

Atmospheric Ignition Chemistry of Green Hypergolic Bipropellant 1-Ethyl-3-Methylimidazolium Cyanoborohydride – Hydrogen Peroxide in an Acoustic Levitator: Exploring a Potent Universal Propellant

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Hypergolic ionic liquids (HILs) represent a critical pool of reactive ionic liquids which ignite spontaneously in absence of oxygen when mixed with an oxidizer such as white fuming nitric acid (WFNA, HNO_3) or hydrogen peroxide (H_2O_2). These HILs have emerged as greener alternatives to the toxic hydrazine family of fuels for operations in space under anaerobic conditions. Here, we report on the unusual atmospheric ignition chemistry of the 1-ethyl-3-methylimidazolium cyanoborohydride ([EMIM][CBH])– H_2O_2 bipropellant while comparing with the parent hypergolic reaction by exploiting a chirped-pulse triggered droplet merging technique in an ultrasonic levitation apparatus under controlled environment. Significant enhancements of the ignition performance and notice-

able differences of product distribution in the simulated atmosphere containing molecular oxygen are revealed. The critical mechanistic role of the surrounding oxygen plausibly involves the reaction with a suitable intermediate (iminomethyl)boronic acid, $[(\text{HO})_2\text{BCH}=\text{NH}]$ formed in the initial reactions of the IL and H_2O_2 which eventually generates catalytic hydroperoxyl ($^*\text{HO}_2$) and hydroxyl ($^*\text{OH}$) radicals – further promoting the ignition reaction. This systematic case study conceptually demonstrates that under atmospheric conditions, well-defined HIL – oxidizer combinations provide excellent ignition performance and effectively be used as universal fuel both in space and in the terrestrial atmosphere simplifying the multistage propulsion system.

Introduction

A hypergolic bipropellant constitutes a highly reactive fuel-oxidizer combination, which ignites spontaneously, i.e. without any ignition source, upon contact with each other. These propellants have been dedicatedly exploited as rocket fuels for deep space missions under anaerobic combustion conditions circumventing the need for complex cryogenically-cooled liquid oxygen operated propulsion systems.^[1] Traditional hypergolic bipropellants include hydrazine (N_2H_4) and its derivatives such as methylhydrazine ($\text{H}_2\text{NNH}(\text{CH}_3)$) and unsymmetric dimethyl hydrazine (UDMH, $(\text{CH}_3)_2\text{N}_2\text{H}_2$) in combination with oxidizers such as white fuming nitric acid (WFNA, HNO_3) or dinitrogen tetroxide (N_2O_4). Hypergolic ionic liquids (HILs), a special pool of ionic liquids (liquid salts at room temperature) that undergo self-ignition with oxidizers like WFNA, N_2O_4 or concentrated hydrogen peroxide (H_2O_2) have emerged as efficient green bipropellants by replacing the highly toxic, volatile and carcinogenic hydrazine family fuels, yet possessing comparable combustion performances to the latter.^[2,3] Since the discovery

of the HILs by Schneider et al. through reporting the hypergolicity of 1-allyl-3-methylimidazolium dicyanamide with WFNA^[4] numerous chemically distinct HILs have been synthesized with a goal to enhance the efficiency and performance while simultaneously aiming at more environment-friendly options.^[5–21] In general, the recently reported HILs have low vapor pressures and tend to be chemically inert when exposed to air thus providing a significant advantage of convenient storage and handling.^[9,11–14]

Currently, HIL-based research is rapidly expanding; however, there lies a severe concern in the performance analysis of the hypergolic reactions, as evaluated by conventional *drop tests*, where a tiny IL droplet is allowed to fall in a reservoir of liquid oxidizer followed by ignition. These tests are unable to avoid significant surface contributions from the vessel containing the oxidizer and the excess of the latter during primary reactive contact leads to ambiguous determination of performance parameters, e.g. *ignition delay* (ID) values, which vary largely within different experimental groups. Unlike the usual *drop tests*, it is known that the liquid fuel (ionic liquid) and the oxidizer initially interact as droplets inside the combustion chamber of rocket after being injected.^[22,23] Driven by the need to eliminate surface reaction contributions, through contactless merging of IL and oxidizer droplets in a ultrasonic levitator apparatus (Figure 1) under controlled conditions in a closed process chamber, systematic analysis of hypergolic as well as non-hypergolic reactions have been performed recently.^[24–26]

Here, we explore the atmospheric combustion of the hypergolic bipropellant pair 1-ethyl-3-methylimidazolium cya-

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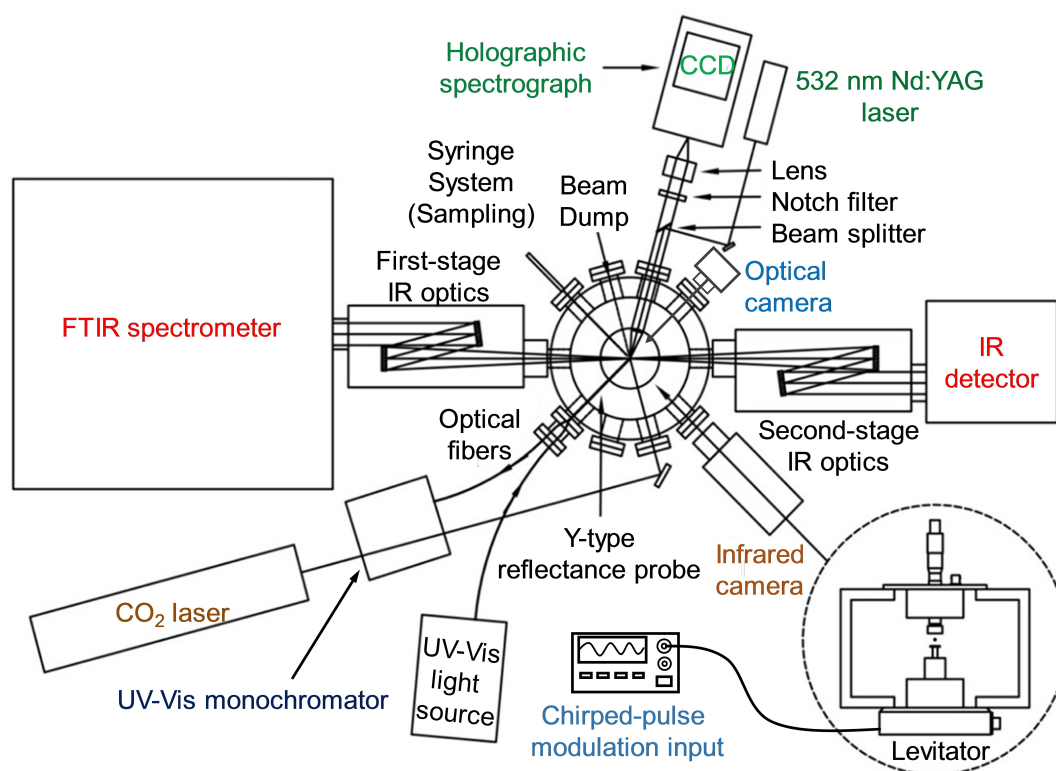


