RDECOM

Dihydroxylammonium 5,5'-bis-tetrazole-1,1'-diolate (TKX-50) Synthesis and Lab Scale Characterization

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

Briefed by: Steve Nicolich
973-724-3016
steven.m.nicolich.civ@mail.mil

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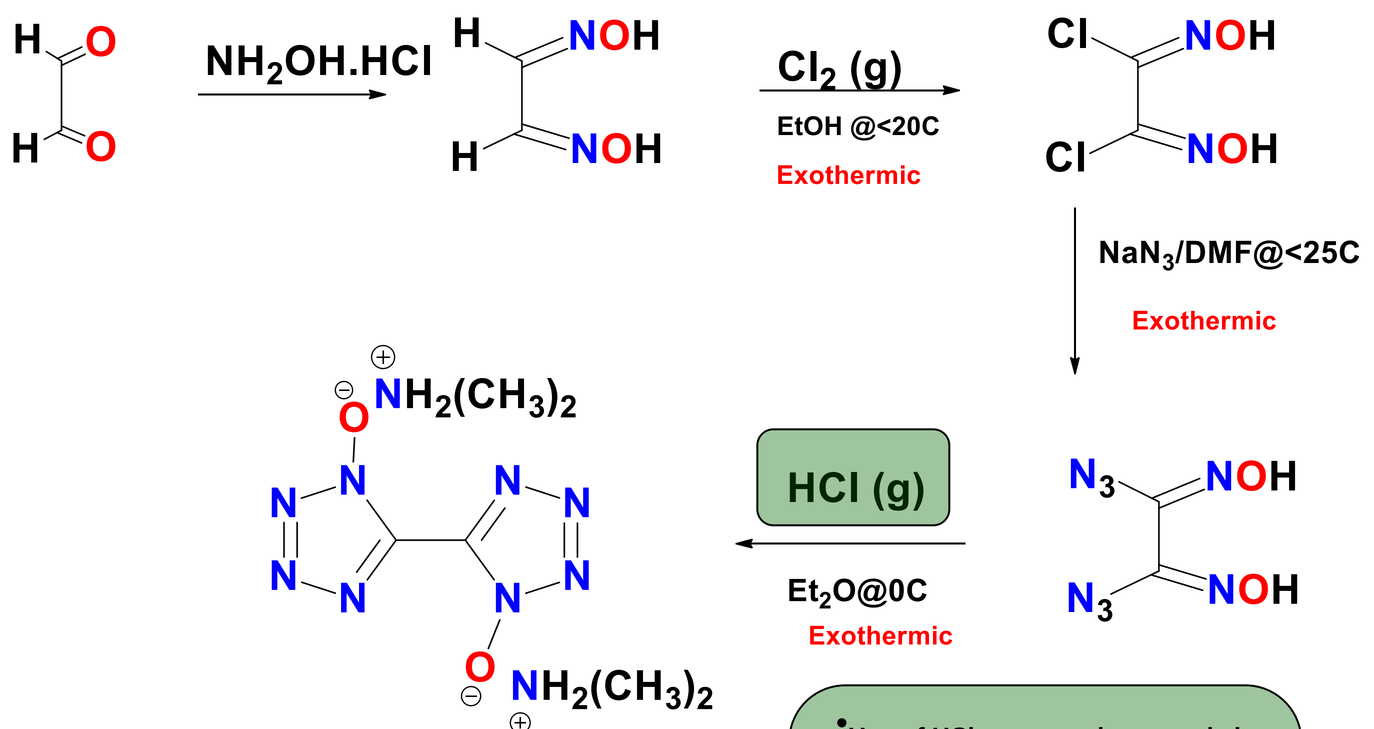
Briefing Overview

- TKX-50 Synthesis/scale up with multiple steps defined individually
- Various Characterizations
- Thermo Chemical Calculations
- Future work
- Conclusions

