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Sandia National Laboratories, Albuquerque, NM
National Renewable Energy Laboratory, Golden CO
Operated for the United States Department of Energy

Advanced Thermal Storage Fluids for Solar Parabolic Trough Systems

GCEP Solar Energy Workshop

October 18-19, 2004
Stanford University
Palo Alto, CA

Presented
by
Luc Moens

NREL
National Renewable Energy Laboratory

FLUIDS R&D

Alternative Solvents & Reaction Media

- *aqueous*
- *organic*
- *ionic liquids*
- *fluorous*
- *supercritical*
- *subcritical*
- *biobased*

- synthetic chemistry
- bioreactions
- fractionation & separation
- advanced materials
- nanocatalysts

Fuels

- *oxidative stability*
- *physico-chemical properties*
- *purity*

Functional Fluids

Thermal Fluids

heat transfer fluids
thermal storage fluids

Bio-Lubricants

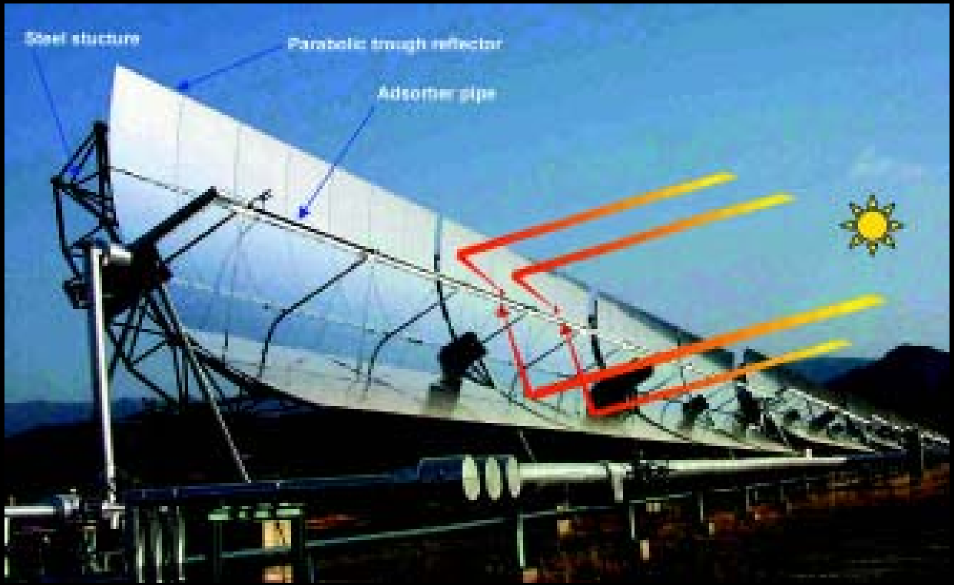
plant oils
carbohydrate derivatives

Luc Moens

Fluids R&D

National Bioenergy Center

Transfer of Solar Heat



- Current System Components:

  Heat Transfer Fluid

  Heat exchanger

  High-Pressure Superheated Steam

Solar Parabolic Trough Plants

Review : Price *et al. J. Solar En. Eng.* **2002**, *124*, 109-25

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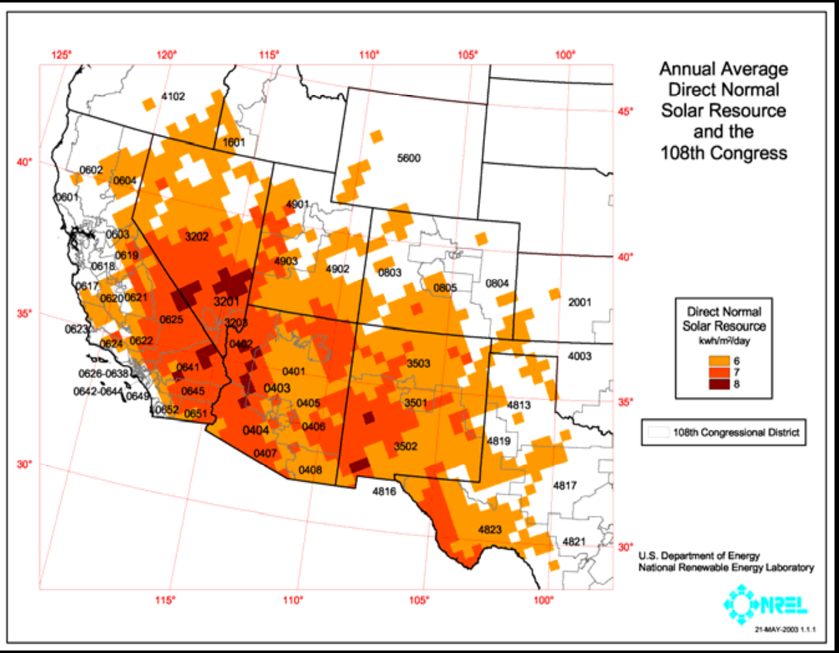
Southwest 1000 MW Strategy

Resource Availability:

State	Solar Capacity (MW)	Land Area (Sq Mi)
AZ	1,652,000	12,790
CA	742,305	5,750
NV	619,410	4,790
NM	1,119,000	9,157
Total	4,132,715	32,487



The table and map represent land that has no primary use today, exclude land with slope > 1%, and do not count sensitive lands.

Solar Energy Resource ≥ 7.0 kWhr/m²/day (includes only excellent and premium resource)

Current total generation in the four states is 83,500 MW.

