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Ionic Liquids as Hypergolic Fluids

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Contents

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Hypergolic Ionic Liquids

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- Hypergolic – spontaneous reaction of one chemical (fuel) when contacted with another (oxidizer)
- Hypergolic bipropellants - fuel and oxidizer combinations that react chemically to release enough heat to spontaneously ignite, eliminating the need for an additional ignition source.
- Why hypergols? – efficient propellants to replace volatile and carcinogenic hydrazines.
- Desirable properties –
  - low vapor pressure - low toxicity
  - high thermal and hydrolytic stability
  - short ignition delay time (< 5 msec)
  - low impact sensitivity
  - low viscosity - high density
  - high specific impulse (> 300 s)
  - environmentally friendly

Commonly Used Oxidizers

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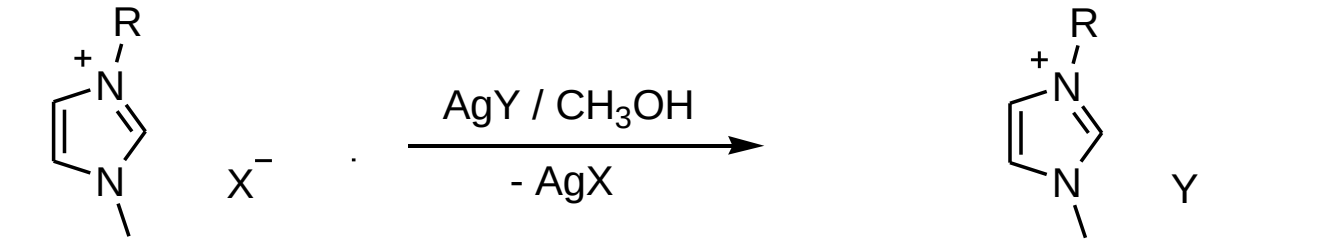
- IRFNA – inhibited, red-fuming nitric acid (83% HNO_3 + 14% N_2O_4 + ~ 2% H_2O + 0.6% HF)
- WFNA – white fuming nitric acid (~100% HNO_3)
- N_2O_4

Azolium Nitrocyanamide and Dicyanamide Salts



X = Cl, Br, or I

Y = $N(CN)_2$, $N(NO_2)(CN)$

Y = $N(CN)_2$; R = propargyl (**1**), allyl (**2**)
Y = $N(NO_2)(CN)$; R = ethyl (**3**), *n*-butyl (**4**), allyl (**5**), 2-methoxyethyl (**6**)

Properties of azolium nitrocyanamide and dinitrocyanamide salts

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Compd	$T_g(T_m)$[a] [°C]	T_d[b] [°C]	d[c] [g/cm³]	η[d] [cP]	ID[e] [ms]	ΔH_f[f] [kJ/g]	I_{sp}[g] [s]
1[h]	-61(17)	144		110	43		
2[h]	-85	207		42	15		
3[i]	(-73)	253	1.18	23	78	0.80	192
4[i]	(-90)	256	1.13	57	81	0.57	186
5[i]	(-91)	220	1.11	44	46	1.31	197
6[i]	(-82)	266	1.21	54	65	0.19	187
7[h,j]	-66	143		92	31		
8[h,i,k]	-6(-90)	240	1.06	33 (20°C)	47	1.30	165
9[h,l]					44		
10[h,m]					37		

[a] glass transition (melting point); [b] decomposition onset; [c] density; [d] viscosity, 25 °C; [e] ignition delay (WFNA); [f] enthalpy of formation; [g] specific impulse (Cheetah 5); [h] Ref. (*1, 2)*; [i] Ref. (*5)*; [j] 1-methyl-4-amino-1,2,4-triazolium; [k] 1-butyl-3-methyl-imidazolium; [l] 1- butyl-1-methyl-pyrrolidinium; [m] n-butyl-3-methylpyridinium.