Dimethylammonium Salt Synthesis

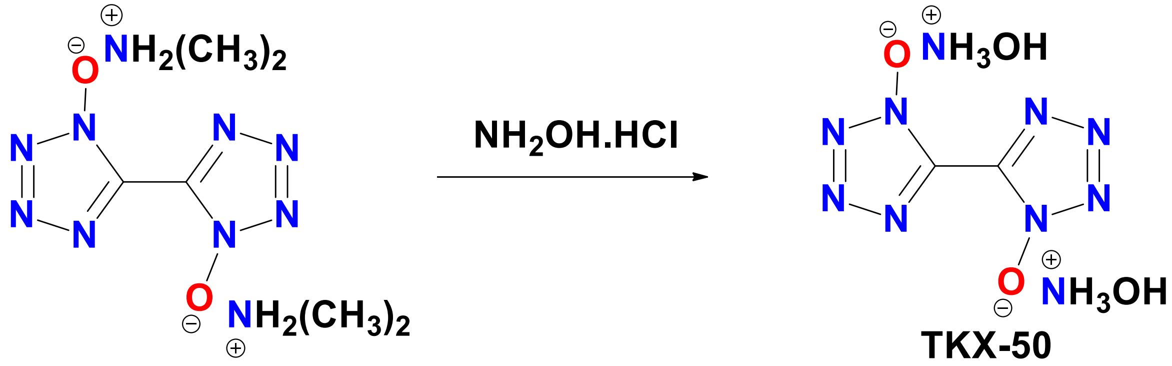


TKX-50 Precursor

- Use of HCl gas on a large scale is dangerous
- Use of HCl solution in Dioxane has been developed in its place

Unclassified

SYNTHESIS OF DIHYDROXYLAMMONIUM 5,5'-BISTETRAZOLE-1.1'-DIOLATE (TKX-50)



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Dichloroglyoxime Synthesis

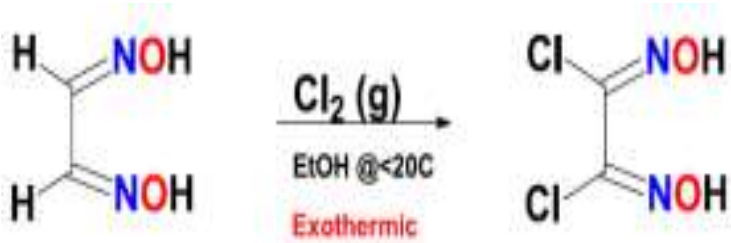
Chlorination Synthesis and Initial Scale-Up

Set-up & Initial Experiments

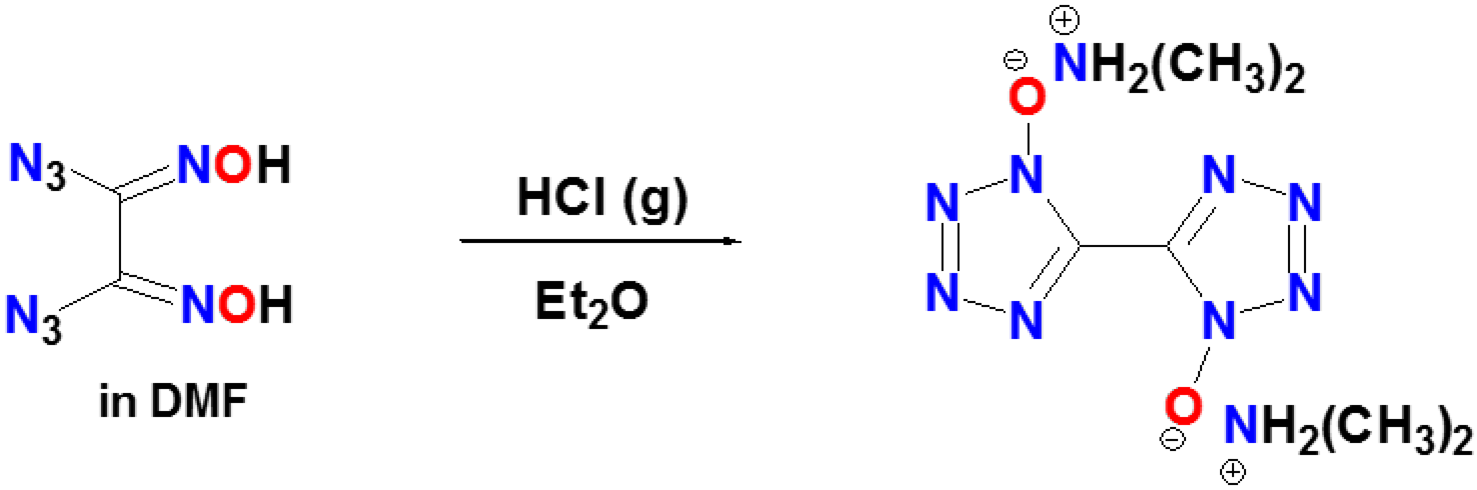
- 1-L and 3-L chlorination experiments set-ups and procedures established
- Established approximate chlorine flow rates at low temperature with rotameter
- Small-scale synthesis of glyoxime (20g)

