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Article

Synthesis and Physical and Chemical Properties of Hypergolic Chemicals such as *N*,*N*,*N*-Trimethylhydrazinium and 1-Ethyl-4-Methyl-1,2,4-Triazolium Salts

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Abstract: Hypergolic chemicals *N*,*N*,*N*-trimethylhydrazinium iodide, $[TMH]^+[I]^-$, and 1-ethyl-4-methyl-1,2,4-triazolium iodide, $[EMT]^+[I]^-$ were firstly synthesized by nucleophilic substitution (S_N2). The successful synthesis of hypergolic chemicals $[TMH]^+[I]^-$ and $[EMT]^+[I]^-$ was confirmed by IR and ^{1}H-NMR spectroscopy and, GC-mass spectrometry. Subsequently the hypergolic chemicals $[TMH]^+[X]^-$ ($X = CN^-, N_3^-, NO_3^-, NO_2^-, ClO_4^-, AlCl_4^-$) were prepared via an ion exchange reaction from $[TMH]^+[I]^-$ and $[EMT]^+[I]^-$, respectively. After that, a mixture of hypergolic chemicals was prepared by dissolving the synthesized hypergolic chemicals in 2-hydroxyethylhydrazine ($HOCH_2CH_2NHNH_2$). The physical and chemical properties of the mixture such as decomposition temperature (T_d), density (d), viscosity (η), and decomposition energy (ΔH_d) was then evaluated to determine suitability for use as liquid rocket fuels. The ignition delay (ID) time of the mixture of hypergolic chemicals with $[TMH]^+[N_3]^-$ and $[TMH]^+[CN]^-$ using H_2O_2 as an oxidizer was determined as 55.6 ms and 97.4 ms; respectively. The ID time of the mixture of hypergolic chemicals with $[EMT]^+[N_3]^-$; $[EMT]^+[CN]^-$; $[EMT]^+[AlCl_4]^-$; and $[EMT]^+[I]^-$ using H_2O_2 as an oxidizer was also determined as 18.0 ms; 32.6 ms; 27.6 ms; and 7.96 ms; respectively. The synthesized mixture of hypergolic chemicals could thus be used as a rocket propellant liquid fuel.

Keywords: hypergolic chemicals; rocket propellant fuel; *N*,*N*,*N*-trimethylhydrazinium salts; ethyl-methyl-triazolium salts

1. Introduction

Typical applications of propellant include fuel-like functions such as driving turbines, moving pistons, pumping fluids, starting aircraft engines, *etc.* [1]. For military applications, propellants are employed for firing bullets, missiles, and rockets, as well as ejecting pilots [2]. More commonly used high explosives such as RDX (1,3,5-trinitroperhydro-1,3,5-triazine) [3] or TNT (2,4,6-trinitrotoluene) [3] are inappropriate for rocket propellant due to poor performance, high sensitivities, high production costs, and detrimental decomposition gases [4–6]. Hydrazine and its methylated derivatives have become more and more important in the world of both war and peacetime propellants [7–9]. Furthermore, hydrazine (H_2N-NH_2) and methylated hydrazines have been widely used as hypergolic bipropellants in combination with oxidizers such as LOX (liquid oxygen), RFNA (red fuming nitric acid), or N_2O_4 (NTO = nitrogen tetroxide) [10–13].

In order to prevent an unwanted collection of fuel and oxidizer, it is important for the reactions to progress as rapidly as possible (minimal ignition delay time). In previous studies, 50 ms was the target for the maximum acceptable time for ignition delay; now the target may be as low as a few milliseconds depending on the application [14]. The phenomenon of spontaneous ignition after the reaction between the fuel and oxidizer is called Hypergol. After the first report of a hypergolic ionic liquid (IL) in 2008 [15], researchers have focused on synthesizing hypergolic ILs with low melting points, wide liquid ranges, high thermal stabilities, and short ignition-delay (ID) times [16–23]. Furthermore, hypergolic ILs could serve as bipropellant fuels over a variety of conditions due to the high thermal and chemical stabilities, low volatilities, and long liquid ranges [2,15]. A new family of dicyanoborates ILs has been synthesized in water with substituted nacyclic, N-cyclic, and azolium cations to meet the desired criteria required for well-performing fuels [2,15].

There is a great need for alternate oxidizers and hypergolic fuels that will have low toxicity, high density, long-term storability, and excellent performance. The extremely carcinogenic nature of hydrazine as well as its volatility presents difficulties for its handling [1,2,4]. Finding a way to replace hydrazine is one of the main goals of researchers in this field. The conversion of hydrazine and its derivatives into energetic ionic liquids (EILs) can be an alternative path of investigation for the replacement of hydrazine. Sabaté and Delalu [7] used *N*,*N*-dimethyl hydrazine dihydrochloride to synthesize a family of new hydrazinium salts, but these salts failed to detonate when exposed to a Bunsen burner flame. Salt-based energetic materials have lower vapor pressures and higher densities than neutral compounds [4]. Furthermore, salt-based energetic materials have lower sensitivities and higher thermal and chemical stabilities than commonly used high explosives. Salts based on fewer oxidizing anions were found to be more resistant to impact and friction, showing no signs of decomposition at the maximum loading for friction tests (FS > 360 N) [2]. For hypergolic EILs to successfully replace hydrazine they must possess shorter ignition delay (ID) times than the conditions leading to their own detonation.

