Computational Investigations into Hypergolic Ionic Liquid Reactions
Using VENUS Dynamics Simulation, Kinetics Modeling and Spectral Analysis

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Introduction

Hypergolic ionic liquids (ILs) ignite spontaneously upon contact with an oxidizer and present low vapor toxicities and environmental hazards. They have become of interest within the aerospace community as green propellant alternatives to hydrazine for rocket propulsion applications.

The designability of hypergolic ILs includes the choice of cation, anion and the introduction of functional groups, each of which may be modified independently.

We have investigated thermal decomposition and oxidation of various ILs which consist of 1-methyl-4-amino-1,2,4-triazolium (MAT$^+$) and dialkyl imidazolium (dialkyl-IM$^+$) cations and dicyanamide (DCA$^-$) and dicyanoborohydride (DCBH$^-$) anions. The work was to reveal preignition kinetics and dynamics of individual constituent ions and their combinations.

Approaches and Computational Methodologies

- **Purpose of Direct Dynamics** Oxidation and decomposition of energetic ILs are vigorous, and the reactions may go to completion within a few nanoseconds. These features make it a challenge to experimentally detect, in situ, all of the generated transient species. Moreover, IL reactions may be autocatalytic and non-statistical distributions among multiple channels may arise. Accordingly, use of chemical intuition may be inadequate to predict IL reactions.

  Direct dynamics trajectories explore multiple minima in the conformational landscape and the reaction potential energy surface (PES), all under specific experimental conditions. The motions of the molecules are directly followed, thus allowing the molecules to show what the preferred pathways are.

- **Methodologies**
  - Direct dynamics trajectory simulation using Hase's VENUS was sued to identify IL reaction pathways;
  - Followed by PES mapping and Rice-Ramsperger-Kassel-Marcus (RRKM) kinetics modeling to pinpoint the most probable reaction mechanisms and products;
  - Theoretical results were validated by comparing product structures and spectroscopy with available experimental data.

Results from Reaction Dynamics to Potential Surfaces, Kinetics and Spectroscopy

1. Dominant Role of Anions in Preignition

Anions are directly associated with IL hypergolicity and play a decisive role during the induction stage of ignition. DCA$^-$ (i.e. N(CN)$_2^-$) and DCBH$^-$ (i.e. BH$_2$(CN)$_2^-$) are the two well known choices based on their hypergolicity in propellant formulations and low viscosity. In the following, their oxidizability by nitric acid are compared.

- Formation of O$_2$N-NHC(O)NC(O)NH-NO$_2^-$ (DNB$^-$) is exclusively important in the preignition of DCA$^-$.

- Oxidation of DCBH$^-$ presents the same type of reactions that have occurred to DCA$^-$, but these pathways are minor in DCBH$^-$ preignition.

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Kinetics Analysis using RRKM Theory

temperature	300 °C	450 °C	600 °C	750 °C	900 °C
	DCA$^-$ + 2HNO$_3$				
$E_{internal}$ (kJ·mol^{-1})	93	130	171	213	258
k_{DCA^-} (s^{-1})	2.4×10^5	1.1×10^6	4.0×10^6	1.2×10^7	3.0×10^7
	DCBH$^-$ + 2HNO$_3$				
$E_{internal}$ (kJ·mol^{-1})	101	144	189	237	288
k_{DCBH^-}	2.15×10^2	1.5×10^4	3.75×10^5	4.5×10^6	3.3×10^7
$k_{DCBH^-} : k_{DCA^-}$	< 0.01	0.014	0.1	0.4	1.1
	DCBH$^-$ + 3HNO$_3$				
k_{DCBH^-} (s^{-1})	4.3×10^5	4.6×10^6	3.8×10^7	2.0×10^8	7.5×10^8
$k_{DCBH^-} : k_{DCA^-}$	1.8	4.2	10	17	25

- The preignition of DCBH$^-$ with HNO$_3$ mostly results from the boron-hydride-specific reactions, of which the most important one is H$_2$ elimination via the combination of a hydride in DCBH$^-$ and a proton in HNO$_3$.

- Kinetics analysis suggests that H$_2$ elimination becomes overwhelmingly dominant in the HNO$_3$ oxidation of DCBH$^-$.
- The phenomenological rate constant of DCBH$^-$ is an order of magnitude higher than that of DCA$^-$.

  - The combination of the fast reaction k, the large exothermicities of H$_2$ elimination, the high heat of combustion of H$_2$ product, and the low viscosity of the DCBH$^-$-ILs may rationalize the shortened ID time and enhanced preignition of DCBH$^-$ over DCA$^-$.

2. Participation of Cations in Preignition

Cations not only tune IL physicochemical properties but participate in preignition via intra-ion-pair reactions. The cation's capability of proton transfer and alkyl abstraction by anion may significantly affect IL oxidizability.

