



Coulomb explosion and ultra-fast hypergolic ignition of borohydride-rich ionic liquids with WFNA

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ABSTRACT

In this work, the hypergolic ignition process of 8 recently synthesized ionic liquids (I.L.s) with $[\text{BH}_3(\text{CN})\text{BH}_2(\text{CN})]^-$ anions with white fuming nitric acid is experimentally investigated by using droplet test method and long distance microscope-high speed photography techniques. Results show that the hypergolic ignition process of the present I.L.s is of a completely different three stage nature and ultra-fast hypergolic ignition is observed for this family of I.L.s (< 5 ms). Specifically, at the very first stage upon contact (within a fraction of millisecond), 'coulomb explosion' like behavior in terms of fast and vigorous ejection of liquid spikes that protrude from mixing layer is observed, and this phenomenon has never been reported in previous hypergolic test for I.L.s or conventional hydrazine based fuels. The 'coulomb explosion' delay time (CEDT) is found to be correlated with the side alkyl functional group, which indicates the I.L. structure (characterized by the side alkyl functional group and the heterocyclic core) effects on shifting the Rayleigh instability limit ($E_{\text{coulomb}}/2E_{\text{surface}} > 1$). Subsequently in the second stage, liquid spikes that are ejected into the oxidizer pool during CEDT significantly increase the reactive surface area underneath the liquid surface. As a consequence, local temperature increases, gas phase intermediate product and oxidizer/fuel vapor accumulate due to the continuous liquid phase reaction underneath the surface. When the local pressure overcomes the surface tension, disintegration of the surface in terms of larger ligaments and secondary droplets ejection was observed, together with shooting out of the vapor/smoke. Finally, in the third stage when the local temperature and the vapor concentration increase sufficiently, further gas phase reaction leads to ignition. Fine and stable flame with strong bright and green luminescence continuously evolve from the initial mixing layer. Some red and dark smokes are gradually generated above the burning bright and green flame until finally the flame dies out. The ignition delay time (IDT) decreases with the increase of unsaturation index of the heterocyclic core in the cation, and also the decrease of CEDT. The enthalpy of formation of the I.L.s for different cation structures are correlated with IDT, which represents both the fuel structure chemistry and the 'coulomb explosion' enhances mixing effect on the overall reactivity of this diffusive system.

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1. Introduction

Liquid propellants have been widely used in launching vehicles for satellite and ballistic missile and for orbit maneuvering of space shuttle. Though liquid propellant rocket engines have more complex structures than their solid propellant counterparts, they offer the advantages such as high specific impulse, and being able to be throttled. As such, the acceleration, deceleration, and restart can be simply achieved by controlling the flow rate of the propellants. Hypergolic propellants in the liquid propellant family, are even more

attractive because the fuel and oxidizer ignite simultaneously upon contact with each other such that the engines are more reliable because no separate ignition system is needed. Conventional hypergolic fuels including hydrazine, monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH) and extensive investigations have been conducted to understand the hypergolic ignition behavior of these hydrazines and their derivatives [1–5]. Specifically, Forness et al. [1] conducted a series of drop test experiments on MMH/WFNA (white fuming nitric acid) with different droplet impact velocities and angles and they found three impact outcomes: bounces, splashes and explosions. They proposed that the impact angle and the Weber number are the two primary factors that influence the impact and liquid reactions. Daimon et al. [2] studied the nature and mechanisms of explosions caused by

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dropping hypergolic fuels (N_2H_4 , MMH, or UDMH) into oxidizer pools (NTO, nitrogen tetroxide, or RFNA, red fuming nitric acid). The explosion phenomena were classified into three types: 1) sudden gasification of a superheated liquid layer occurs spontaneously at the mixing layer and a detonation-like reaction proceeds in the reactive mixture produced. 2) sudden gasification caused by the shock of a local ignition, and a turbulent-combustion reaction proceeds in the reactive mixture produced. 3) relatively weaker gasification occurs spontaneously as in the case of 1). They concluded that the vapor layer, which is formed between reactive fuel droplet and pool liquid, plays an important role for the occurrence of explosion. These studies have improved the fundamental understanding of hypergolic ignition behaviors of hydrazine based propellants. However, they also outlined that these hydrazine based hypergols are extremely toxic, carcinogenic and of high vapor pressure. A small amount of fuel leakage can cause acute poisoning to technical staff as well as atmosphere, water, and soil pollution, thus the storage and handling are of high risk and expense.

Searching for less toxic and easily storable green hypergolic propellants to reduce costs and increase handling safety has raised significant attention in the past few decades [6–12]. Specifically, the concepts of hydrazine gelling have been proposed for reducing vapor pressure [7], and the spray and atomization of gelled propellants remain to be challenges due to their non-Newtonian and high viscous nature. Pichon et al. [8] attempted to replace MMH by examining the hypergolicity of gaseous ethanol with NTO in a combustion chamber. However, no hypergolic ignition was achieved though room temperature reactions between gaseous ethanol with NTO were detected. Kang et al. [9] tested the hypergolic ignition between an HTP (high-test peroxide) droplet and a shallow pool of sodium borohydride based fuel and hypergolic ignition was found. Willits et al. [10] examined the hypergolic ignition behavior by dropping a WFNA droplet into small amount of amine boranes (triethylamine borane, ethylenediamine bisborane and diisopropylethylamine borane). Vigorous ignition with adequately small ignition delay times was found. In addition, several green high performance propellants with the objectives of hydrazine replacement have been proposed by the relevant institutions in the U.S. [11] and European Union [12].