In the review article of Sebastiao and her co-authors [2], they summarized the developing trends in the field of new energetic materials with emphasis on propulsion applications. Schneider *et al.* [15] developed new green hypergolic bipropellants that contain hydrogen peroxide and hydrogen-rich ionic liquids. They claimed that this class of ILs has the potential for providing non-cryogenic, high-performing, green bipropulsion for the first time. In the last few years, many salt-based compounds have been synthesized in which the salt contains anions of an inorganic nature (e.g., perchlorate, nitrate, and azide) as well as organic (e.g., 3-nitrotriazolate, picrate, and 5,5-azotetrazolate) [1,2,4]. Derivatives of hydrazine such as MeNH-NH_2, Me_2N-NH_2, and MeNH-NHMe [7,9,10] have also been studied to some extent.

The combination of an azo group with high-nitrogen heteroaromatic rings has been used to increase the heat of formation as well as to desensitize where the azo group is bonded to carbon and are known as diazoic dyes. The creation of a rather long chain of catenated nitrogen atoms by the attachment of an azo group to the nitrogen atoms of heteroaromatic rings generates unique properties in the synthesis material. Furthermore, in contrast to the toxicity of many azobenzene-based compounds, these high-nitrogen azo compounds are nontoxic and harmless [24,25]. Recently, Liu *et al.* [24] reported a new family of nitrogen-rich energetic salts based on 3,3′-diamino-4,4′-azo-1,2,4-triazole containing an *N*-*N*′-azo linkage and these salts exhibited excellent thermal stabilities, high detonation properties and reasonable sensitivities. To fulfill our interests for the synthesis of rocket propellant, TMH and EMT salts were prepared in the laboratory with various counter anions: CN^-, N_3^-, NO_3^-, NO_2^-, ClO_4^-, $AlCl_4^-$. To the best of our knowledge, there are no that show the synthesis route of *N,N,N*-trimethylhydrazinium and 1-ethyl-4-methyl-1,2,4-triazolium salts with these counter anions.

2. Experimental

2.1. Materials and Methods

The starting materials dimethylhydrazine and 1,2,4-triazole used in this study were of analytical reagent grade and used directly as purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Ethyl iodide, methyl iodide, acetonitrile, 2-hydroxyethylhydrazine, and sodium salt with varying anions CN^-, N_3^-, NO_3^-, NO_2^-, ClO_4^-, $AlCl_4^-$ were received from Sigma-Aldrich in an analytical grade. DSC (DSC 800, PerkinElmer, Seoul, Korea) was used to measure the decomposition temperature (T_d) and decomposition energy (ΔH_d). The FT-IR spectrum was taken using a ThermoFisher scientific IR spectrophotometer. ^1H-NMR spectra were recorded at room temperature on a Varian Inova 600 NMR spectrometer with tetramethyl silane as an internal standard and DMSO as a solvent. The TMH and EMT salts with the variation of counter anions I^-, N_3^-, CN^-, NO_2^-, NO_3^-, ClO_4^-, and $AlCl_4^-$ were subjected to ignition tests to determine their ignition delay time with common propulsion oxidizer (98%, H_2O_2). A high-speed camera was used to take the picture of ID time test. Also, collected gaseous products were collected by using gas sampling bag after the ignition of hypergolic chemicals and H_2O_2 in home-made gas reactor and analyzed by FT-IR spectrometer.

2.2. Synthesis of *N,N,N*-Trimethylhydrazinium Salts, $[TMH]^+[X]^-$

N,N,N-trimethylhydrazinium iodide, $[TMH]^+[I]^-$, was prepared by following the previously reported method by S_N2 nucleophilic substitution reaction as shown in Figure 1 [8,26]. 1,1-dimethylhydrazine (1.26 mL, 20.1 mmol) was dispersed in 20 mL of dry THF and then the methyl iodide (20.1 mmol, 2.98 mL) was added by dropping with continuous stirring. The reaction continued for 8 h at 25 °C. Here, the methyl iodide reacted with 1,1-dimethylhydrazine in THF at room temperature by vicarious nucleophilic substitution of hydrogen to produce TMH iodide. Purification of the TMH iodide was performed by washing several times with ether before it was then dried in a vacuum oven at room temperature for 6 h. Next, the ion exchange reaction was performed by the further treatment of TMH iodide (0.02 mmol) with NaX (X = CN^-, N_3^-, NO_3^-, NO_2^-, ClO_4^-, $AlCl_4^-$) (0.02 mmol) in the medium of acetonitrile as solvent at room temperature for 72 h. The resulting reaction mixture was filtered and the acetonitrile was evaporated from the filtrate to obtain the final product.

