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)) \(^{-}\) and DCBH\(^{-}\) (i.e. H\(_{2}\)) are the two well-known choices based on their hypergolicity in propellant formulations and low viscosity. In the following, their oxidizability by nitric acid \(\Delta H(\text{reaction})\) and their contribution to preignition kinetics and dynamics of individual constituent ions and their combinations are explored.

- Formation of N=NHCOCONH=NO\(^{-}\) (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.

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.

- \(\Delta H(\text{reaction})\) of the reaction: 1.22 (0.81) for BMIM\(^{+}\) DCA\(^{-}\) vs. 1.01 (0.08) for HDCA\(^{+}\) DCA\(^{-}\) (0.86).
- \(\Delta R(\text{reaction})\) of the reaction: 1.56 (1.51) for BMIM\(^{+}\) DCA\(^{-}\) vs. 1.01 (0.08) for HDCA\(^{+}\) DCA\(^{-}\) (0.86).

3. Verification of Computational Results: Product Spectral Analysis

- 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\(^{-}\).

4. Application of Reactive Molecular Dynamics

- Intra-Ion Pair Reactions of MAT\(^{+}\)DCA\(^{-}\):
  - Probability for PT: BMIM\(^{+}\) has 13 H (CH\(_{3}\)) and C2-H available for PT, followed by 9 in AMIM\(^{+}\) (CH\(_{3}\), CH\(_{2}\) and C2-H) and then 6 in MAT\(^{+}\) (NH\(_{3}\), CH\(_{3}\), and C2-H).
  - A unique PT in dialkyl-IM\(^{-}\)DCA\(^{-}\) is the concerted H\(^{+}\)-transfer and elimination of alkene, which is missing in MAT\(^{-}\)DCA\(^{-}\).
  - Dialkyl-IM\(^{-}\)DCA\(^{-}\) have exoergic S,\(_{2}\) alkyl abstraction, which releases heat to promote other reactions. The order of ion-pairing (eV) of MAT\(^{-}\)DCA\(^{-}\), dialkyl-IM\(^{-}\)DCA\(^{-}\)

5. 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 ILs toward enhanced H\(_{2}\) elimination capability.
- The oxidation reactivity are in the order of BMIM\(^{+}\)DCA\(^{-}\) > AMIM\(^{+}\)DCA\(^{-}\) > MAT\(^{+}\)DCA\(^{-}\).

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References