleable
- Each step has been run under different conditions multiple times at the 500g to 1kg scale and high purity material obtained
- Reagents are all readily available and of reasonable cost
- Significant reaction optimization has been completed
- There appear to be few reaction scale issues that would prevent this chemistry from being further scaled up