Energetic 2,2-dimethyltriazanium Salts

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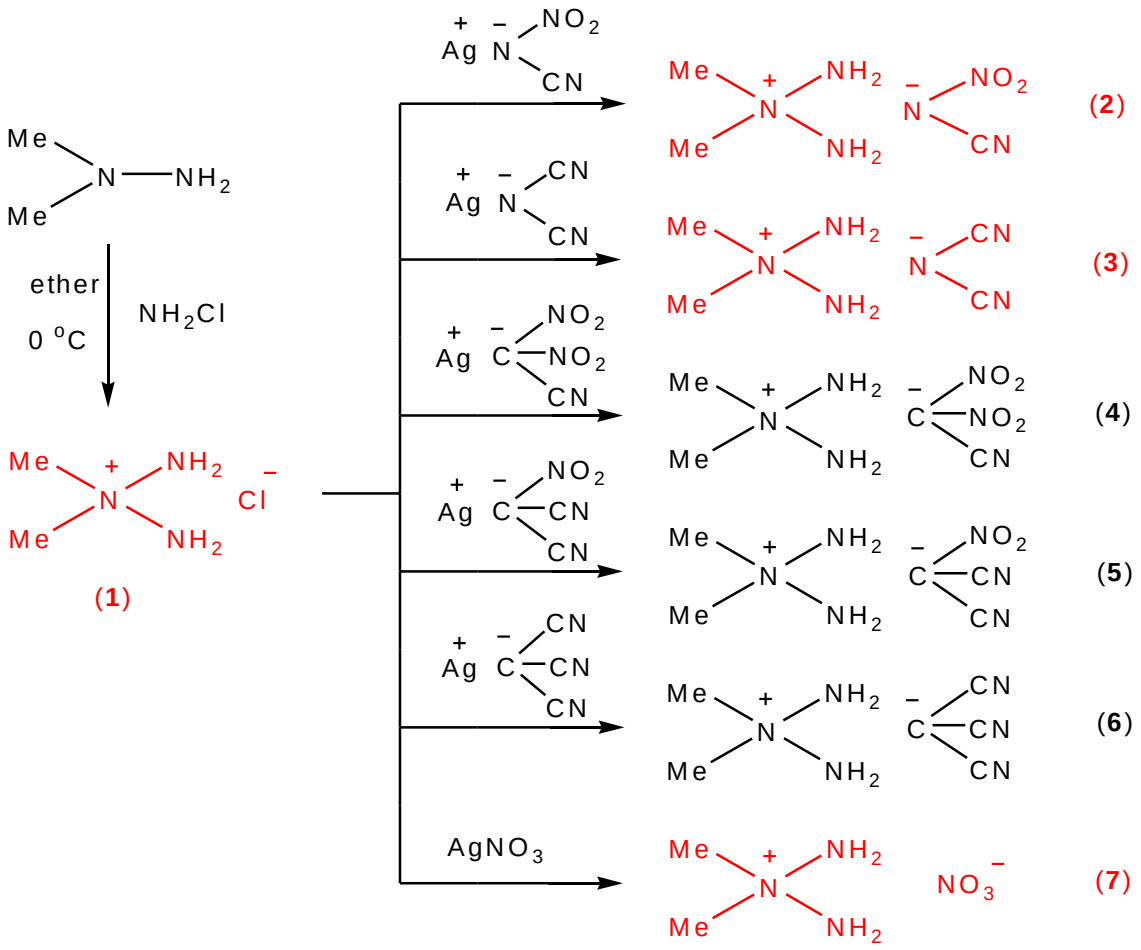