Figure 1. Schematic top view of the levitator apparatus displaying the ultrasonic levitator, process chamber, carbon dioxide laser, Raman, FTIR and fiber optic UV-Vis spectrometer along with high-speed infrared and optical cameras.

noborohydride ([EMIM][CBH]) with concentrated hydrogen peroxide (H_2O_2 , 92% w/v) as a case study (Figure 2) and

compare both the qualitative and quantitative findings such as reaction products and ignition delays to that of the parent

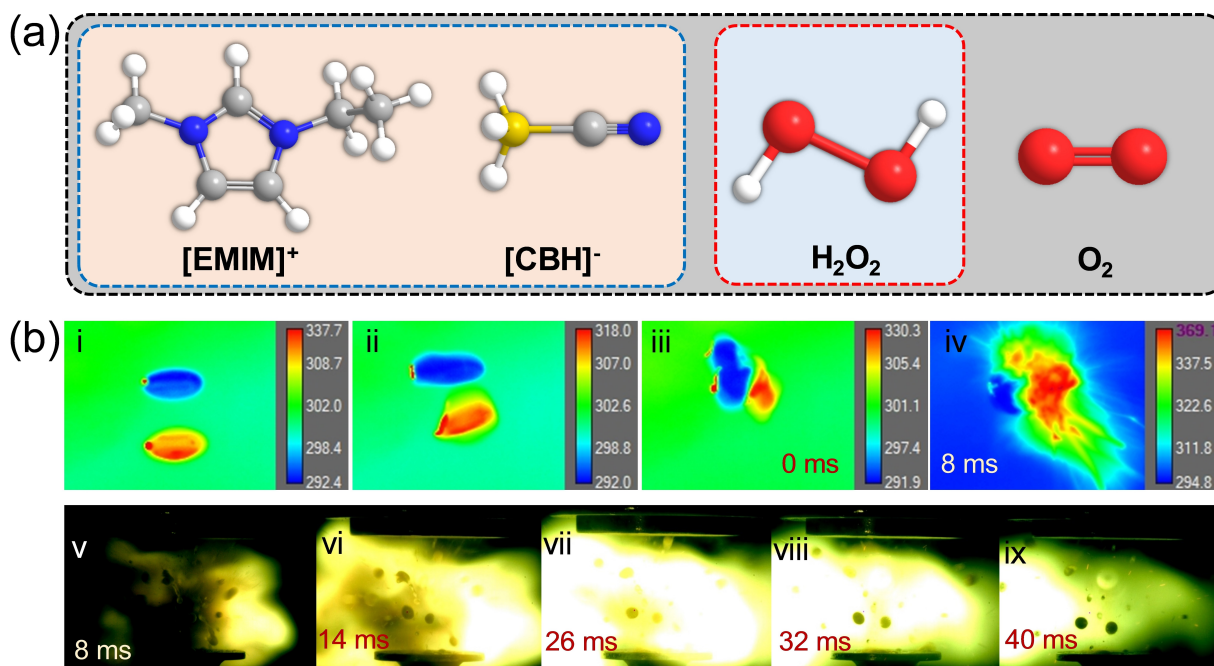


Figure 2. (a) The hypergolic bipropellant 1-ethyl-3-methylimidazolium cyanoborohydride ([EMIM][CBH]) and concentrated hydrogen peroxide (H_2O_2 ; 92% w/v) in varying molecular oxygen (O_2) – argon (Ar) environments. (b) Synchronized, temporally resolved complementary infrared and optical camera images of the droplet merging event followed by ignition between [EMIM][CBH] and 92% w/v H_2O_2 in simulated atmosphere (mixture of 20% O_2 and 80% Ar by volume).

hypergolic reaction. The primary objective of the study is to conceptually assess the feasibility of using HIL-oxidizer combinations as primary lift-off or booster rocket propellants, thus expanding HIL's operational range in both air and anaerobic environments to enable their use as universal propellants while unifying the multistage propulsion system to a single unit. The chosen ionic liquid, [EMIM][CBH] advantageously exhibits exceptional thermal stability, extremely low vapor pressure, moisture-insensitivity with a preferable density (0.98 g cm^{-3}) and low viscosity (19 mPa s),^[13,27] it further possesses high energy-content even compared to energy-rich borohydrate ILs.^[13] The low viscosity of this IL helps the contact and mixing with the oxidizer, which is desirable for smooth engine operations. For the bipropellant pair, H_2O_2 serves as a cleaner and ecofriendly oxidizer compared to toxic white/red fuming nitric acid (HNO_3) or dinitrogen tetroxide (N_2O_4).^[28–31] To simulate the ignition event via chirped-pulse triggered merging of quantifiable, individually *levitated* reactant droplets, the closed process chamber is filled with pure argon (Ar, 100%), and mixtures of Ar and molecular oxygen (O_2) gases of two different compositions – 90%:10% and 80%:20%, respectively. Alongside synchronized high-speed cameras (optical and infrared), multiple spectroscopic tools have been utilized in tandem for the sensitive detection of the gaseous products by Fourier-transform infrared (FTIR) spectroscopy and the key emitting reaction intermediate is identified by time-resolved UV-Vis emission spectroscopy.^[32–35] Notably, the presence of molecular oxygen (O_2) in the reaction environment significantly lowers the *ignition delay* (ID) compared to that of the hypergolic reaction as well as leads to a different gas phase product distribution, indicating a direct reactivity of molecular oxygen during the merging reaction of the IL and oxidizer.

Materials and Methods

In the acoustic levitator (Supporting Information S1), an ultrasonic sound wave produced by a piezoelectric transducer is reflected on a concave plate mounted vertically upwards and generates a resultant standing wave, in which liquid droplet(s) or tiny solid particle(s) can be levitated at the stable pressure minima.^[24,26,36,37] The levitator assembly is enclosed within a pressure-compatible process chamber (Figure S1) surrounded by spectroscopic (FTIR and UV-Vis) as well as visualization tools (high-speed optical and infrared cameras). In the present experiments, the chamber is filled with pure argon and different compositions of argon-molecular oxygen gas mixtures. The ionic liquid and H_2O_2 droplets are loaded in adjacent pressure nodes using two micro needles mounted on a flexible wobble stick and connected to an outside port on the chamber via chemically inert PTFE tubing while sampled by two distinct syringes. Once the reactant droplets are deposited, an amplitude-modulated chirped pulse is applied to trigger the merging motion of the ionic liquid droplet upwards for mixing with the H_2O_2 droplet (Figure S2), eventually resulting in ignition. The electromagnetic radiation emitted by the flame during ignition is collected by a fiber-optic probe attached to an x, y, z manipulator located inside the process chamber and analyzed by a temporally resolved UV-Vis spectrometer in the range of 200–1100 nm. The gaseous products are identified by collecting FTIR absorbance spectra in the 400–4,000 cm^{-1} wavenumber region through the full width of the process chamber using a FTIR spectrometer with two

stages of external copper mirror optics and a liquid nitrogen cooled MCT-B (mercury cadmium telluride, wide band) detector. The merging and ignition events are recorded with complementary high speed optical and infrared cameras. The cameras along with the initial chirp pulse and UV-Vis spectrometer are synchronized and externally triggered by a pulse generator (Figure S3). The 1-ethyl-3-methylimidazolium cyanoborohydride was synthesized in house^[13] and its purity was determined to be 98% by NMR spectroscopy while concentrated hydrogen peroxide (H_2O_2) was enriched from 30% w/v stock (Fisher) by vacuum distillation (Supporting Information S2) and its strength was estimated from the density versus concentration plot. Argon (99.9999%, Ar) and molecular oxygen (100%, O_2) gases to fill the levitator process chamber were procured from Airgas. The gases for calibration purposes were supplied by Matheson Tri-gas: carbon dioxide (CO_2 , purity: 99.999%) hydrogen cyanide (HCN, diluted 5% in helium), methane (CH_4 , purity: 99.999%), carbon monoxide (CO, purity: 99.999%).