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Current HTFs

Fluid	Application T (ºC)	Properties
Synthetic oils e.g. Therminol VP-1 (aromatic HC's)	13 - 395	Flammable
Mineral oils e.g. Caloria (paraffinic HC's)	-10 - 300	Flammable
Silicone oils	-40 - 400	Expensive Flammable
Nitrate salts e.g. HITEC-XL	220 - 500	Freezing point ≥ 120 ºC High T stability

HITEC-XL™ : $Ca(NO_3)_2 + NaNO_3 + KNO_3$

Goal of R&D Project:

Heat Transfer Fluid = Heat Storage Fluid

* *Higher operating temperatures: low vapor pressure fluid needed*

* *Improved cost / performance of solar plant*

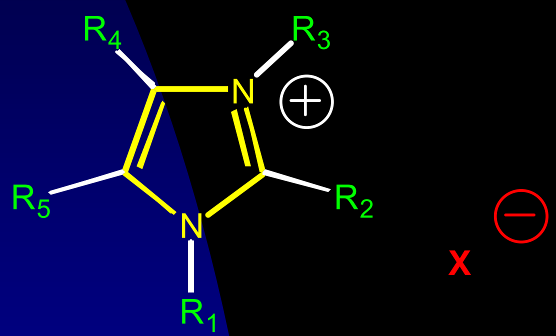
* *Optimized dispatch of power to meet utility peak loads (up to 12 h of storage)*

Desired Properties for ‘ideal’ heat storage fluid

- High thermal stability (up to 425ºC)
- Low freezing point (≤ 0 ºC)
- Non-flammable
- Low vapor pressure (@ high T)
- High boiling point
- Relatively inexpensive

ROOM TEMPERATURE IONIC LIQUIDS

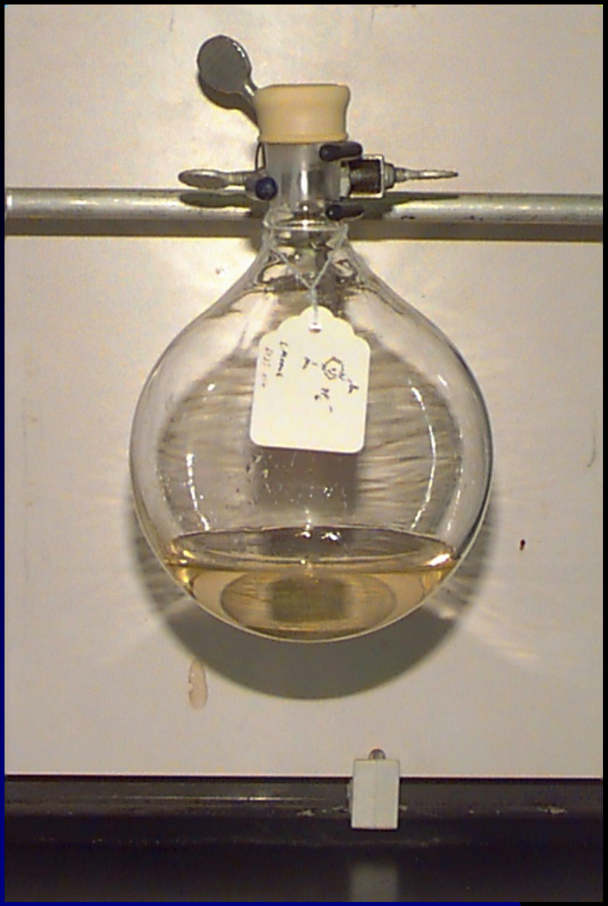
Imidazolium Salts



R	X⁻
Methyl	Cl^{-}
Ethyl	$^{-}OSO_2CH_3$
Butyl	BF_4^{-}
Hexyl	PF_6^{-}
Octyl	
Phenyl	
Silyl	

Ionic Liquids

Imidazolium salts



Ionic Liquids

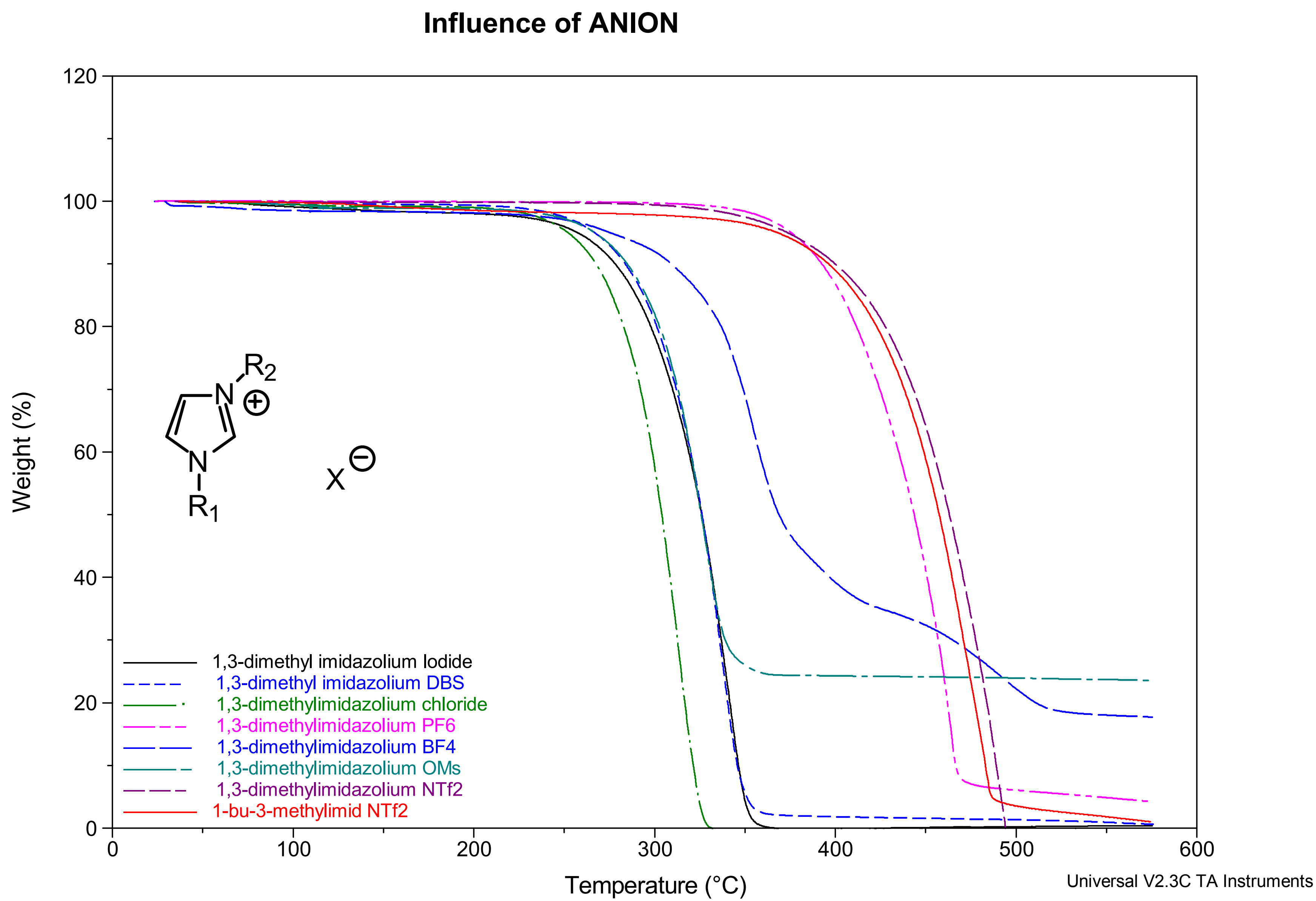
- Organic Salt structure
- Very High Thermal Stability (≥400 ºC known)
- Virtually no vapor pressure
- Low Melting point (some ≤ 0 ºC)
- Not flammable
- Many RTILs identified among imidazolium salts