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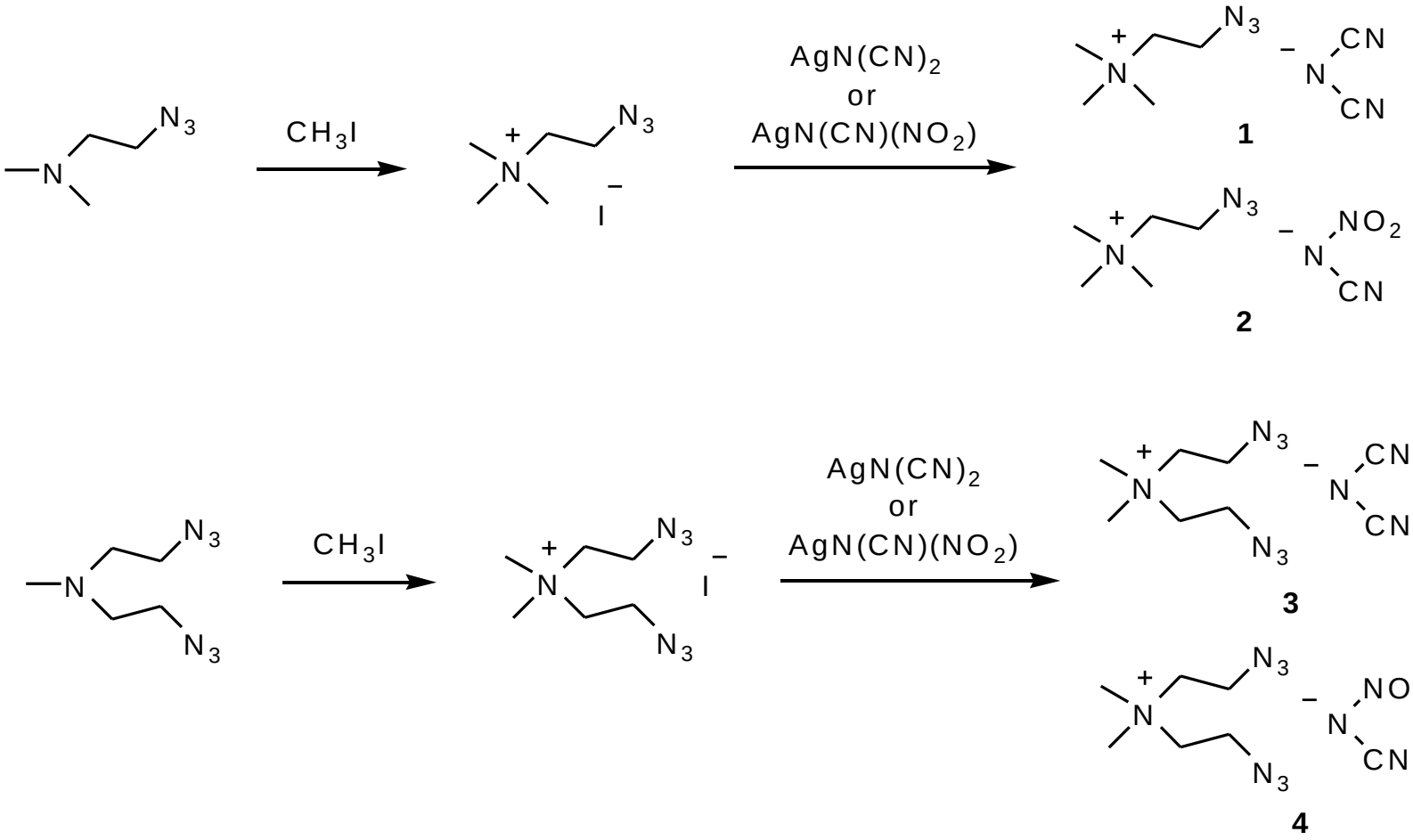
Properties of energetic 2,2-dimethyltriazanium salts

Salts	Density g cm^{-3}	T_m °C	T_d °C	Ignition Delay [ms]		ΔH_f kJ mol^{-1}	P GPa	D m s^{-1}	I_{sp} S	IS J
				N_2O_4	WFNA					
1	1.47		-	26	not hy.	-50	-	-	-	>60
2	1.26	0.2	146	8	16	228	15.9	7169	226	>60
3	1.15	10.7	134	SH	22	364	12.1	6516	201	>60
7	1.47	99.0	146	10	4	-96	22.2	8034	228	>60
IL A*	1.25	61	-	-	15	540	8.9	5721	187	-
IL B*	1.41	66	-	-	31	483	16.2	7158	213	-

*** 1-(2-propargyl)-3-methylimidazolium dicyanamide; 1-methyl-4-amino-1,2,4-triazolium dicyanamide**
Schneider, S. et al. *Energy & Fuels* 2008, *22*, 2871-2872.

Mono- and Diazidoethyl Tri and Dimethyl Ammonium Salts



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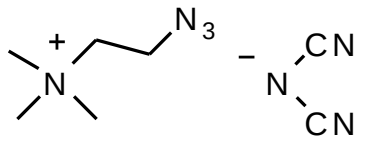
Properties of Mono- and Diazidoethyl Tri and Dimethyl Ammonium Salts



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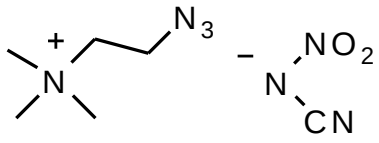

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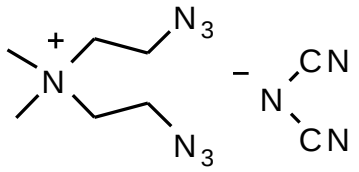

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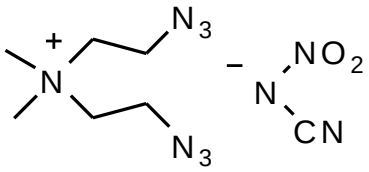