Results and Discussions

Ignition Events by Chirped Pulse-Triggered Droplet Merging

The merging processes of the droplets of [EMIM][CBH] and 92% H_2O_2 loaded in the lower and upper pressure nodes, respectively, followed by ignition events in simulated atmospheres (0, 10, and 20% O_2) were monitored by the high-speed, temporally resolved, synchronized optical and infrared (IR) cameras [Movies S1, S2 (20% O_2); S3, S4 (10% O_2); S5, S6 (0% O_2)]. Series of snapshots captured by complementary IR and optical cameras for the ignition at 20% O_2 – 80% Ar mixture are displayed in Figure 2, while the same for the 10% and 0% O_2 (hypergolic) compositions are depicted in Figures S5, S6, respectively. The IR images show distinct stages of the whole merging process sequentially – (i) levitating reactant droplets (pre-merging), (ii)–(iii) merging motion upon application of the frequency-chirp pulse, and (iv) merging instance resulting to temperature jump (exoergic). Simultaneously, the optical camera operating at 1 kHz captures the ignition and post-ignition (combustion) events by revealing bright greenish flames with yellowish tints. The ignition delays (IDs) are determined from the time difference between the merging and the initiation of ignition. With the increase in molecular oxygen concentration, a significant reduction of the ID is observable. Quantitatively, the ID was reduced from $390 \pm 10\text{ ms}$ at 0% oxygen (hypergolic reaction) to $14 \pm 6\text{ ms}$ at 10% oxygen to $8 \pm 4\text{ ms}$ at 20% oxygen (atmospheric condition). The maximum flame temperature reaches $2,876 \pm 100\text{ K}$ for the atmospheric ignition while that of the hypergolic reaction is determined to be $2,521 \pm 100\text{ K}$ (Supporting Information S3). The evaluated molar ratios of IL to H_2O_2 from the droplet size measurements indicate that about four molecules of the oxidizer react with each IL molecule for the ignition events (Table S1).

Flame Emission Spectra

Spectroscopically, the ignition chemistry was probed by time-resolved ultraviolet – visible (UV-Vis) emission spectroscopy in the 200 to 1,100 nm spectral range (Figure 3). The temporal evolution of emission spectral intensities indicates the onset of the ignition, the spread of the flame to its peak intensity, i.e. the combustion of the ionic liquid droplet, followed by no emission implying the completion of the oxidation process. This time sequence as perceived spectroscopically also mirrors the recordings of the synchronized high-speed cameras (Figure 2(b)). Thus, it is noted that the first appearance of emitting spectral features in the traces since the merging instances as captured by the cameras confirms the determined ID values. A sustainable ignition is also evidenced with the increase in molecular O₂ fraction, i.e. the ignition duration at 20% O₂ is measured to be 46 ms, whereas the same for 10% O₂ and the hypergolic reaction (0% O₂) are 32 and 28 ms, respectively.

Spectral deconvolution of the emission traces (Figure 4(i), Table 1) reveals dominant emission features (bands a–g, j–l) of boron dioxide (*BO₂) radical (547.5 nm (band f); A ²Π_g–X ²Π_g)^[26,38,39]. The strong presence of *BO₂ is attributed to the facile oxidation of sp³ hybridized B-center of the [CBH] anion. However, another emitting intermediate, boron monoxide (*BO),^[40] could not be detected in the emission spectra owing to the intense emissions from boron dioxide. Traces of alkali metals present in the IL are also detectable via their character-

istic atomic emission lines of sodium (Na) [590.3 nm (band h), 2p⁶3p ²P→2p⁶3s ²S; 819.4 nm (band o), 2p⁶3d ²D→2p⁶3p ²P] and potassium (K) [770.5 nm (band n), 3p⁶4p ²P→3p⁶4s ²S].^[41] Band h belonging to Na-atomic emission consistently represents the maximum intensity in the spectral traces. The normalized band intensities of the most prominent transition for *BO₂ (band f) with respect to band h qualitatively suggests greater yield of *BO₂ via facilitated oxidation of the B-center with increasing molecular oxygen content in the reaction chamber. The normalized peak intensity of the *BO₂ transition for the hypergolic reaction (0% O₂) is 0.39, and it increases to 0.71 for the atmospheric ignition process (20% O₂). Temporal profile of the reactive intermediate *BO₂ (Figure 4(ii)) extracted via plotting the peak areas of band h as a function of time reveals extended existence of the species with the increasing fraction of molecular O₂.

Gas Phase Products

The gaseous products generated *in situ* via the hypergolic (0% O₂) and aerobic (10% and 20% O₂) ignition events of the [EMIM][CBH]-H₂O₂ bipropellant combination were detected by FTIR spectroscopy (Figure 5a, Table S2). In all the cases, broad spectral features of water vapor in the region 3950–3490 cm⁻¹ (stretching) and 1910–1320 cm⁻¹ (bending) are observed, since the oxidizer itself contains water as the medium. The strong