Scale up Runs

- Task: batch-wise synthesis of ~1.5kg dichloroglyoxime from glyoxime
    - Purpose: provide material for initial synthesis/DV testing
- Batch size:150-160g product yield (3L reactor)
    - 18 reactions successfully conducted at this scale – approximately 3000g of dichloroglyoxime isolated
    - Upon warming exotherm observed at roughly -10 ^{o}C; warmed up to about 15 degrees C but was controlled by bath



Alternate Method for Cyclization (1 of 3)



Concerns

- Highly flammable solvent (ether); not desirable on an industrial scale
- Application of corrosive HCl gas into the medium until the medium is saturated (meaning uncertain amount of time and careful control of HCl gas addition)

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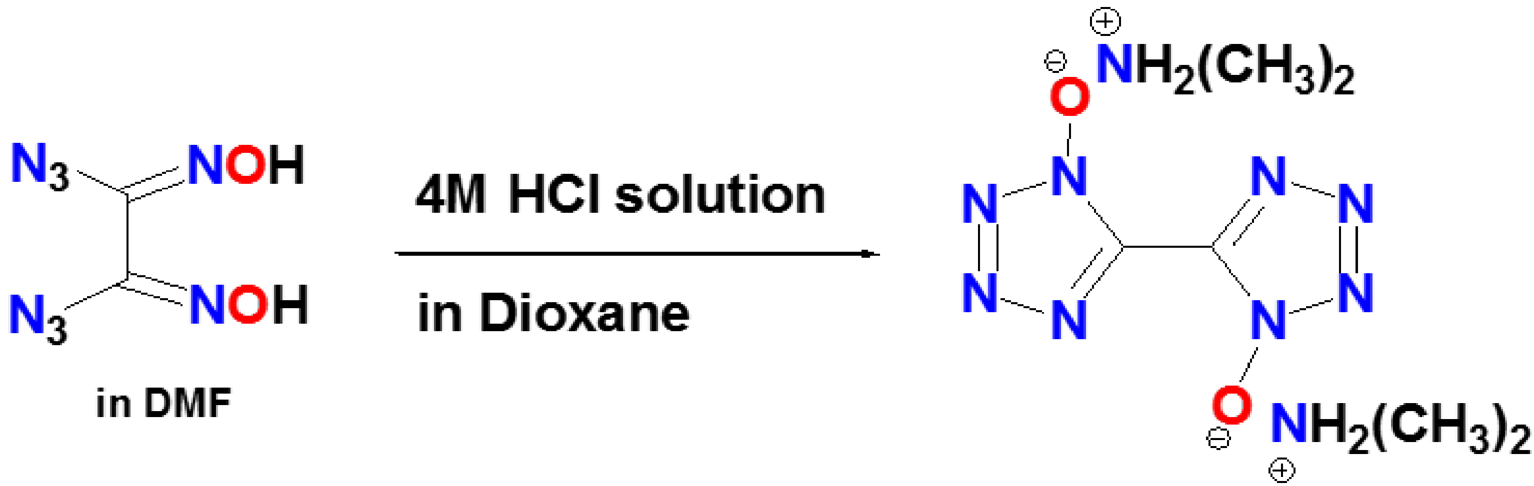