4

Salts	Density cm^{-3}	T_m °C	T_d °C	Ignition Delay [ms]		ΔH_f kJ mol^{-1}	I_{sp} s	IS J
				N_2O_4	WFNA			
1	1.15	9	235	not hy.	20	518	201.5	>60
2	1.24	28	245	not hy.	8	380	217.5	>60
3	1.21	-	222	not hy.	16	894	220.7	>60
4	1.32	-	222	not hy.	226	752	231.3	>60

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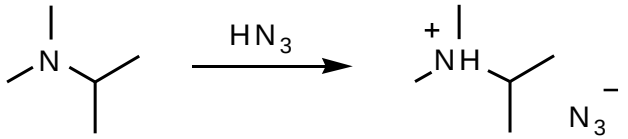
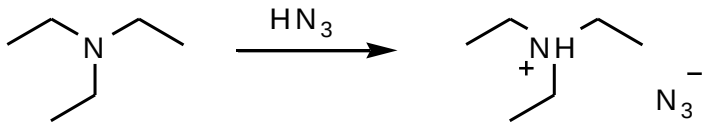
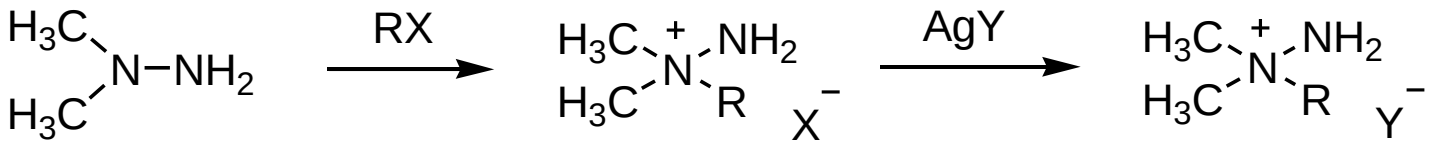
Hypergolic ionic liquids with azide anion





Hypergolic in N_2O_4

N,N-dimethylhydrazinium salts



R	X	
C_4H_9	I	**15**, **19**
CH_2CHCH_2	Cl	**16**, **20**
CH_2CCH	Br	**17**, **21**
CH_2CH_2OH	Cl	**18**, **22**

Y = $N(NO_2)(CN)$ (**15**-**18**)
Y = $N(CN)_2$ (**19**-**22**)

Properties of N,N-dimethylhydrazinium salts

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Compd	T_d[a] (ºC)	d[b] (g/cm^3)	η[c] (cP)	ID[d] (ms)	ΔH_f[e] (kJ/g)	I_{sp}[f] (s)
15	286	1.11	120	228	0.46	201
16	208	1.16	85	130	1.68	221
17	189	1.21	270	134	2.18	227
18	269	1.26	186	247	-0.15	206
19	263	1.01	114	46	1.27	180
20	199	1.05	79	24	2.71	204
21	174	1.13	229	30	3.26	210
22	236	1.15	162	40	0.64	186

[a] decomposition onset; [b] density; [c] viscosity, 25 ºC; [d] ignition delay (WFNA); [e]enthalpy of formation; [f] specific impulse