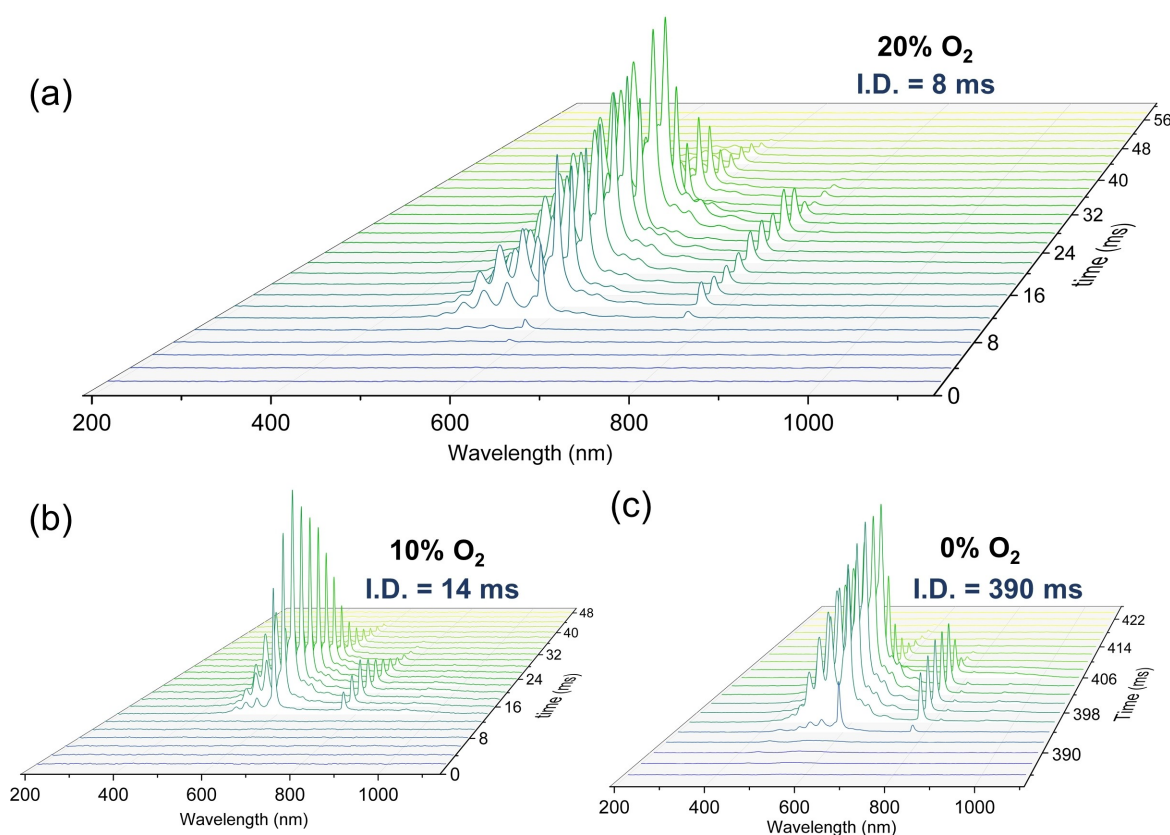


Figure 3. The evolution of the ignition event spectroscopically probed by recording time-resolved emission (UV-Vis) spectra of the [EMIM][CBH]-H₂O₂ (92% w/v) reactions in varying molecular oxygen (O₂)-argon (Ar) environments.

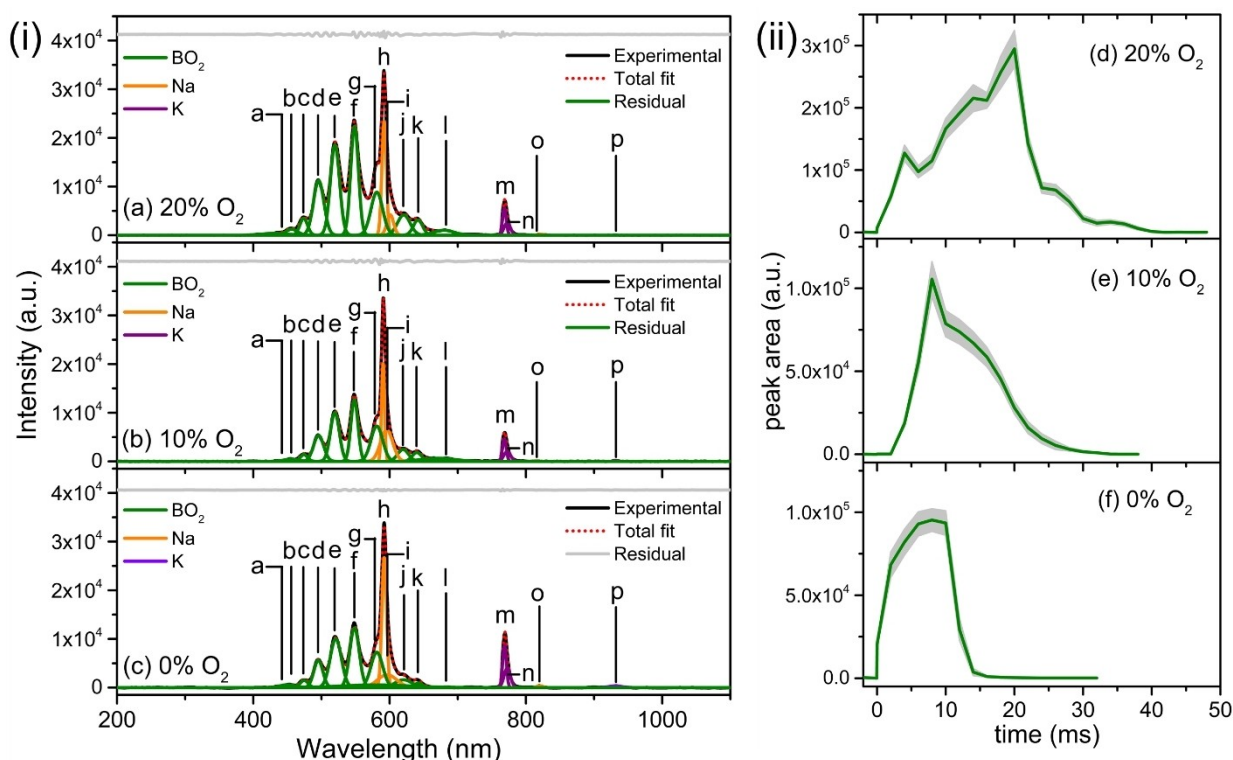


Figure 4. (i) Deconvolution of the most intense flame emission spectra of ignition reactions between [EMIM][CBH] and 92 % H₂O₂ at different molecular oxygen (O₂) concentrations with (ii) temporal profiles of the key emitting intermediate – boron dioxide (*BO₂).

bands at 2350 cm⁻¹ and 667 cm⁻¹ correspond to the asymmetric stretching and bending vibration, respectively, of the primary combustion product, carbon dioxide (CO₂) along with carbon monoxide (CO) which is identifiable by its stretch at 2143 cm⁻¹. In presence of molecular oxygen, the intensity of the CO band becomes weaker. Similarly, characteristic features for hydrogen cyanide (HCN) at band centers of 3311 (C–H stretching) and 712 cm⁻¹ (bending) are noted under hypergolic ignition which are largely diminished in atmospheric combustions. The weak 2269 cm⁻¹ band of isocyanic acid (HNCO) is present in all of the traces depicted in Figure 5a. HCN and HNCO are most likely produced upon decomposition and oxidation of the –C=N functional group existing in [CBH]⁻.

In absence of O₂ in the process chamber during ignition, spectral features of methane (CH₄, 3150–2870 cm⁻¹) and ammonia (NH₃, 950 cm⁻¹) can be easily identified (magnified spectral segments, Figure 5a). However, with the increasing concentration of O₂, a significant decrease in the absorbance of CH₄ and NH₃ bands are noticeable, and formation of methanol (CH₃OH) can be detected via the distinguishable bands at 2999 (C–H perpendicular asymmetric stretching), 2844 (C–H parallel symmetric stretching) and 1033 cm⁻¹ (C–O stretching).