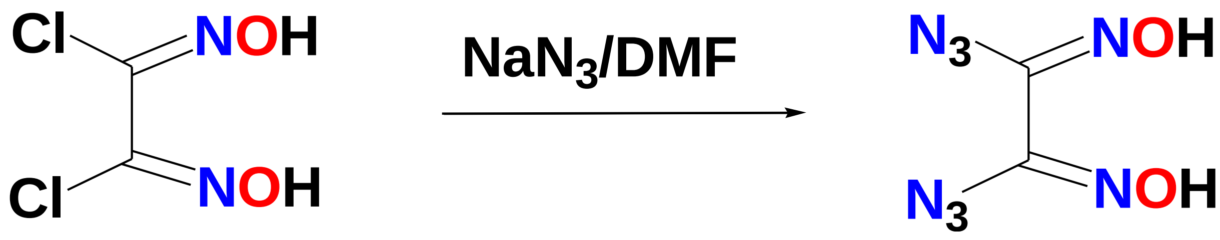
Eliminated

- Use of HCl gas
- Highly flammable diethylether solvent

HCl is in solution form provides more control over the reaction medium

Alternate Method for Cyclization (3 of 3)

Azidation of dichloraglyoxime
Synthesis of diazidoglyoxime



Reagent	Condition	Result
NaN_3	Acetone	The m.p. of TKX prepared from this reaction does not match with the authentic sample
NaN_3	Dioxane	No diazide formation
$TMSN_3$	Toluene, 90°C	Starting material only
	EtOH	Starting material only
	DMF	NMR experiment suggested complete conversion to diazide when used large excess of $TMSN_3$; lab experiment provided mixtures of compounds
NaN_3	DMF (used about half the volume of reported amount)	Diazidoglyoxime