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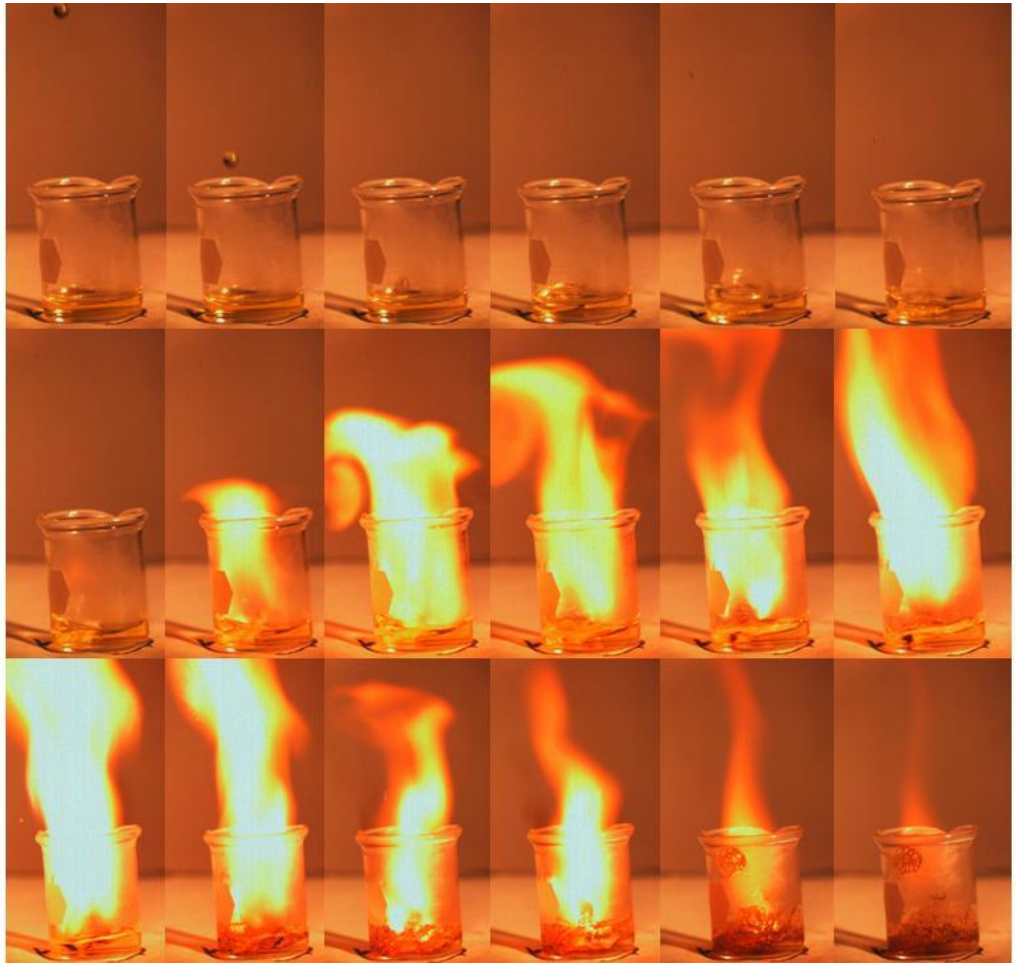
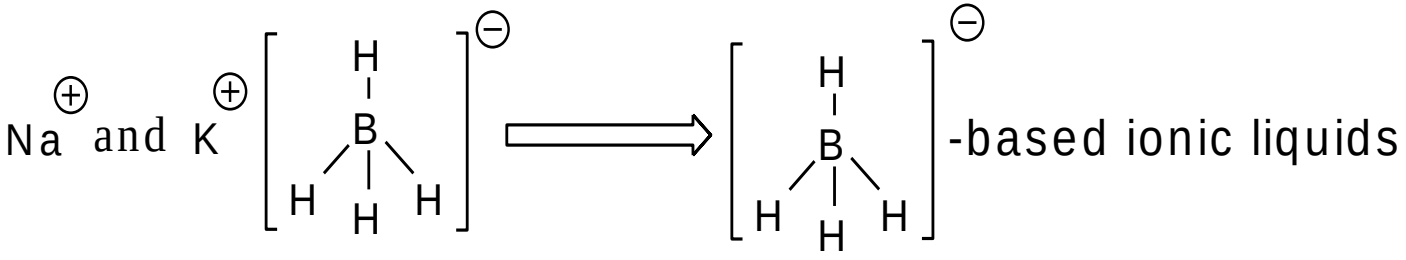


Generalizations

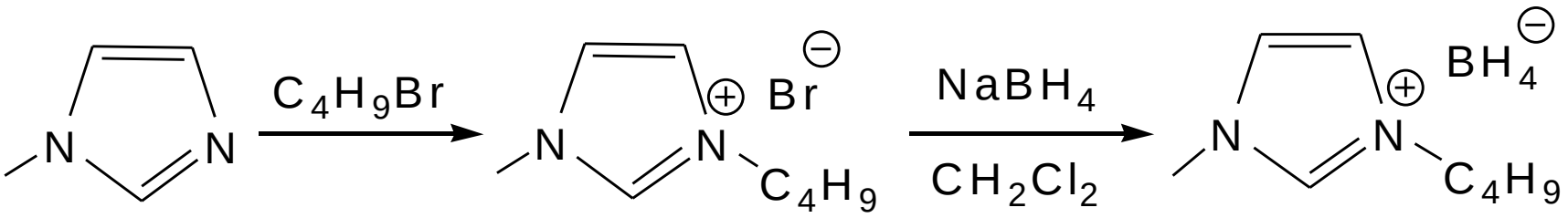
Property	Impact
1) asymmetrically substituted cation	lower melting point
2) < seven carbon atoms	encourages hypergolicity
3) unsaturated side chains, e. g., acetylenic	enhance tendency toward hypergolicity
4) secondary or tertiary amines	alternative to monomethyl hydrazine and unsymmetric dimethyl hydrazine
5) higher positive heat of formation	higher specific impulse
6) oxygen balance in fuel	unimportant - oxidizer provides
7) high specific impulse and density	improve density-impulse – measure of fuel performance
8) absence of N-N single bonds	reduces toxicity but decreases enthalpy
9) low viscosity	enhances flow characteristics and mixing with oxidizer
10) additives	increases density/decreases viscosity
11) anions	may govern viscosity