Quantification of CO, CH₄ and HCN (Figure 2(b)) from the FTIR spectral traces using calibration curves (Figures S7–S9) shows a sharp decline in their amounts with the increase in molecular O₂ in the reaction medium. Essentially, HCN production is absent in the case of ignition at 20% O₂, whereas in the hypergolic event (i.e. 0% O₂), the formation is recognizable

[(8.4 ± 1.3) × 10⁻⁶ moles]. This decrease in the quantity of HCN can be linked to the subsequent oxidation of HCN to nitrogen oxides (NO_x) – primarily nitric oxide (NO) and nitrous oxide (N₂O) with CO₂ and water.^[42] However, the characteristic features of NO and N₂O at 1875 and 2224 cm⁻¹, respectively, are found to be absent indicating either a negligible formation of the species below the detection limit of the spectrometer or a facile consumption of the generated NO_x via thermal decomposition or reduction (e.g. by CO) to produce molecular nitrogen (N₂) in the high temperature process.

The amount of CH₄ is reduced to (3.0 ± 2.0) × 10⁻⁷ moles during atmospheric ignition (20% O₂) from (2.5 ± 0.5) × 10⁻⁶ moles as determined in hypergolic ignition. CH₃OH quantification is performed by utilizing the absorbance cross-section of the 1033 cm⁻¹ band^[43] and its amount remarkably exceeds that of CH₄ at 20% O₂ [(4.1 ± 1.4) × 10⁻⁶ moles versus (3.0 ± 2.0) × 10⁻⁷ moles]. Declining yield of CO with the increase of O₂ in the medium [(11.6 ± 1.5) × 10⁻⁶ moles at 0% O₂; (2.1 ± 1.3) × 10⁻⁶ moles at 20% O₂] is the likely consequence of oxidation of these species forming CO₂ under aerobic conditions. The substantial amount of the predominant combustion product, CO₂ increases with the O₂ content in the reaction chamber and measured to be (4.6 ± 0.4) × 10⁻⁴ moles during the atmospheric ignition (20% O₂) indicating a facile oxidation of the IL (Figure S10). Quantitatively, at this condition, the yield or conversion efficiency from the IL reaches the maximum of 87%, where [EMIM]⁺ is assumed to be its primary source because of the six constituent carbon atoms (Table S3). The percentage

Table 1. Peak/band assignments for the deconvoluted flame emission spectra of [EMIM][CBH] – 92 % H₂O₂ ignition reactions in different molecular oxygen concentrations.^[25,26,39,41]

Peak/band	Peak wavelength/ band center (nm)	Species	Reference wavelength (nm)	Transition	Branch; spin-orbit components; vibrational quantum numbers: (v', v'') or (v ₁ ', v ₂ ', v ₃ ') – (v ₁ '', v ₂ '', v ₃ '')
a	434.5 ± 1.2	•BO ₂	431.2 ^x	A ² Π _u –X ² Π _g	(0,2,n)–(0,0,n); (0,3,n)–(1,1,n)
b	450.8 ± 0.5	•BO ₂	448.8 ^x	A ² Π _u –X ² Π _g	(n,2,m)–(n-2,2,m); (n,3,0)–(n-1,3,m)
c	473.5 ± 1.1	•BO ₂	469.6 ^x	A ² Π _u –X ² Π _g	(n,2,m)–(n-1,2,m); (n,1,m)–(n-2,1,m)
d	495.2 ± 0.8	•BO ₂	492.7 ^x	A ² Π _u –X ² Π _g	(n,0,m)–(n-2,0,m); (n,1,m)–(n-1,1,m)
e	519.4 ± 0.5	•BO ₂	518.1 ^x	A ² Π _u –X ² Π _g	(n,0,m)–(n-1,0,m); (n,1,m)–(n-1,1,m)
f	547.5 ± 0.8	•BO ₂	546.5 ^x	A ² Π _u –X ² Π _g	(n,0,m)–(n,0,m)
g	581.2 ± 0.7	•BO ₂	581.2 ^x	A ² Π _u –X ² Π _g	(n,0,m)–(n+1,0,m)
h	590.3 ± 1.5	Na	589.0 ^y	2p ⁶ 3p ² P ^o –2p ⁶ 3s ² S	3/2–1/2
i	591.1 ± 1.3	Na	589.6 ^y	2p ⁶ 3p ² P ^o –2p ⁶ 3s ² S	1/2–1/2
j	621.2 ± 1.1	•BO ₂	620.2 ^x	A ² Π _u –X ² Π _g	(n,0,m)–(n+2,0,m)
k	642.5 ± 1.5	•BO ₂	644.2 ^x	A ² Π _u –X ² Π _g	(n,0,m)–(n+3,0,m)
l	681.8 ± 1.1	•BO ₂	687.8 ^x	A ² Π _u –X ² Π _g	(0,0,m)–(1,2,m)
m	767.8 ± 0.6	K	766.5 ^y	3p ⁶ 4p ² P ^o –3p ⁶ 4s ² S	3/2–1/2
n	770.5 ± 0.5	K	769.9 ^y	3p ⁶ 4p ² P ^o –3p ⁶ 4s ² S	1/2–1/2
o	819.4 ± 0.4	Na	818.3 ^y 819.5 ^y	2p ⁶ 3d ² D–2p ⁶ 3p ² P ^o	5/2–3/2; 3/2–3/2; 3/2–1/2
p	932.6 ± 1.8	K	934.7 ^y	3p ⁶ 8p ² P ^o –3p ⁶ 3d ² D	1/2–3/2

x – Ref. [25, 26, 39]; y – Ref. [41].

yield is significantly higher as compared to that of the parent hypergolic reaction (59%) suggesting a nearly complete oxidation of the IL.

Atmospheric versus Hypergolic Ignition

Summarizing the above results of both the atmospheric and hypergolic ignition events, the following key observations can be highlighted. *First*, a remarkable decrease in the ignition delay from 390 ± 10 ms for hypergolic ignition to only 8 ± 4 ms for atmospheric ignition is noted. *Second*, presence of molecular oxygen in the reaction medium also positively influence the ignition duration, for instance, at 20% oxygen, the ignition lasted 18 ms longer than the hypergolic one. Spectroscopically, the emission features of •BO₂ is more intense in oxygen rich conditions. *Third*, the yield of the major combustion product, CO₂ increases with the rise in O₂ concentration indicating more efficient oxidation of the IL. Besides, formation of CH₃OH is exclusively detected in presence of oxygen. *Fourth*, the quantity of some of the trace gaseous products such as CO, HCN and CH₄ drastically decreases with the increasing share of molecular oxygen in the process chamber.

These salient observations evidently reveal a critical role of the molecular oxygen in the reaction and largely facilitates the

oxidation as compared to that in the parent hypergolic event. Quantitatively, all ignition events are initiated with an approximate 1:4 (IL:H₂O₂) reactant ratio as determined from the droplet volumes (Table S1). According to the recent electronic structure theory calculations,^[26] the hypergolic reaction originates due to a termolecular reaction of the more reactive anion ([CBH][–]) in the IL with two molecules of H₂O₂ leading to the formation of •BO₂ (Figure 6).