Ionic Liquids

- New to synthetic / process chemistry
- Chemical industry interest is growing
- Data on physical / engineering / toxicology growing rapidly
- Cost for production unknown
- Commercially available in research quantities, but laboratory synthesis straightforward (kilogram-scale)

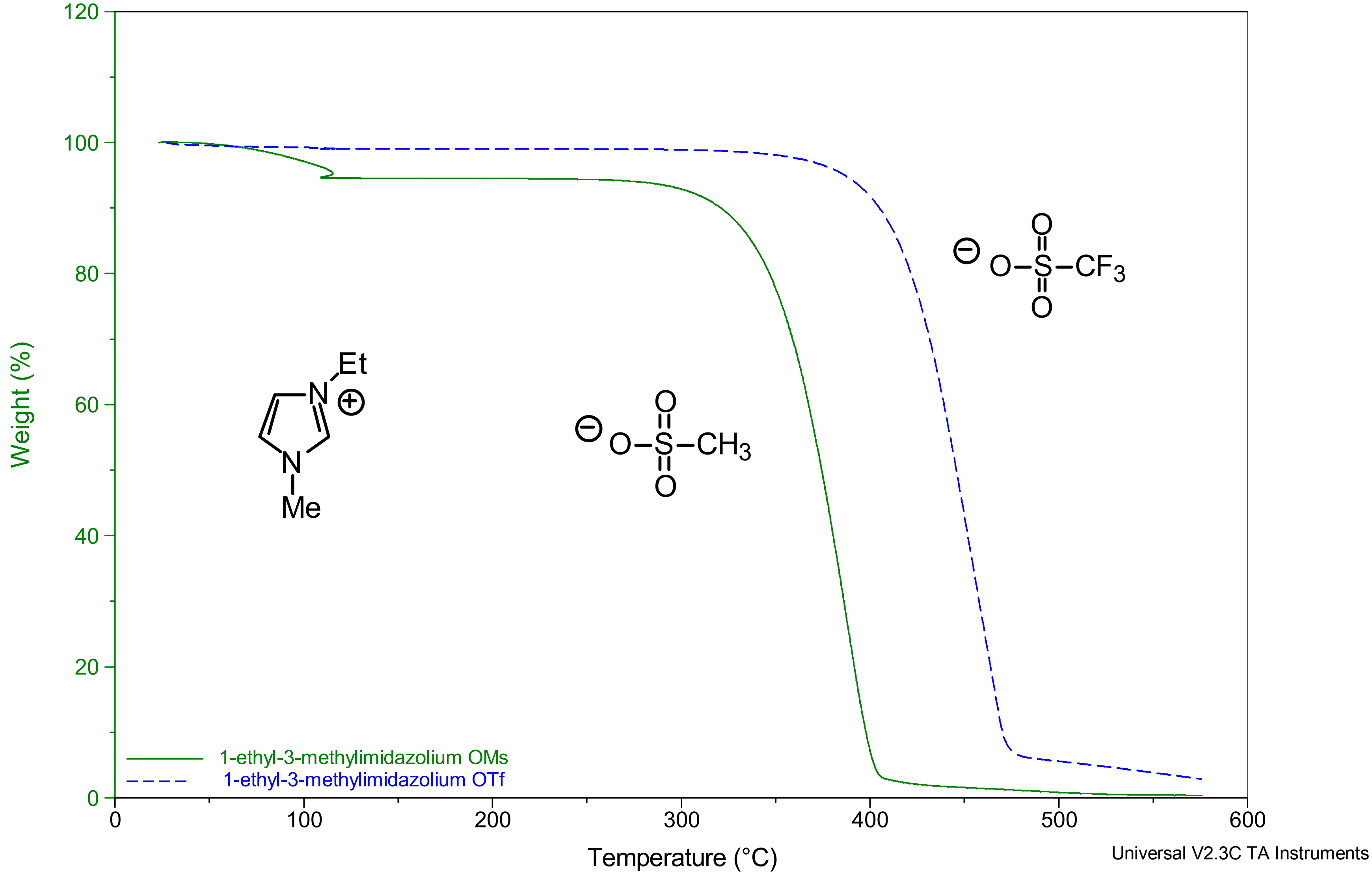
Dynamic viscosity

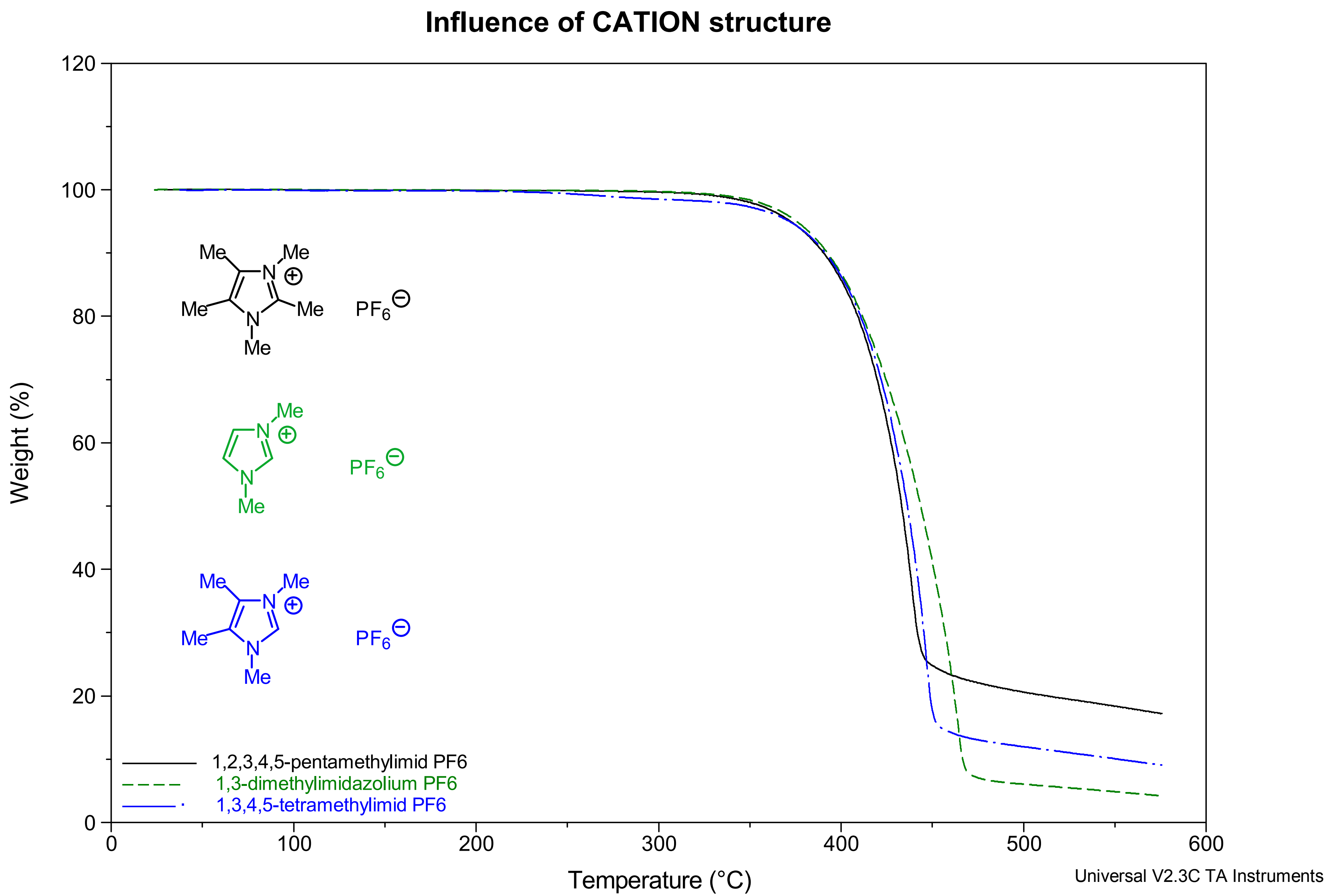
Fluid	T (ºC)	η (cP)
VP-1	15 300	4.98 0.22
HITEC-XL	120 300	138.99 6.37