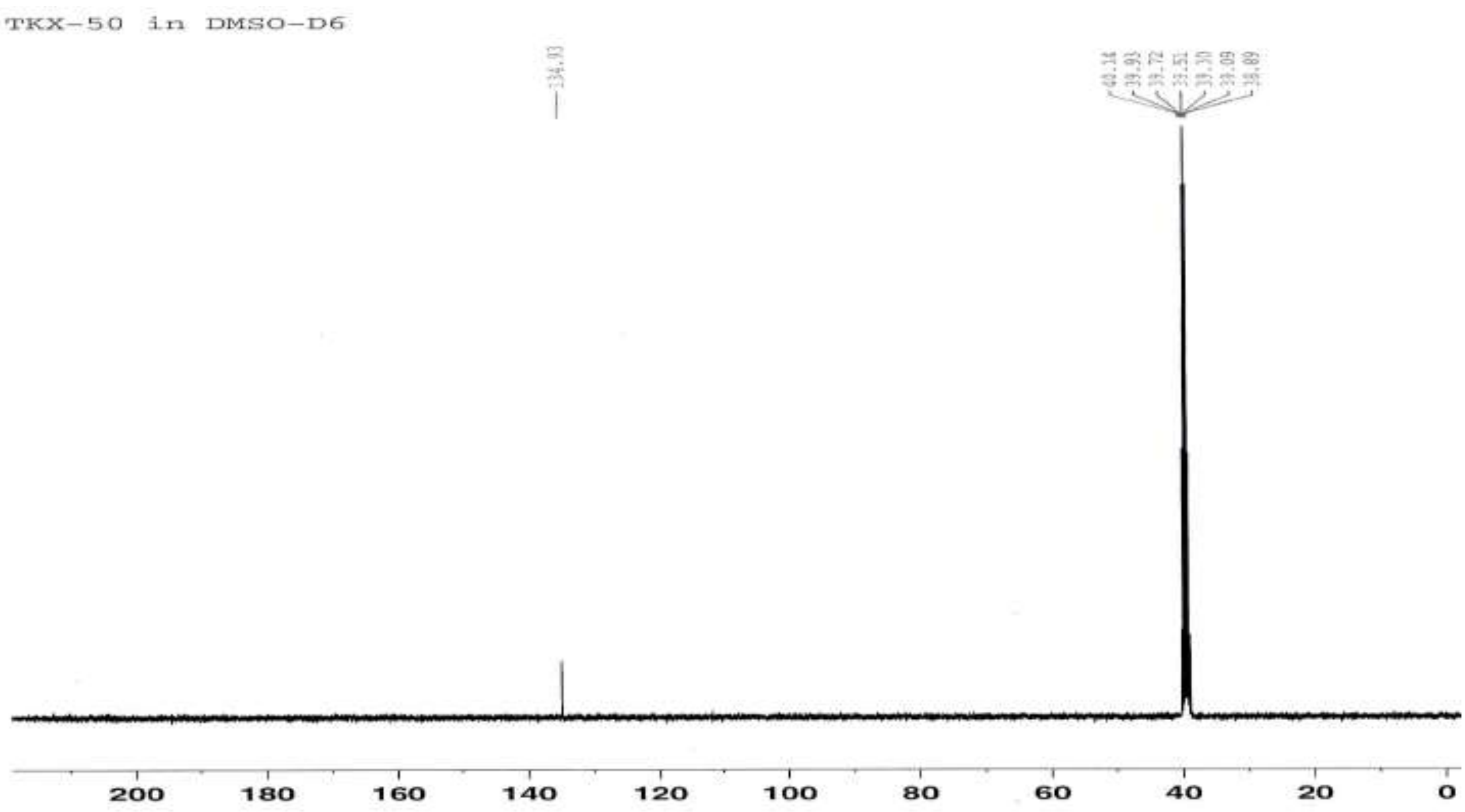
Synthesis of TKX-50

- Develop a procedure for **preparation of glyoxime** in house
  - AlfaAesar sells glyoxime as 20% water wet
  - Cost: $197 / 50 grams
    - In-house process now available with minimum costs
- **Chlorination**
  - Eliminate Chlorine gas: Investigate chlorination process with alternate reagents (ex. SO_2Cl_2, NCS, bleach, $CaCl_2$-H_2O_2)
  - Address the exotherm part by developing a continuous chlorination process to produce dichloroglyoxime
- Perform research on using **dibromoglyoxime** instead of dichloroglyoxime
- **Cyclization**
  - DMF is a high boiling solvent and tough to remove from the medium. Investigate **azidation** with *alternate reagents* in other organic solvents such as ethanol as an alternative to use of DMF