Hypergolic Borohydride Salts



hypergolic with white-fuming nitric acid (WFNA)

Borohydride-Based Ionic Liquids

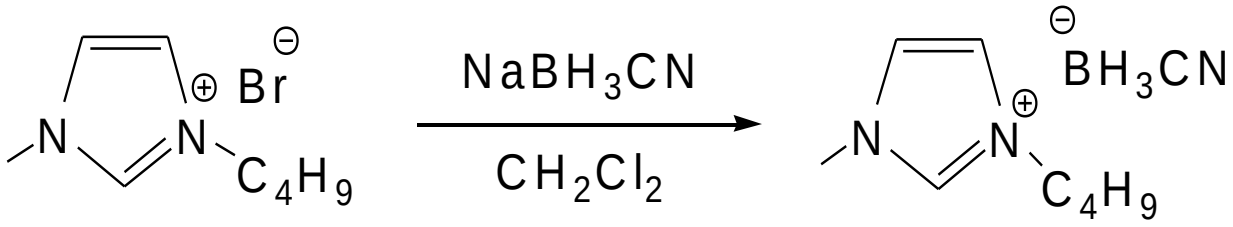


[Bmim]Br [Bmim]BH_4

Hypergolic (white fuming nitric acid)

Very water-sensitive

Cyanoborate-Based Salts



[Bmim]Br [Bmim]BH_3CN

Hypergolic (white fuming nitric acid)

Less water-sensitive

$$BH_3CN + 2\,H_2O \longrightarrow BO_2 + HCN + 3\,H_2$$

Dicyanoborate-Based Salts

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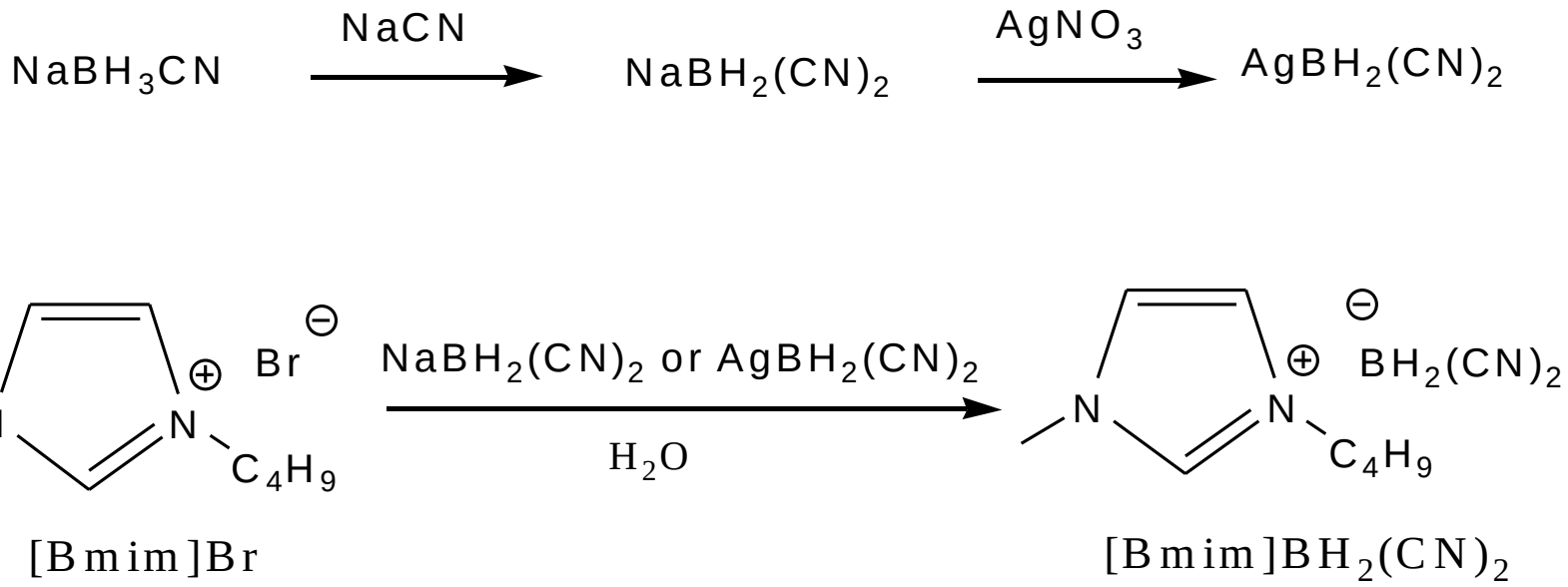