$EmimBF_4$ (ionic liquid)	26 300	43 1.5 (calc)



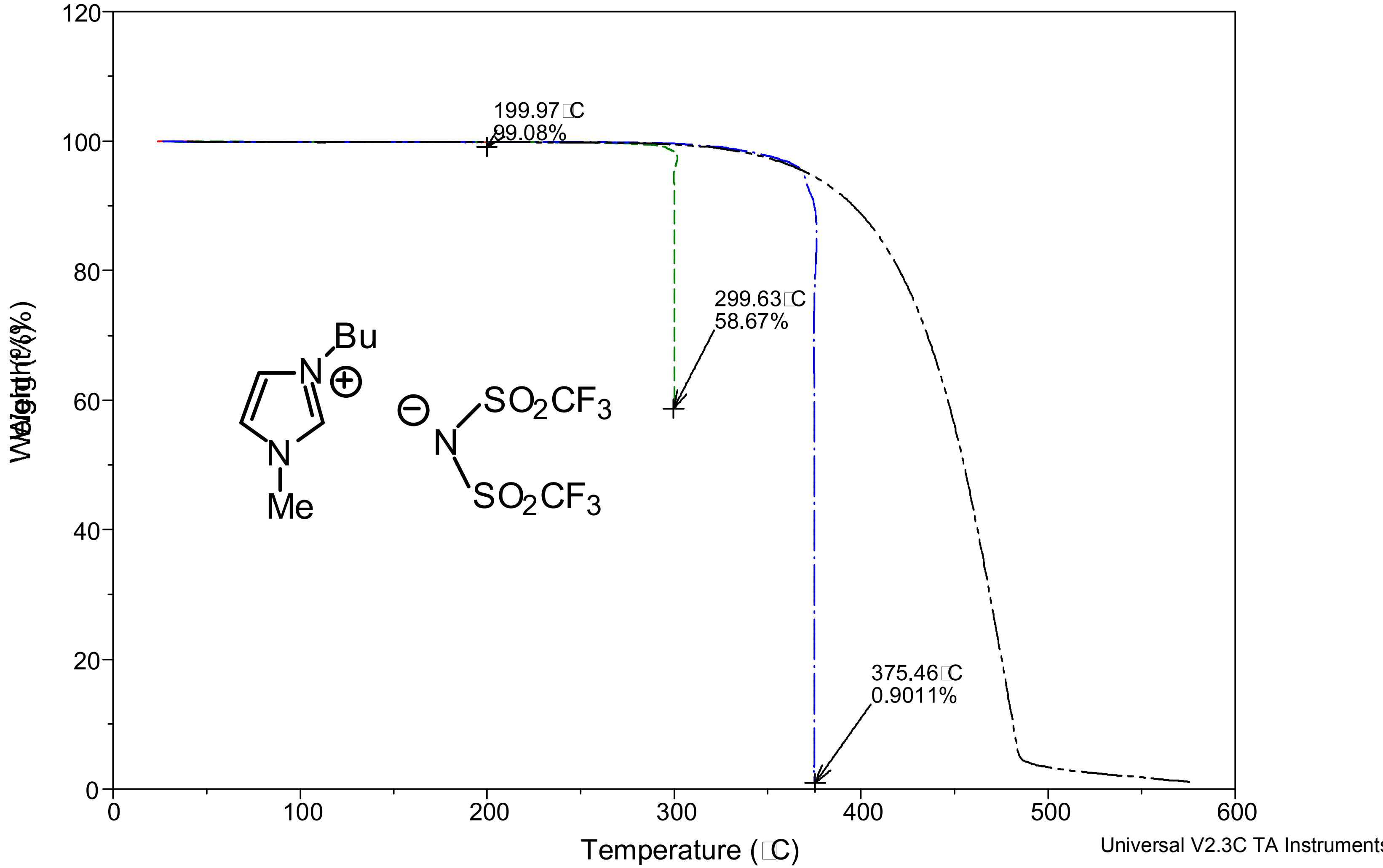
Influence of ANION
Weight (%)
Temperature (°C)
120
100
80
60
40
20
0
0
100
200
300
400
500
600
R2
N
N
R1
X
1,3-dimethyl imidazolium Iodide
1,3-dimethyl imidazolium DBS
1,3-dimethylimidazolium chloride
1,3-dimethylimidazolium PF6
1,3-dimethylimidazolium BF4
1,3-dimethylimidazolium OMs
1,3-dimethylimidazolium NTf2
1-bu-3-methylimid NTf2
Universal V2.3C TA Instruments