  - Find the conditions that would utilize the minimum amount of HCl required for the **cyclization**
  - Generate HCl insitu from acetyl chloride and alcohol; this would eliminate use of HCl gas
  - Research on using hydrochloric acid as a catalyst or dimethylammonium chloride (or hydroxylammonium chloride) as an acid source in the cyclization
  - Investigate use of alternative acid catalyst such a Lewis acids

^{13}C NMR of TKX-50

Unclassified

CARBON-13 NMR DATA



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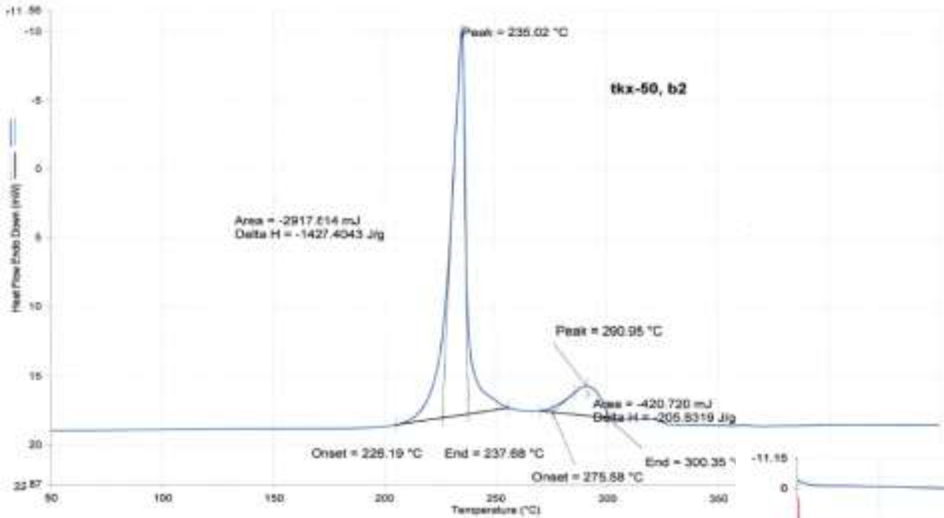
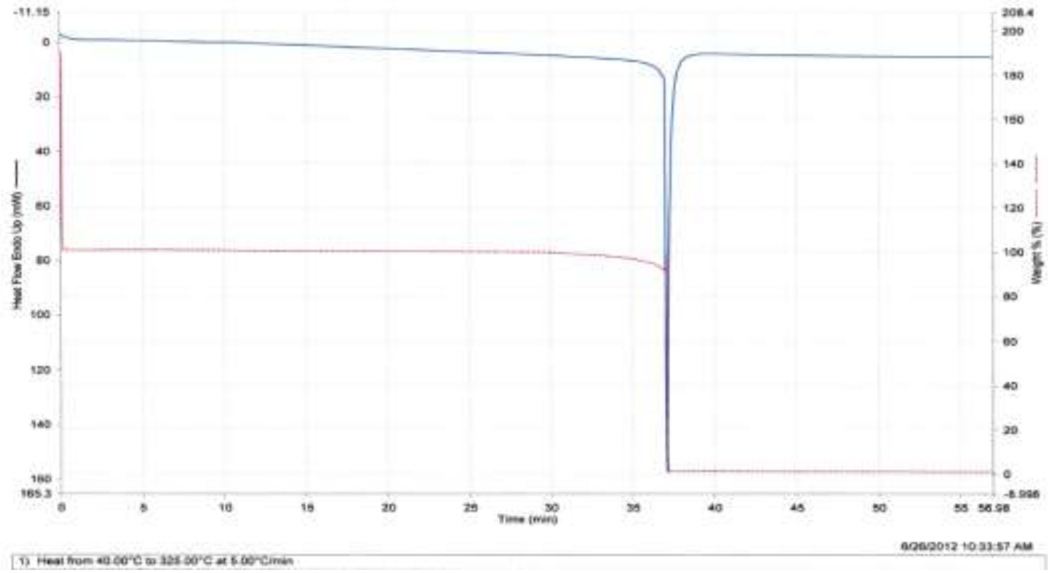
TKX-50 Thermal Data