The mechanistic pathway essentially represents a sub-merged potential energy surface (PES) as compared to the separated reactants. This spontaneous exothermic reaction channel drives a subsequent termolecular reaction of [EMIM]⁺ with two molecules of H₂O₂ possessing a high energy barrier (172 kJ mol^{–1}) at the entrance channel. Nevertheless, the individual bimolecular reactions of H₂O₂ with the anion and cation shows significant initial energy barriers (35 and 210 kJ mol^{–1}, respectively).^[26]

Although the overall termolecular reaction [CBH][–] + 2 H₂O₂ is found out to be energetically submerged with respect to the separated reactants, the individual steps have energy barriers up to a maximum of 355 kJ mol^{–1} linked to the immediate intermediate. From a chemical viewpoint, any suitable reactive intermediates on the PES upon reaction with the molecular oxygen can lower the corresponding energy barriers, resulting in an overall energetically favored pathway as compared to the

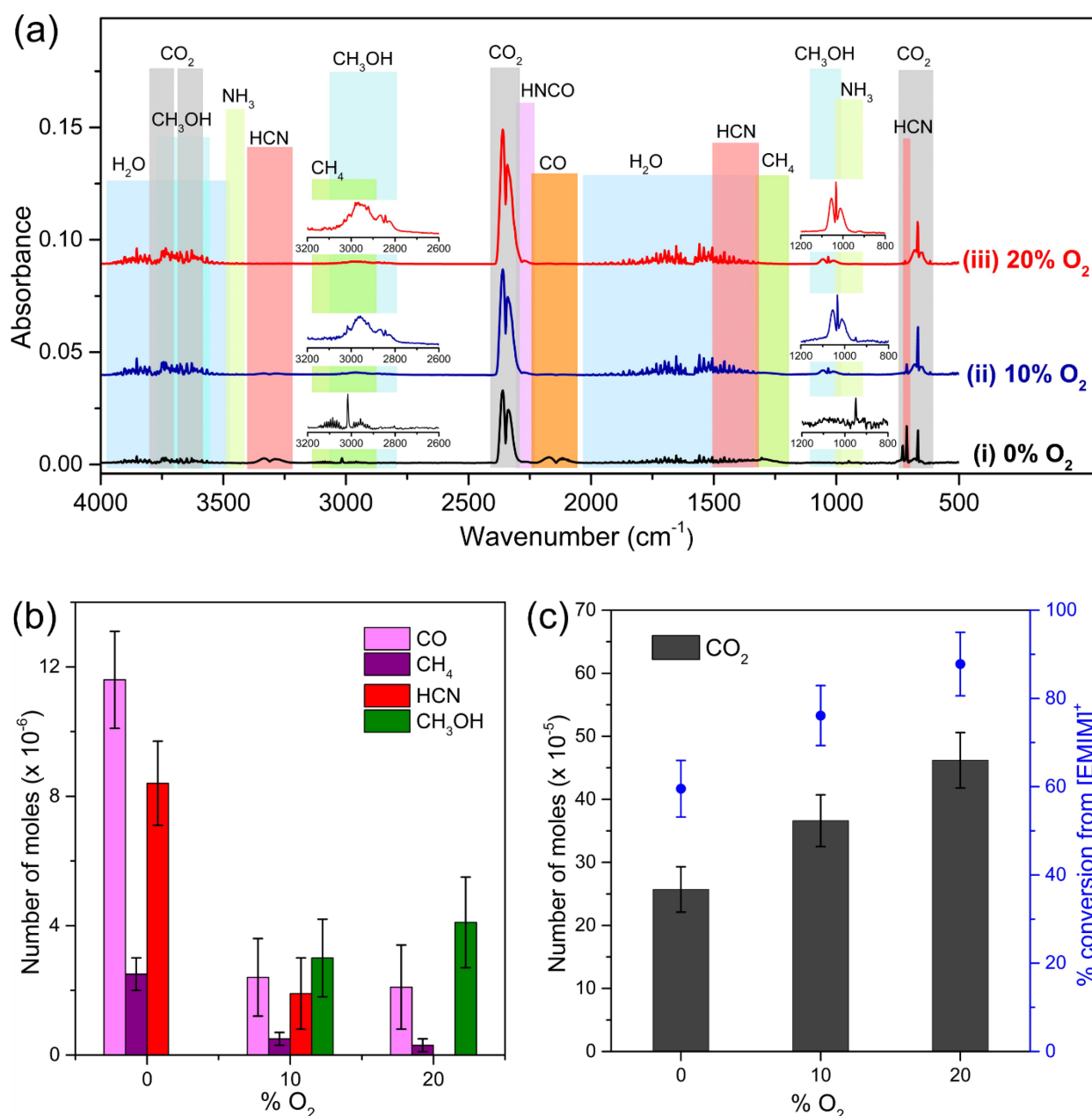


Figure 5. (a) FTIR spectra of the gas phase products formed in the reaction of ionic liquid [EMIM][CBH] and 92% hydrogen peroxide (H₂O₂) at different molecular oxygen (O₂) concentrations. Magnified sections depict exclusive formation of methanol (CH₃OH) vapor in presence of O₂ in the reaction environment. (b) Quantification of the major gaseous products [carbon monoxide (CO), methane (CH₄), hydrogen cyanide (HCN) and methanol (CH₃OH)] during the reactions as a function of molecular oxygen contents. (c) Amount of the primary combustion product carbon dioxide (CO₂) and its percentage conversion from the [EMIM]⁺ ion.

parent termolecular reaction. It is worth mentioning that the IL is inert to a molecular oxygen environment, that is, the latter does not directly react with the IL. Therefore, a possible reactive candidate could be the *in situ* generated intermediate (imino-methyl)boronic acid [(HO)₂BCH=NH, **i5**] (Figure 6, Scheme 1), which is formed due to successive hydroxyl (–OH) group insertions at the boron center of the anion from H₂O₂ molecules with accompanying products such as water (H₂O) and the hydroxyl ion (OH[–]) [Scheme 1, step 1]. The intermediate is also the global minimum on the PES for the original termolecular reaction ([CBH][–] + 2 H₂O₂) explaining the hypergolic ignition. In

i5, a hydrogen atom migration occurs from one of the hydroxyl group to the carbon atom followed by the cleavage of boron-carbon bond forming metaboric acid (HOB(O)OH) and methanimine (H₂C=NH) [step 2]. Further, the hydrogen atom transfers from HOB(O)OH to either carbon or nitrogen center of H₂C=NH results into [•]BO₂ and methylamino (H₃CNH[•]) [**p1**] or 1-amino-methylene ([•]H₂CNH₂) radicals [**p2**], respectively [step 3] with exoergic energy release in the range of 210 to 236 kJ mol^{–1} with respect to the separated initial reactants [**r1**].