Influence of ANION

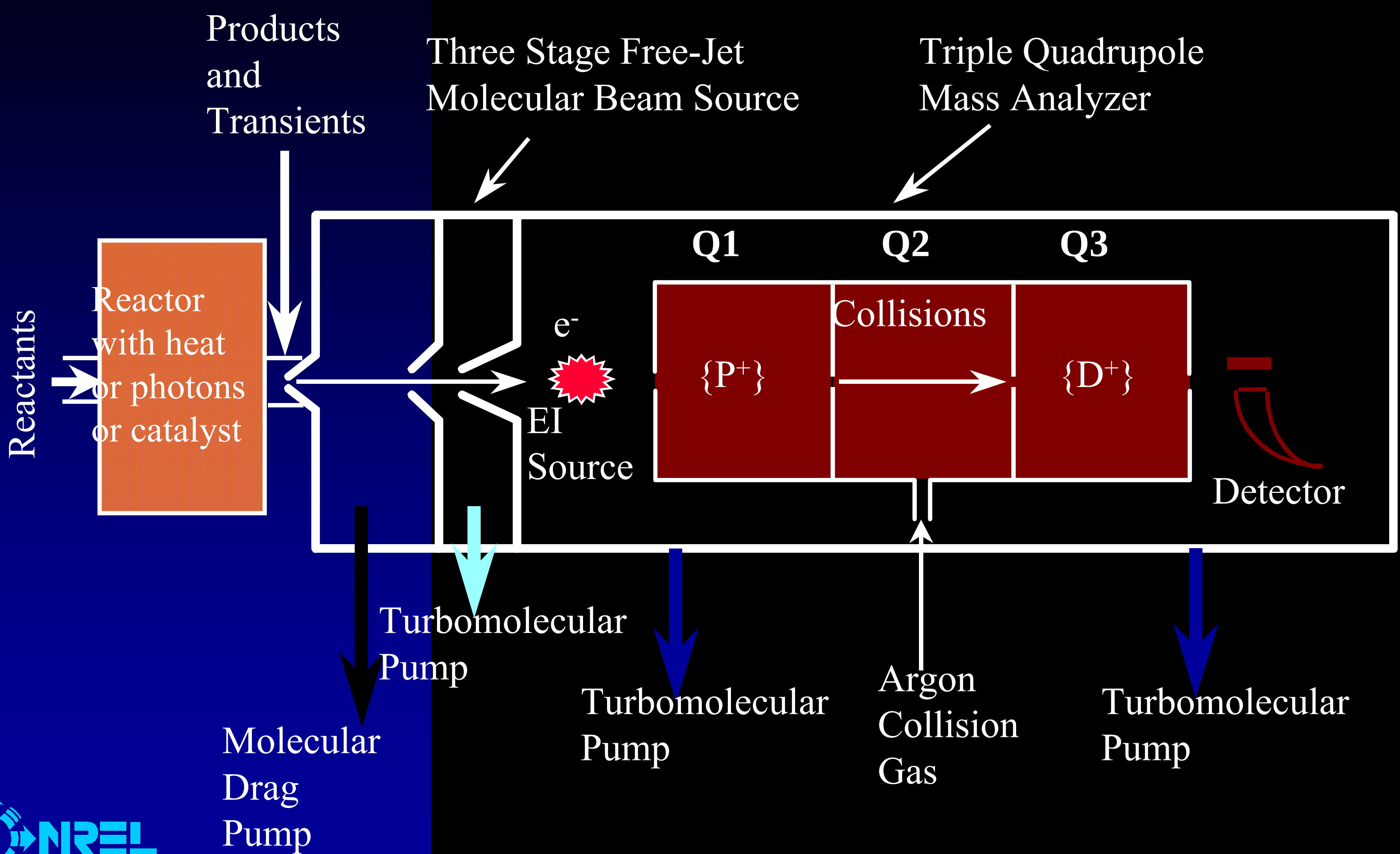



Influence of CATION structure
Weight (%)
Temperature (°C)
Universal V2.3C TA Instruments
1,2,3,4,5-pentamethylimid PF6
1,3-dimethylimidazolium PF6
1,3,4,5-tetramethylimid PF6
Me
N
PF6
0
20
40
60
80
100
120
0
100
200
300
400
500
600