THERMAL DATA : DSC



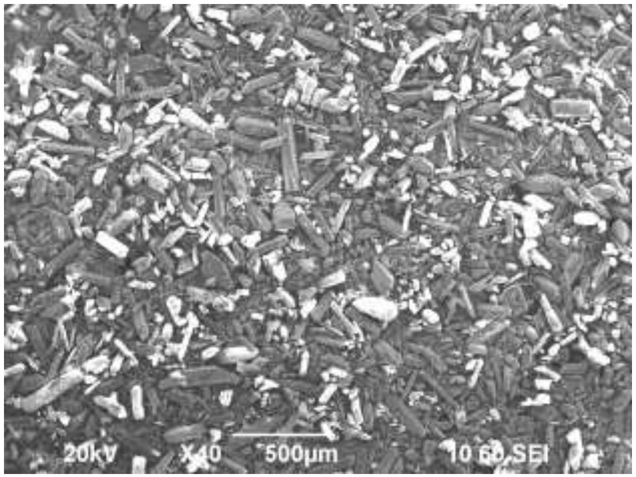
THERMAL DATA : TGA

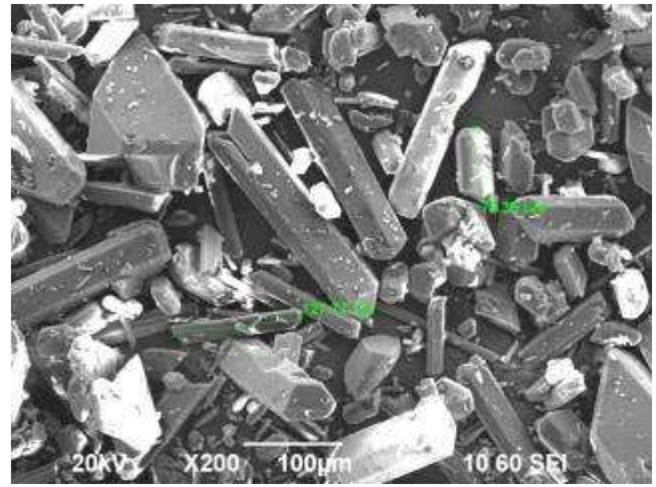


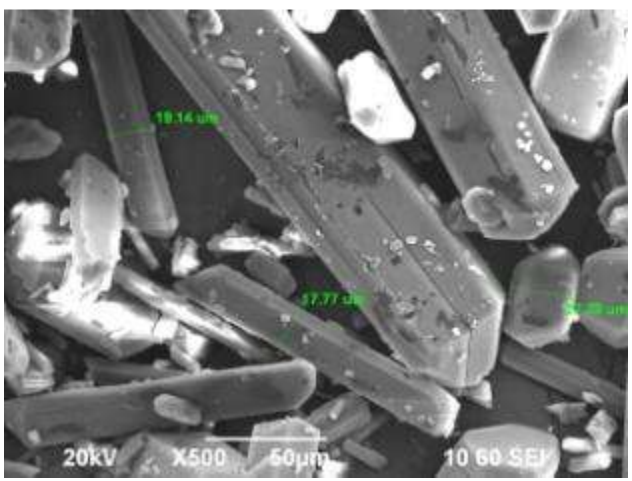
Heat from 30C to 450C at 5C/min

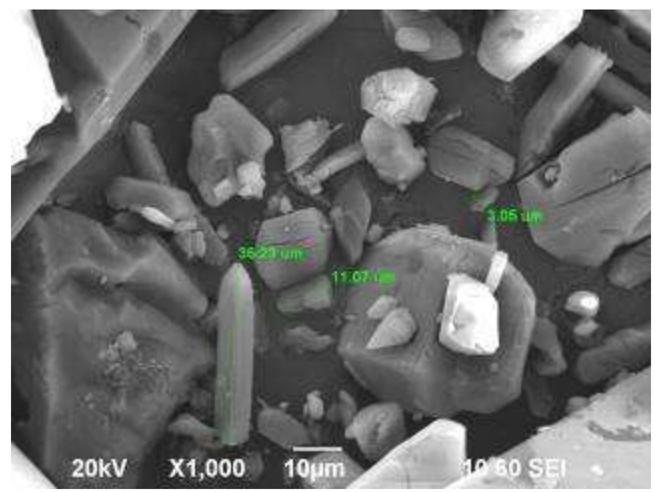
SEM of TKX-50

SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS:



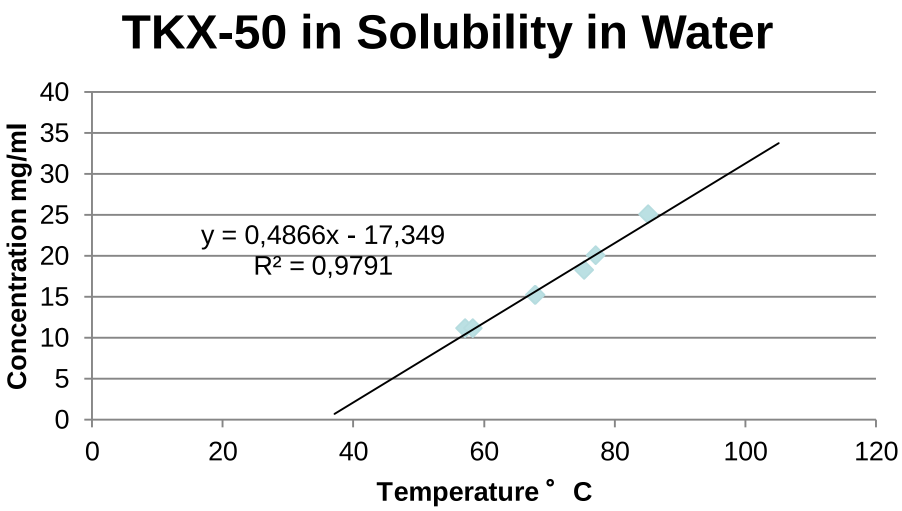






TKX-50 Water Solubility

Unclassified



Clear Point Temperature	Concentration
ºC	mg/ml
57.1	11.2
58.3	11.2
67.8	15.2
67.9	15.2
75.3	18.3
77.1	20.1
85.1	25.1

TKX-50 Safety Test Results

Unclassified

Molecule	ERL Impact (cm)	BAM Friction (N)	ABL ESD (J)
TKX-50	45.5	Reacted @ 128N, Did not React in 10 trials @ 120N	Reacted @ 0.128J; Did not React in 20 trials @ 0.09J
RDX (Class I)	33.5	Reacted @ 216N, Did not React in 10 trials at 192N	Reacted @ 0.063J; Did not React in 20 trials @ 0.051J
RDX (Class V)	30.5	Reacted @ 324N, Did not React in 10 trials at 288N	Reacted @ 0.051J; Did not React in 20 trials @ 0.040J
FEM HMX	27.1	Reacted @ 168N, Did not React in 10 trials @ 160N	Reacted @ 0.040J; Did not React in 20 trials @ 0.031J