For the atmospheric ignition, the molecular oxygen (O₂) could abstract a hydrogen atom from one of the hydroxyl

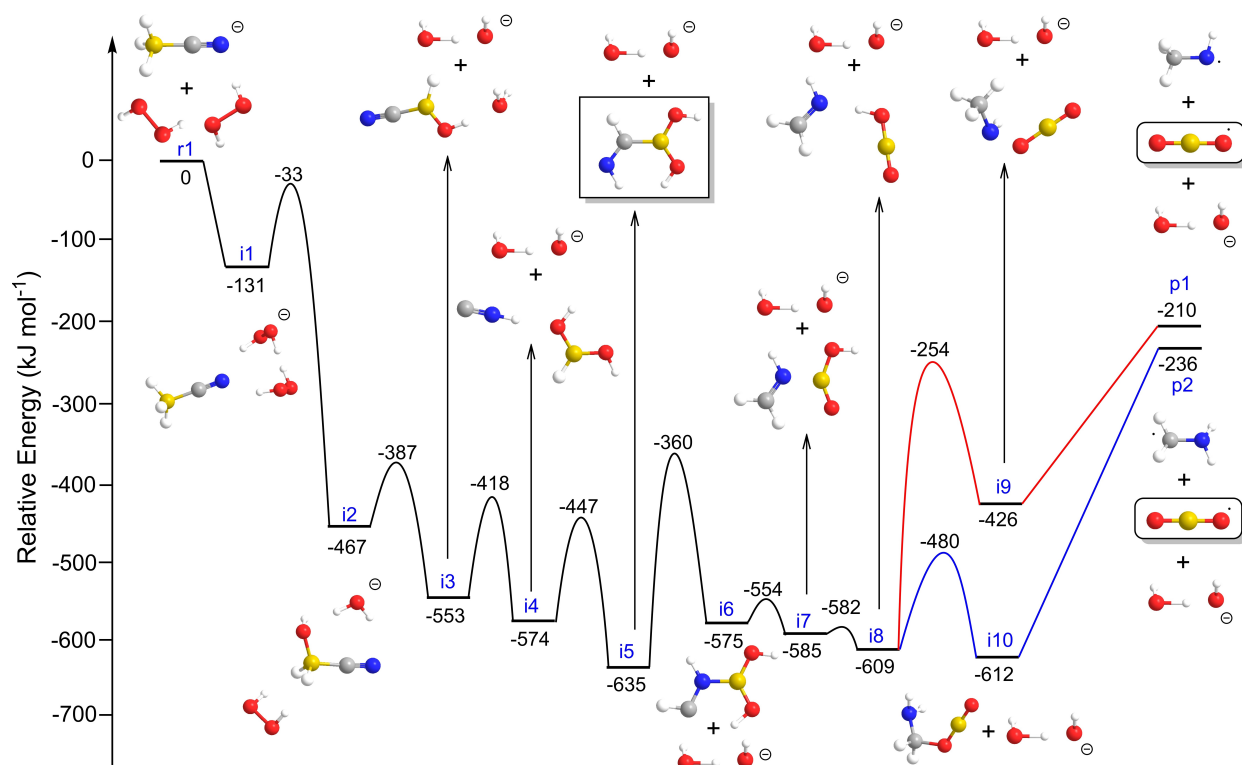
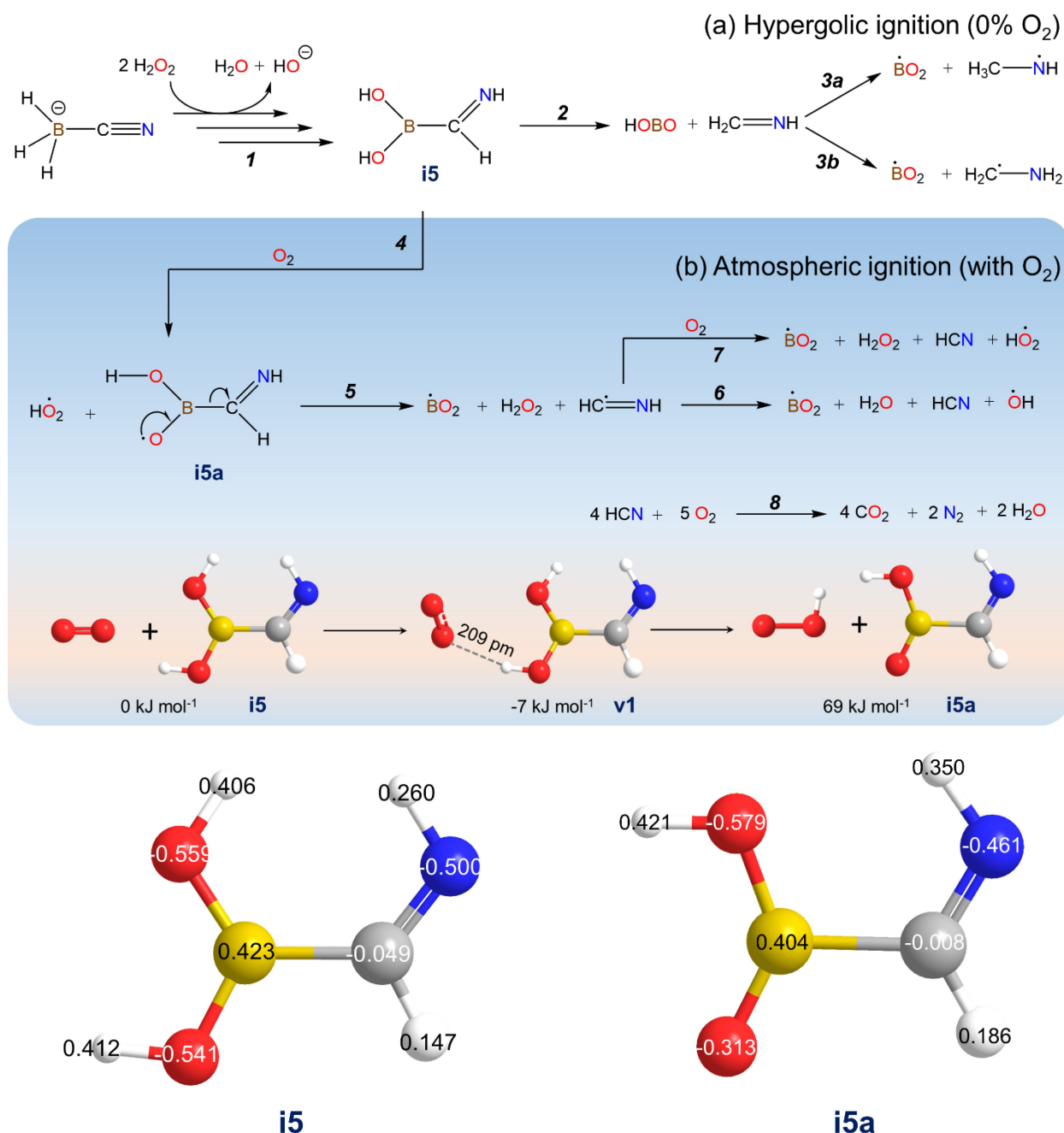


Figure 6. Potential energy surface (PES) for the exoergic termolecular reaction of $[\text{CBH}]^-$ with two molecules of H_2O_2 initiating the hypergolic ignition to yield the primary emitting intermediate boron dioxide ($^*\text{BO}_2$), adapted from Ref. [26]. Copyright 2025 with permission from American Chemical Society.