Ramp 20C/min and Isothermal decomposition over 120 min



Schematic of NREL's MBMS Sampling System



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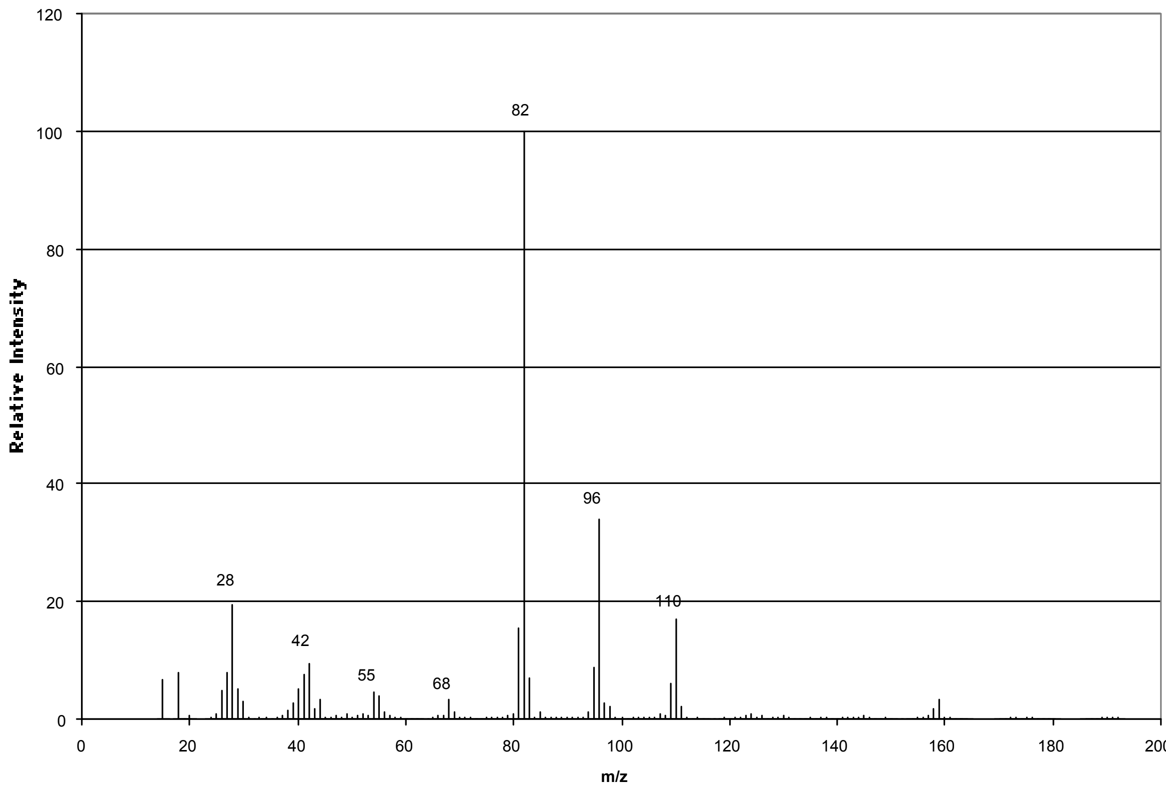
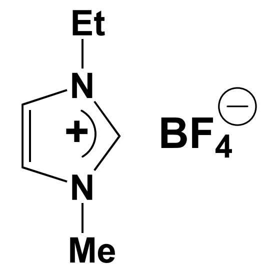
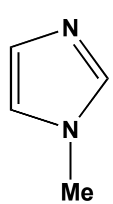
MBMS study of [EtMeIm][BF_4]

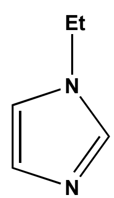




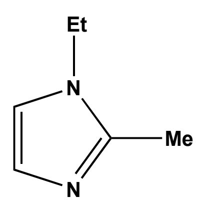
MW = 198



m/z = 82



m/z = 96



m/z = 110

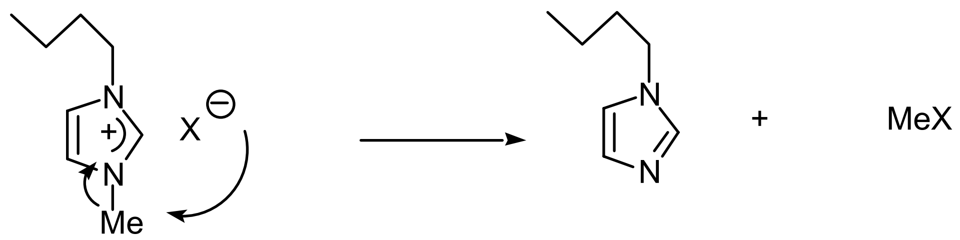
<u>Proposed thermal events</u>:

1) HF liberation at high T

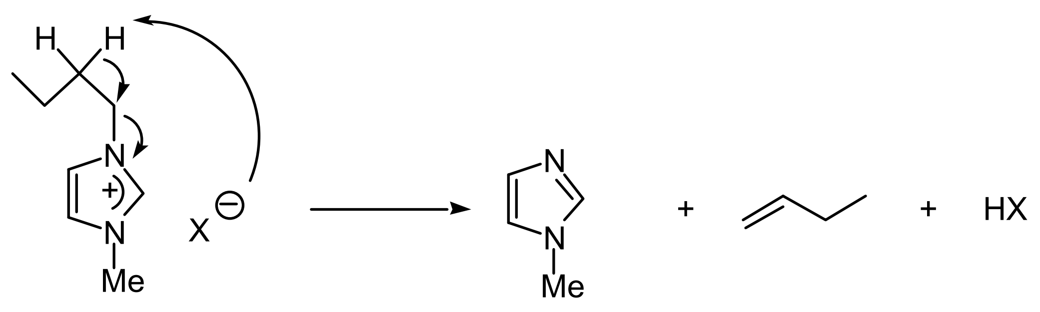
2) de-alkylation of quat. amine salt

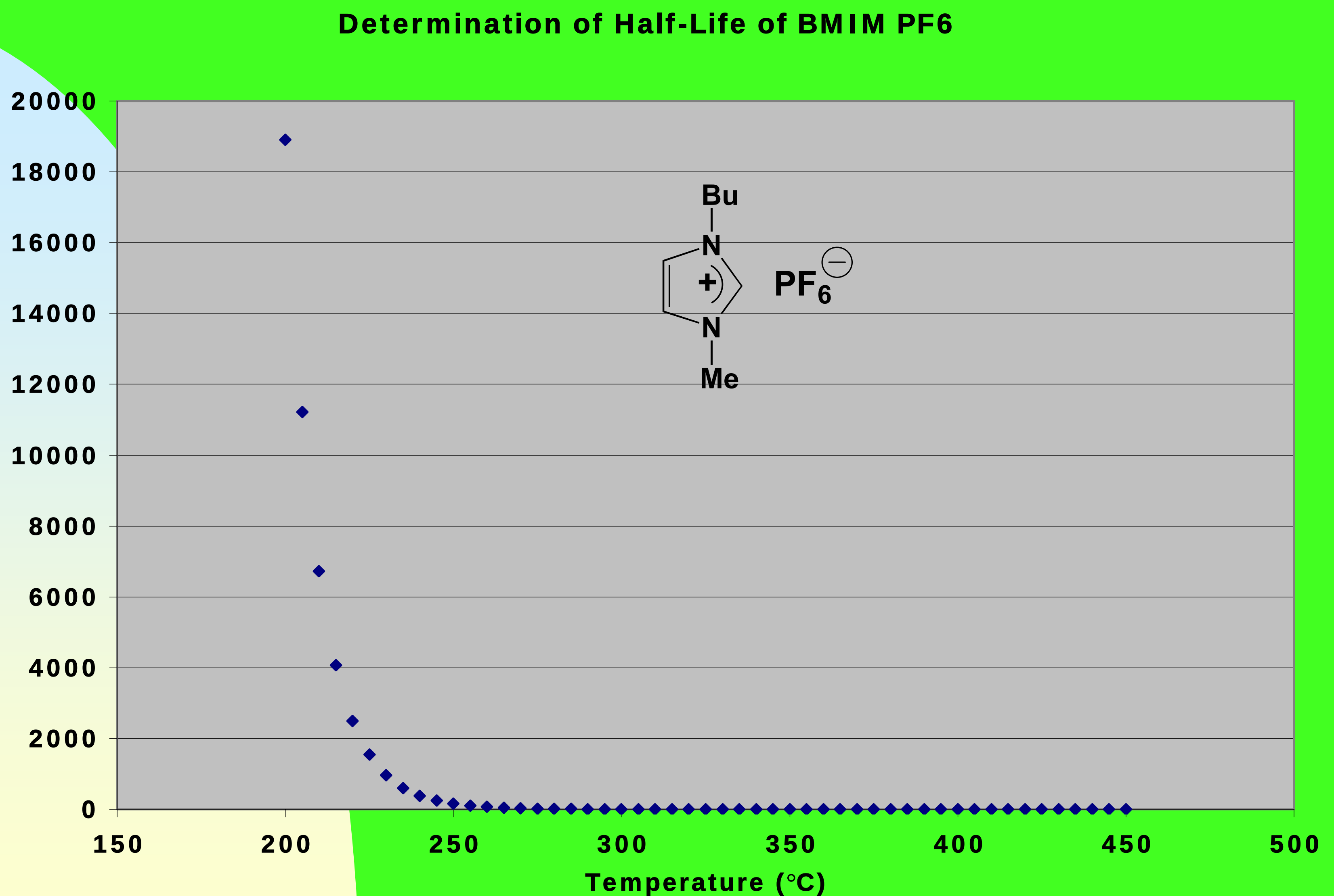
Thermal Decomposition Pathways

Demethylation



Hofmann Type Elimination




Determination of Half-Life of BMIM PF6
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
150
200
250
300
350
400
450
500
Temperature (°C)
Bu
N
N
Me
PF6

Conclusions

- Ionic Liquids are not suitable as heat storage fluids (thermally unstable at T's required for solar trough systems)
- Synthesis straightforward (one-pot)
- Other types of fluids must be explored for use in solar troughs

New Candidate Fluids for exploratory work

- known to (petro)chemical industry
- large-scale production possible or existent
- low cost

New Candidate Fluids

- modified commercial fluids (Therminol VP-1™)
- plasticizers
- modified high-performance lubricants (esters)

New Candidate Fluids

- modified commercial fluids (Therminol VP-1™)

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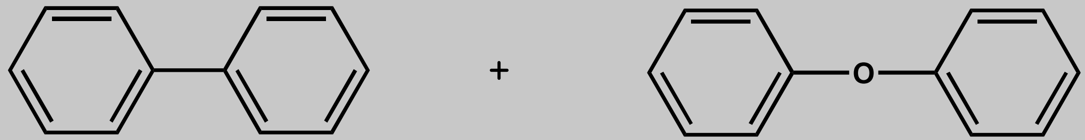
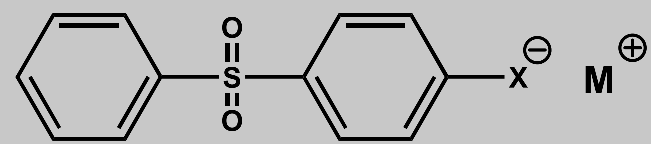
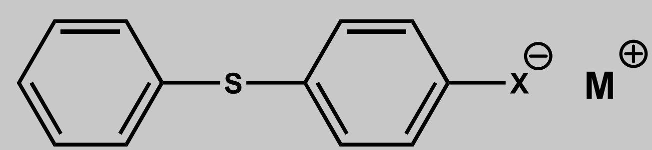
VP-1



Explore new fluids based on modified aromatics :



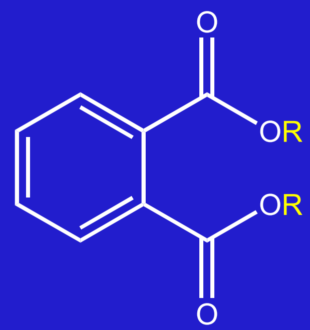


New Candidate Fluids

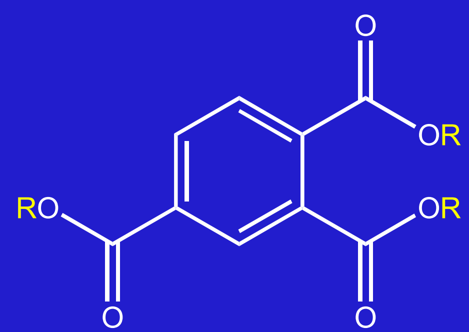
- modified commercial fluids (Therminol VP-1™)
- plasticizers

PLASTICIZERS

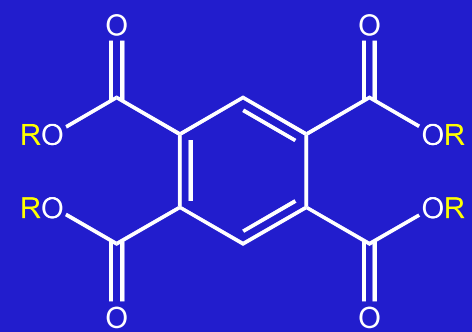
R = alkyl groups (linear or branched)