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Vacuum Thermal Stability Test Results

- Performed vacuum stability testing in accordance to STANAG 4556 ED.1 (Explosives: Vacuum Stability Test)
- The materials were tested for 40 hours at 100 degrees Celsius
- Compatible Material Range 0.0 – 3.0

ml gas of 1:1 mix	Reactivity of mix (ml)	Result
TKX-50	0.067	pass
TKX-50 & CUO(II)	0.62	pass
TKX-50 & Steel shavings	Negligible	pass
TKX-50 & Al powder	0.13	pass
TKX-50 & R8002	2.4	pass
TKX-50 & BDNPA/F	0.94	pass
TKX-50 & Chlorez wax	negligible	pass
TKX-50 & Viton	negligible	pass
TKX-50 & DNAN	negligible	pass
TKX-50 & TNT	negligible	pass
TKX-50 & DEMN	9.84	fail
TKX-50 & NTO	negligible	pass
TKX-50 & HMX	negligible	pass
TKX-50 & PrNQ	1.2	pass

TKX-50 Thermo-Chemical Calculations

Cheetah 6.0 EXP6.3 Library

Formulation	Density (g/cc) [98%TMD]	Detonation Velocity (Km/s)	CJ Pressure (Gpa)	Gurney
PBXN-5 (Baseline)	**1.86**	**8.75**	**35.32**	**3.11**
Comp A5 (Baseline)	**1.75**	**8.25**	**30.73**	**2.95**
PBXN-9 (Baseline)	**1.72**	**8.43**	**29.52**	**2.90**
PAX-46 (Baseline)	**1.77**	**8.47**	**31.25**	**3.07**
TKX-50	1.83	9.5	37.5	3.02
95% TKX-50, 5% Viton A	1.83	9.23	35.62	2.96
98% TKX-50, 2% Stearic Acid Wax	1.79	9.19	33.63	2.9

Jaguar 10*

Explosive	Formula	Density	ΔH_f	Det Vel	C-J P	CJ T	Gurn Vel(3)	Gurn Vel(7)	E0
		g/cm^3	kJ/mol	km/s	GPa	K	km/s	km/s	kJ/cm^3
TKX-50	$C_2H_8N_{10}O_4$	1.877	193	9.83	42.1	2433	2.66	2.9	-9.72
TNT	$C_7H_5N_3O_6$	1.654	-63	6.89	19.8	3092	2.20	2.43	-7.11
RDX	$C_3H_6N_6O_6$	1.816	70	8.76	34.8	3708	2.73	3.01	-10.88
HMX	$C_4H_8N_8O_8$	1.905	75	9.09	38.7	3514	2.76	3.04	-11.38

*Professor Leonard Stiel

Future Work

- **Solubility is an important factor for formulations efforts**
- **Need to conduct solubility studies of TKX-50 in a variety of solvents using the Crystal 16 unit**
- **Perform process development/optimization studies using Easymax reactor system**

Crystal-16

Easymax Reactor

Conclusions

- Developed a reproducible process for the purification of DCG
- TKX-50 passes compatibility with standard binders and materials for pressing/handling
- Determined scale-up synthesis of TKX-50 from DCG
- Looking to establish one-pot procedure of TKX-50 in DMF
- Initial experiments at gram scale one pot synthesis look encouraging for scale up
- Investigated EtOH and DMF chlorination rates / heats of reaction as function of temperature (EasyMax / RC1)
- Completed In situ monitoring of diazidoglyoxime intermediate formation (EasyMax)
- Determined kinetics of reactions from IR data

Participants

- Reddy Damavarapu, PhD
- Alex Paraskos, PhD
- Victor Stepanov, PhD
- Paula Cook
- Edward Cooke
- Kelley Caflin, PhD
- Raja Duddu, PhD (Leidos)
- Peggy Sanchez
- Rodger Cornell
- Erik Wrobel
- Brian Travers
- Ralph Acevedo
- Brad Sleadd, PhD (Indian Head)
- Heather Hayden, PhD (Indian Head)
- Lori Nock (Indian Head)