Hypergolic (white fuming nitric acid)

Water stable

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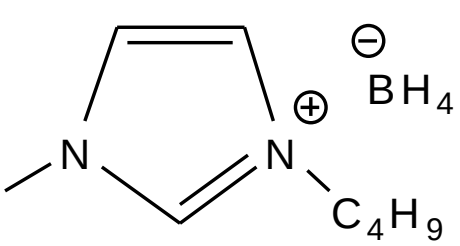
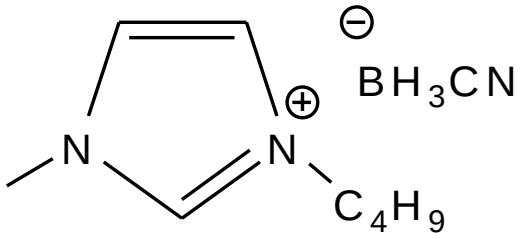
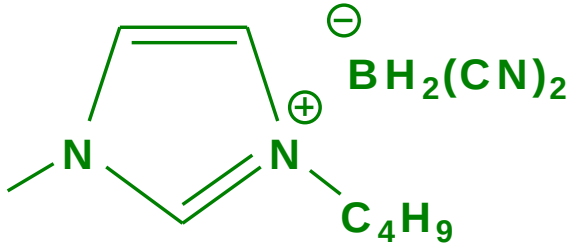


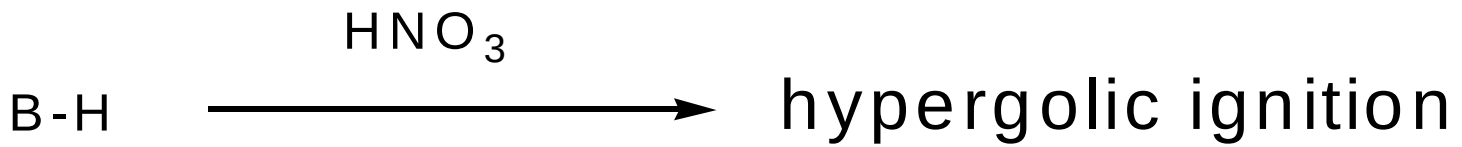




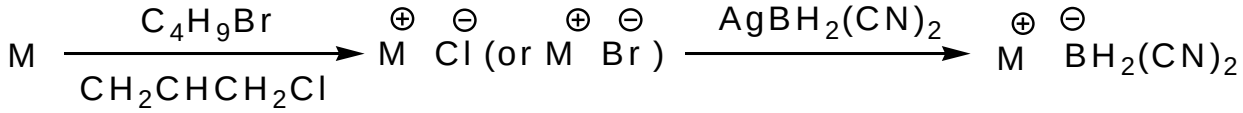
H_2O-sensitive

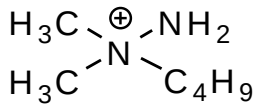
less H_2O-sensitive

H_2O-stable



Synthesis



M = 

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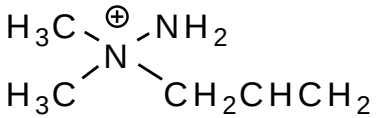

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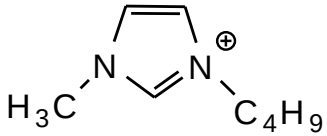

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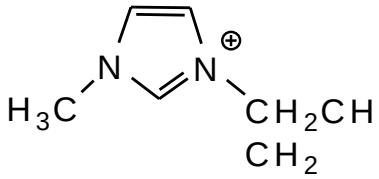