Recently, energetic ionic liquids have attracted significant interests from the community of chemical synthesis as well as combustion and propulsion [13–22]. Energetic ionic liquid (I.L.) is a kind of salt in liquid state at room temperature. They are typically composed of organic cations and inorganic/organic anions. Compared to the molecules of ordinary liquids, the I.L.s are more stable and have extremely low vapor pressure because their ionic bond is usually stronger than the Van der Waals force between ordinary molecules [20]. In addition, I.L.s are insensitive towards destructive stimulations such as impact, friction, or electrostatic discharge. Furthermore, I.L.s can be produced with the designed performance of the energy density, oxygen balance, freezing point, solubility and liquid viscosity by adjusting the structure of the anion and cation [13]. All these properties and characteristics make energetic I.L.s storage and handling easy and they hold superior potential as green hypergolic propellants.

However, not all energetic I.L.s are hypergolic. When they are synthesized to be used as propellants, their hypergolicity with certain oxidizers needs to be examined. Recently, a great many of I.L.s have been synthesized, as reviewed by Zhang and Shreeve [13] and Zhang et al. [14]. However, all these studies only emphasize the I.L. fuel synthesis and do not improve our understanding on the hypergolic ignition and combustion process. Schneider et al. [15] reported the hypergolicity behavior of selected I.L.s by using the drop test method and they found that several dicyanamide anionic I.L.s ignite hypergolically with WFNA and RFNA. However, the reported ignition delay times were from tens to hundreds of milliseconds,

which are too large and will be prone to cause hard-start issue when used in rocket engines [16]. In addition, because the images they reported were of low spatial and time resolution, no interpretation of the hypergolic ignition process is provided. McCray et al. [17] investigated the hypergolic ignition of 38 ionic liquids comprised of 13 cations and they found that the reactivity of these ionic liquids correlates strongly with the electron density in the cation and subtle change in chemical structure of cation would influence the hypergolic ignition. We recently investigated the hypergolic ignition between a superbase-derived ionic liquid drop with WFNA, RFNA, and NTO liquid pool and found that initial contact dynamics and liquid phase mixing could affect the subsequent hypergolic ignition [18].

The objectives of this work is the following. Since the structures of I.L.s are different from the structures of ordinary molecular liquids such as MMH or UDMH, the initial liquid phase reaction mechanism upon contact between hypergolic I.L.s and oxidizer may be different from that of conventional hypergolic propellants. We recently synthesized several borohydride-rich ionic liquids and 8 of them have the same anions $[BH_3CNBH_2CN]^-$. For this family of I.L.s, one cyano group serves as a stabilizing ligand to bridge two hydrogen-rich $\{BH_3\}$ and $\{BH_2CN\}$ moieties. In addition, the electron-withdrawing cyano groups improve the chemical stability of negatively charged hydrogen atoms [19]. Our first objective is to examine the very early stage upon the contact of these 8 I.L.s with specially designed anion structures with WFNA to see if any unexpected phenomenon can be observed. Later we will show that indeed, new phenomenon (coulomb explosion) that has never been reported previously was observed for this kind of I.L.s. In addition, when new I.L.s are synthesized as hydrazine replacement fuel propellants, understanding their hypergolic ignition is critical for developing safe and efficient hypergolic rocket engine techniques. We note that the hypergolic ignition and subsequent flame behavior involve complex coupling of fluid mixing dynamics, liquid phase reaction, phase change, heat and mass transport, and gas phase reaction kinetics. Thus our second objective is to scrutinize the whole combustion process of these hypergolic I.L.s to characterize the key features during different stages of combustion. Finally, because the I.L.s studied in this work have the same anions, the time scales of coulomb explosion delay time (CEDT) and hypergolic ignition delay time (IDT) will be compared to extract their correlations with the cation structures. In the following, we will specify our experimental apparatus and procedures first. Then experimental observations and detailed analysis on different stages of hypergolic ignition will be presented, followed by comparison of the characteristic parameters of I.L.s with different cation structures.

2. Experimental specifications

Details of the experimentations can be found in Ref. [18]. Briefly, Fig. 1 shows the sketch of the drop testing experimental system. Ionic liquid droplets (fuel) are generated at the tip of a hypodermic needle that is mounted on a three dimensional positioner. 8 ionic liquids are tested and the diameter of the generated droplet (D_0) is around 2.25 mm. Before the experiment, the petri dish filled with WFNA is covered by a glass plate to minimize the effect of WFNA vaporization. The plate is then removed immediately before the ionic liquid drop falls down. We assume that several fuel drops and reaction do not contaminate the oxidizer because the oxidant liquid volume is more than ten thousand times larger than that of the fuel droplet, so that we do not need to refresh the oxidizer for every dropping. However, after about 5 droppings, we still renew the WFNA pool with fresh oxidizer. The depth of the oxidizer pool is 20 mm ($\sim 10 D_0$) and the diameter of the petri dish ($\sim 50 D_0$) is sufficiently large such that the impact and subsequent reactions will not be affected by the dish wall. The

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