Phthalate esters



Trimellitate esters



Pyromellitate esters

Adipate esters

Plasticizers - US production

	2002 (10^3 metric tons)	Average annual growth (%)	2003 price ($ / lb)
Diisodecyl phthalate	125	2.6	0.66
Dioctyl phthalate	120	1.6	0.66
Diisononyl phthalate	110	2.9	0.66
Linear C7-C11 phthalates	110	2.1	0.74 Š0.90
Trioctyltrimellitate	28	4.4	1.05
Dioctyl adipate	25	3.0	0.89

	Therminol VP-1	Phthalates	Trimellitates/Pyromellitates	Adipates
Freezing point (°C)	13	-58 to 0	-56 to Š30	-70 to +8
Bp (°C)	257	283 to 523	414 to 430	222 to 509
Flash point (°C)	124	146 to 254	246 to 266	145 to 243
Viscosity (cP)	4.98 (@ 15°C)	11 to 320 (@ 20°C)	138 to 340 (@ 22°C)	4.8 to 26 (20°C)
Specific heat (kJ/kgK)	1.53	1.57 to 1.8	(?)	1.76 to 2.5

VAPOR PRESSURE OF PLASTICISERS AT VARIOUS TEMPERATURES

	Vapor Pressure (mbar) at different temperatures				
	80°C	100°C	140°C	180°C	250°C
DBP	0.02	0.082	0.87	6.08	86.67
DOP		0.001	0.039	0.571	20.75
DIDA		0.001	0.023	0.282	9.697
L79P			0.025	0.371	13.74
DIDP			0.009	0.143	5.144
L911P			0.005	0.087	4.099
TOTM				0.015	1.005

DBP = di-*n*-butyl phthalate
DOP = di-2-ethylhexyl phthalate
DIDA = di-isodecyl adipate
L79P = di-(*linear C7/C8C9*) phthalate
DIDP = di-isodecyl phthalate
L911P = di-(*linear C9/C10C11*) phthalate
TOTM = tri-2-ethylhexyl trimellitate

(Source: BP Chemicals)

VAPOR PRESSURE OF VARIOUS FLUIDS AT DIFFERENT TEMPERATURES

	Vapor pressures (atm) at different temperatures	
	300°C	400°C
Therminol VP-1™	2.4	10.8
Diphenyl ether	2.3 *	10.5 *
Di-*n*-butyl phthalate	0.4 *	2.9 *

*calculated values using equations

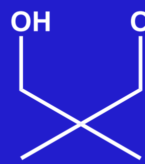
Diphenyl ether P_{vapor} = 10^{4.13678-[1800.415/(T-95.324)]}

Di-*n*-butyl phthalate P_{vapor} = 10^{4.30568-[2083.175/(T-131.7)]}

New Candidate Fluids

- modified commercial fluids (Therminol VP-1™)
- plasticizers
- modified high-performance lubricants (esters)

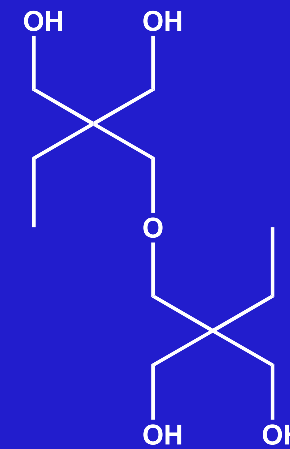
Known building blocks for esters used in high-performance lubricants



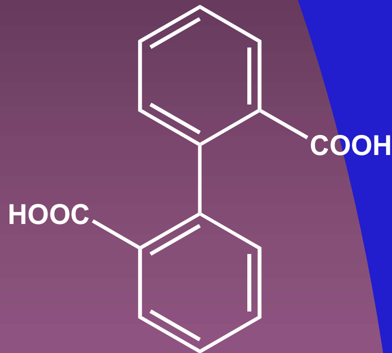
neopentyl glycol

trimethylolpropane

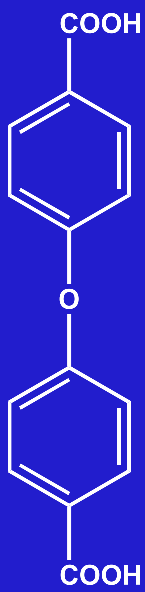
pentaerythritol



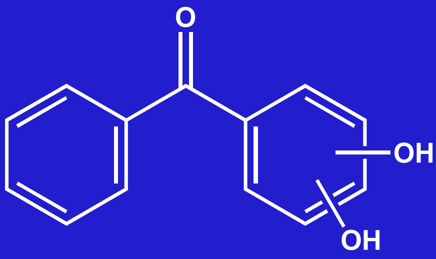
di(trimethylolpropane)



diphenic acid



4,4'-oxybis(benzoic acid)



dihydroxybenzophenone

Challenges for new Thermal Storage Fluids

1. Long-term stability @ 300 - 400ºC
   (~ 20-30 yrs. through kinetic modeling)

2. Thermal decomposition:

   - decomposition products

   - influence of impurities at high T

   - oxidation @ high T (antioxidants needed?)

   - kinetic data

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Challenges for new Thermal Storage Fluids

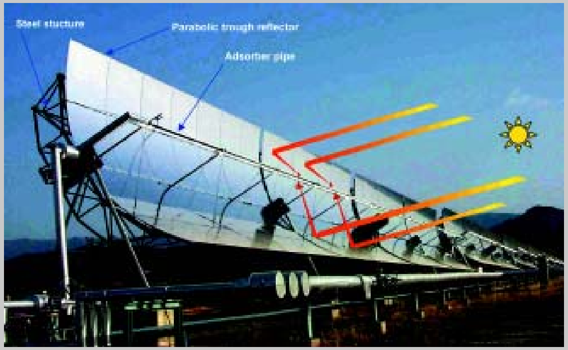
3. Hydrolysis by traces of water @ high T

   (esp. for esters)

4. Vapor pressure:

   - high boiling point esters

   - negligent in case of salts



Challenges for new Thermal Storage Fluids

3. Low melting point (pref. ≤ 0ºC) to avoid need for heat tracing for receiver tubing during cold periods

4. Low viscosity (avoid use of ‘visc. modifiers’)

5. Explore fluid formulations for optimization of physico-chemical properties

6. NEW IDEAS ??????

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