2.1 PT of Imidazolium-DCA and Effects of Alkyl Substituents

EMIM$^+$DCA$^-$ BMIM$^+$DCA$^-$ AMIM$^+$DCA$^-$

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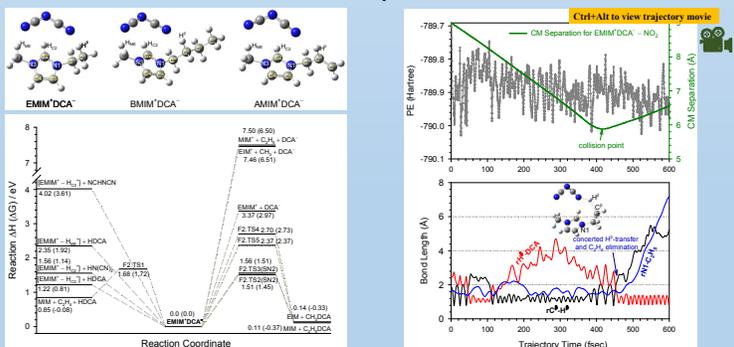
Transfer of a H$^\beta$ proton from the alkyl to a terminal N of DCA$^-$ represents the most important intra-ion-pair reaction, triggering the dissociation of the C-N1 bond and producing the following products:

	ΔH (eV)	ΔG (eV)	Reaction Statics Factor (number of available H$^\beta$)
EMIM$^+$DCA$^-$ → MIM + C$_2$H$_4$ + HDCA	0.85	-0.08	3
BMIM$^+$DCA$^-$ → MIM + C$_4$H$_8$ + HDCA	0.73	-0.23	2
AMIM$^+$DCA$^-$ → MIM + C$_3$H$_4$ + HDCA	1.01	0.08	1

  - Reactivity of intra-ion-pair PT correlates well with the high reactivity of EMIM$^+$DCA$^-$, followed by BMIM$^+$DCA$^-$ and AMIM$^+$DCA$^-$.

2.2 S$_N$2-alkyl Abstraction by DCA$^-$ Leads to Neutral Imidazole and Alkyl-DCA, all of which are reactive toward an oxidant (e.g. NO$_2$)

2.3 Comparison of MAT$^+$ with Dialkyl-IM$^+$: Missing of H$^\beta$ and the Consequences

- Probability for PT: BMIM$^+$ has 13 H (CH$_3$, C$_4$H$_9$ and C2-H) available for PT, followed by 9 in AMIM$^+$ (CH$_3$, C$_3$H$_5$ and C2-H) and then 6 in MAT$^+$ (NH$_2$, CH$_3$ and C2-H).

- A unique PT in dialkyl-IM$^+$DCA$^-$ is the concerted H$^\beta$-transfer and elimination of alkene, which is missing in MAT$^+$DCA$^-$.

- Dialkyl-IM$^+$DCA$^-$ have exoergic S$_N$2 alkyl abstraction, which releases heat to promote other reactions and thus accounts for their higher reactivities than MAT$^+$ DCA$^-$.

- Order of ion-pairing (eV)   ΔH   ΔG
  - dialkyl-IM$^+$DCA$^-$ 3.35   2.92
  - MAT$^+$ DCA$^-$ 3.97   3.49

Intra-Ion Pair Reactions of MAT$^+$DCA$^-$

MAT$^+$DCA$^-$	Products	ΔH (eV)	ΔG (eV)	ΔH(TS) (eV)	ΔG(TS) (eV)
PT_1	[MAT$^+$ – H^a]·HDCA	0.47	0.33	0.41	0.30
	and [MAT$^+$ – H^a]·HDCA	0.99	0.51		
PT_2	[MAT$^+$ – H^b] + HN(CN)$_2$	1.34	0.84	—	—
PT_3	[MAT$^+$ – H$_{imine}$]·HDCA	1.34	0.86		
→	MAT$^+$	DCA$^-$	3.97	3.49	

3. Verification of Computational Results: Product Spectral Analysis

- The computationally-predicted oxidation products include nitrites (RONO), nitroamines (RR'NNO$_2$), aromatic nitro compounds (ArNO$_2$) and carbonitrates (RR'C=NO$_2^-$), as well as a carbonyl group in higher-order products.

- The SMD-GIL//DFT-calculated product Infrared and Raman spectra of MAT$^+$DCA$^-$, BMIM$^+$DCA$^-$ and AMIM$^+$DCA$^-$ reproduced the spectroscopic features detected in the oxidation of IL droplets by the Kaiser laboratory (U Hawaii, *J. Phys. Chem. Lett.* 2017, *8*, 6053; *J. Phys. Chem. A* 2018, *122*, 7351; *J. Phys. Chem. A* 2019, *123*, 400)
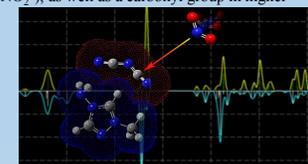
Conclusions

- ❖ Dynamics and kinetics modeling has captured the distinctive preignition chemistry for ILs of various constituent ions.
- ❖ Key reactions of boron-hydride in preignition suggest the design of new IL anions toward enhanced H$_2$-elimination capability.
- ❖ The oxidation reactivity are in the order of BMIM$^+$ DCA$^-$ > AMIM$^+$ DCA$^-$ ≫ MAT$^+$ DCA$^-$

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