groups in **i5** yielding **i5a** [$^*\text{O}(\text{HO})\text{BCH}=\text{NH}$] and hydroperoxyl radical ($^*\text{HO}_2$) [step 4] at elevated temperature of the merged droplet (Figure 2). It is to be noted that the prior intermediates, **i1** to **i4** on the PES (Figure 6) are already bound complexes, and an approach by the molecular oxygen would be energetically unfavorable. Electronic structure calculations at the B3LYP/6-31G* level of theory predicts that **i5** and molecular O_2 forms a bound complex (**v1**) stabilized by 7 kJ mol^{-1} with respect to the separated reactants (**i5** and O_2) and undergoes an endoergic (69 kJ mol^{-1}) hydrogen atom transfer generating $^*\text{HO}_2$ and **i5a**. The endoergicity is compensated by the merging enthalpy (Table S4) evolved due to overall exoergic initial reactions in between $[\text{CBH}]^-$ and H_2O_2 (Figure 6). Subsequently, the second hydrogen atom transfer from **i5a** by the highly reactive $^*\text{HO}_2$ radical is very likely to occur followed by the boron-carbon bond cleavage, which produces $^*\text{BO}_2$, $^*\text{HC}=\text{NH}$ radicals and H_2O_2 [step 5]. The latter radical spontaneously reacts with the recycled H_2O_2 generating HCN, hydroxyl ($^*\text{OH}$) radical and water (H_2O) [step 6].^[44] The liberated $^*\text{OH}$ radical can essentially trigger facile oxidative decomposition of the initial intermediates in the primary termolecular reaction ($[\text{CBH}]^- + 2 \text{H}_2\text{O}_2$) energy profile. On the other hand, reaction of molecular oxygen (O_2) and $^*\text{HC}=\text{NH}$ radical regenerates $^*\text{HO}_2$ radical [step 7], which may further participate in the chain reactions, ultimately showing catalytic effects in the atmospheric ignition process. Starting from intermediate **i5**, intuitively it can be perceived that the interim stages to the $^*\text{BO}_2$ formation in presence oxygen [steps 4–7] are of lower energy barriers than those in the anaerobic case [steps 2–3]. It is also expected that the

exoergicity of the overall reaction steps in the presence of O_2 exceeds that of the reactions in hypergolic conditions and this is also corroborated in the higher maximum temperature recorded in the atmospheric ignition ($2,876 \pm 100 \text{ K}$) as compared to the hypergolic one ($2,521 \pm 100 \text{ K}$). The produced HCN via steps 6, 7 can undergo facile oxidation in excess molecular O_2 (number of moles $\sim 0.15 \pm 0.02$) at elevated temperature yielding CO_2 , N_2 and H_2O (step 8) via a complicated reaction sequence.^[42] Similar to HCN, gases like CO and CH_4 are subsequently oxidized *in situ* eventually forming CO_2 as the end product. These secondary formation channels of CO_2 also contribute to the higher yield of the species, implying the anion is also a minor source while the major source is the cation. It should be noted that similar reaction of the surrounding molecular oxygen is also reported in the case of the [EMIM][CBH]-WFNA reactant pair, where the bipropellant pair only ignited in presence of oxygen and deemed to be non-hypergolic under our droplet merging conditions with IL-to-oxidizer ratio up to 1:5 in a pure argon environment. Obviously the chosen intermediate in the present case could be one of many reactive intermediates which can react spontaneously with oxygen and facilitate the overall reaction sequence. Further computations are required to illustrate the hypothesis considering the reactivities of the appropriate intermediates towards molecular oxygen. A minor source of O_2 could be the decomposition of the oxidizer H_2O_2 , but its quantity is negligible compared to the abundant O_2 in the simulation environment. Moreover, it is evident from the differences in the experimental results that the molecular O_2 in the buffer gas



Scheme 1. Plausible reaction path of the (a) hypergolic and (b) atmospheric ignition events for the primary termolecular reaction involving [CBH][−] with two molecules of H₂O₂ yielding the key reaction intermediate [•]BO₂ via intermediate i5 [(iminomethyl)boronic acid]. Below, the Mulliken charge distribution on the optimized geometry of intermediates i5 and i5a are displayed.

mixture is actually responsible for the atmospheric ignition chemistry. The exclusive formation of methanol (CH₃OH) in the atmospheric ignition events could be plausibly attributed to the incomplete oxidation of the alkyl side chains of [EMIM]⁺.

Conclusions

This systematic study exploiting the novel droplet merging technique in an ultrasonic levitator apparatus reveals the

atmospheric ignition chemistry of a green hypergolic ionic liquid ([EMIM][CBH]) with oxidizer 92% H₂O₂. Notably, the ignition performance is greatly enhanced in the presence of molecular oxygen, such as significant shortening of *ignition delay* to 8 ± 4 ms, and extended the ignition duration along with more intense signal of the key emitting intermediate, boron dioxide ([•]BO₂). These observations are in line with the primary outcomes of our previous study of the [EMIM][CBH]-WFNA pair,^[25] where no ignition was noted in absence of molecular oxygen; yet a short *ignition delay* of 12 ± 5 ms was

achieved for the reaction in the simulated atmosphere with 20% oxygen. In the present study, the identified gaseous combustion products and their quantification reveals more carbon dioxide (CO₂) formation in aerobic conditions reflecting a nearly complete oxidation process. As an added advantage, formation of some of the toxic and pollutant gases, such as carbon monoxide (CO), hydrogen cyanide (HCN) and methane (CH₄) are suppressed due to subsequent oxidation by surrounding O₂ in the reaction medium at elevated temperatures. However, methanol (CH₃OH) is detected only in the case of atmospheric ignition reactions. The superior atmospheric ignition performance could be attributed to the plausible spontaneous reaction of a suitable intermediate species formed during the primary termolecular [CBH][−] + 2 H₂O₂ reaction, with molecular oxygen in the medium. Possible *in situ* formations of hydroxyl (*OH) and hydroperoxyl radical (*HO₂) can serve as catalysts further facilitating the reaction. Finally, this work as a case study introduces a conceptual advancement in the fundamental chemistry of bipropellants expanding their application range irrespective of the presence of molecular oxygen in the operational medium. Since the noted ignition delay for the parent hypergolic reaction is sluggish compared to the desirable ignition delay of ~10 ms or below, certain energetic materials as additives can be explored to promote the reaction faster. Nevertheless, further practical trials are necessary to implement the energetic ionic liquids (EIL) as next generation high performance universal propellants, applicable both in anaerobic space and in Earth's atmosphere, especially considering their expensive and challenging synthesis routes that require multiple extraction steps for extensive purification of the product.

Supporting Information

The Supporting Information contains detailed experimental methods, temporally resolved visualization of hypergolic ignition and ignition at 10% oxygen, flame temperature determination, quantification of molar ratios, assignments of the bands in FTIR spectra of the gas phase products, calibration curves of the major gaseous products, percentage yield of carbon dioxide (CO₂) from the [EMIM]⁺, and enthalpy changes during merging.

Other Supporting Materials

Supporting Movies S1 to S6 for the droplet merging events at 20, 10 and 0% oxygen.

Author Contributions

R.I.K. designed the experiments; S.B., and M.M. carried out the experiments; S.D.C., and S.S. performed the synthesis; S.B. wrote the original draft, S.B., R.S., and R.I.K. revised the draft and all of the authors discussed the data.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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