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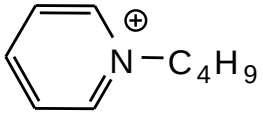

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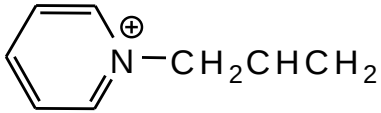

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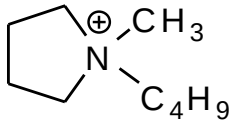

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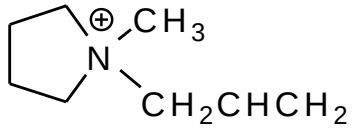

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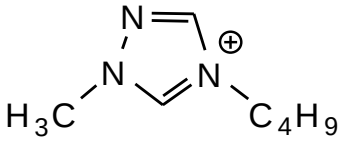

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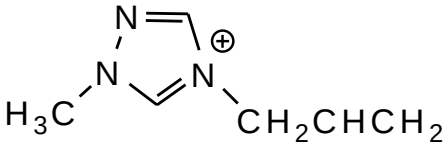

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Properties

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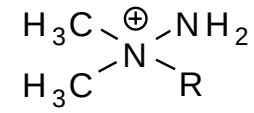
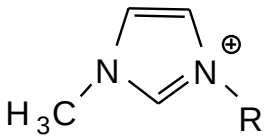
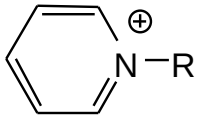
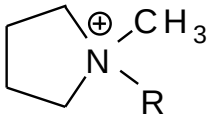
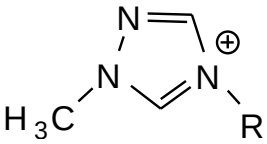
	NO	T_m (°C)	T_d (°C)	d (gcm^{-3}, 25 °C)	η (cP, 25 °C)	*ID (ms)*
	1	< -80	222	0.908	39.44	6
	2	< -80	189	0.929	34.98	4
	3	< -80	307	0.956	17.28	28
	4	< -80	266	0.986	12.37	8
	5	< -80	252	0.963	19.79	18
	6	< -80	203	0.995	13.53	6
	7	< -80	303	0.923	22.33	26
	8	< -80	259	0.943	16.61	8
	9	< -80	220	0.990	29.94	32
	10	< -80	217	1.028	20.96	6

R group: butyl (black), allyl (red).

Properties of dicyanoborate-based salts compared with corresponding nitrocyanamide and dicyanamide analogues

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$^{-}BH_2(CN)_2$

Compd.	T_m/T_g [a] °C	T_d [b] °C	d [c] g cm^{-3}	η [d] cP	ID [e] ms
1 [f]	<-80	222	0.91	39.4	6
1 (NCA) [g]	9	286	1.11	119.5	228
1 (DCA) [h]	20	263	1.01	113.9	46
2 [f]	<-80	189	0.93	35.0	4
2 (NCA) [g]		208	1.16	84.9	130
2 (DCA) [h]		199	1.05	78.6	30
3 [f]	<-80	307	0.96	17.3	28
3 (NCA) [g]	-90	256	1.13	57	81
3 (DCA) [h]					47
4 [f]	<-80	266	0.99	12.4	8
4 (NCA) [g]	-91	220	1.11	44	46
4 (DCA) [h]	-85	207		42	43

[a] Phase-transition temperature; [b] Decomposition temperature (onset);
[c] Density (25 °C); [d] Viscosity (25 °C); [e] Ignition delay time (WFNA).
[f] $^{-}BH_2(CN)_2$; [g] [NCA] nitrocyanamide as anion with common cation;
[h] [DCA] dicyanamide as anion with common cation.

SUMMARY

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- Several hypergolic salts with a variety of cations and a few different anions have been synthesized.
- Anions seem to be controlling although cations appear to have marginal influence on hypergolic properties.
- In general, with a common cation, dicyanamide anions tend to give salts with lower ignition delay times; however nitrocyanamide sometimes wins.
- Borohydride, cyanoborate, and dicyanoborate-based ionic liquids are hypergolic with WFNA.
- Dicyanoborate-based ionic liquids with good properties (wide liquid range, low viscosity, high stability, and short ignition delay time), exhibit serious potential as bipropellants.

ACKNOWLEDGMENTS

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National Science Foundation

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