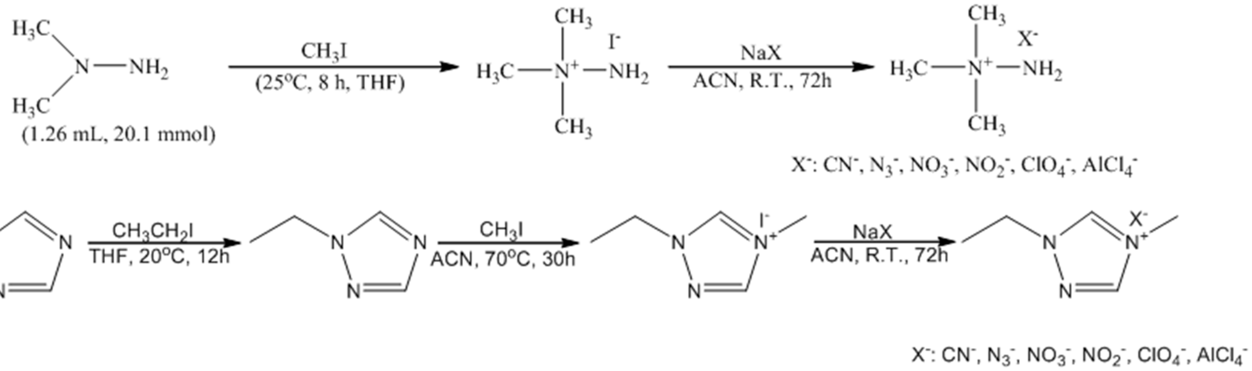

Figure 1. Schematic synthesis of *N*,*N*,*N*-trimethylhydraznium salts, $[TMH]^+[I]^-$, (upper) and 1-ethyl-4-methyl-1,2,4-triazole salts, $[EMT]^+[X]^-$, (down) by ion-exchange reaction after S_N2 reaction.

2.3. Synthesis of 1-Ethyl-4-Methyl-1,2,4-Triazolium Salts, $[EMT]^+[X]^-$

Figure 1 shows the synthesis of the hypergolic chemical with $[EMT]^+[I]^-$. In detail, 1,2,4-triazole (2.50 g, 36.2 mmol) was dissolved in THF (100 mL) and the ethyl iodide (2.98 mL) was added by dropping. The reaction was performed at 20 °C for 12 h. The resulting product was further treated with methyl iodide (3.50 mL, 43.5 mmol) in the medium of acetonitrile (100 mL) at 70 °C for 30 h with continuous stirring. Then, the reaction mixture was washed with ether and dried in a vacuum oven at room temperature. Next, the EMT iodide (0.02 mmol) was treated with 0.02 mmol of NaCN in acetonitrile (100 mL) at room temperature for 72 h. The resulting product was filtered, and the filtrate was evaporated to get EMT cyanide. The same process was repeated to obtain EMT salts with various counter anions; N_3^-, NO_2^-, NO_3^-, ClO_4^-, $AlCl_4^-$.

3. Results and Discussion

We believe that a better understanding of existing systems is necessary for the effective design of energetic materials for the replacement of conventional hypergolic bipropellants. All oxidizers such as RFNA, NTO, cryogens, *etc.* are extremely hazardous by their nature and so reduction of those hazards is beneficial, even though the resulting materials might not be completely harmless. Due to the less-toxic vapor, high performance, and environmentally benign decomposition products of hydrogen peroxide, it appears to be a promising oxidizer with considerably fewer difficulties in handling than nitric acid and N_2O_4. Here, we synthesized TMH and EMT hypergolic chemicals to take an important step towards a lower-toxicity propulsion system with hydrogen peroxide as oxidizer. As you can see in Figure 1, the S_N2 nucleophilic substitution reactions of dimethylhydrazine with methyl iodide [8] and subsequent ion exchange reactions with sodium salt were easily performed. Here, $[TMH]^+[I]^-$ was produced after the reaction of methyl iodide with dimethyl hydrazine and the ion exchange reaction was performed with NaX (X = CN^-, N_3^-, NO_3^-, NO_2^-, ClO_4^-, $AlCl_4^-$). The formation of EMT salts by nucleophilic substitution reactions (two times) followed by ion exchange reaction was also performed. Methyl iodide (first) and ethyl iodides (second) were used in the two nucleophilic substitution reactions.

Figure 2a shows the ^{1}H-NMR spectrum of the synthesized $[TMH]^+[I]^-$. In the ^{1}H-NMR spectra of $[TMH]^+[I]^-$ with $CDCl_3$ as solvent and tetramethyl silane (TMS) as an internal standard, two resonances were observed. The hydrogen atoms of the $-CH_3$ groups resonate at approximately $\delta = 3.29$ ppm, whereas the protons of the $-NH_2$ groups have resonances in the 6.10 ppm [7]. In the IR spectrum, Figure 2b, the most intense vibration corresponds to the out-of plane bending of the N–H and C–H bonds ($\nu \approx 1090$ and ~900 cm^{-1}). The remainder of the vibrations can be assigned as follows (ν = stretching, δ = in-plane bending, γ = out-of-plane bending): 2950–3005 [ν_s(N–H) and ν_{as}(N–H)], 2750–2860 [ν_s(C–H) and ν_{as}(C–H)], 1550–1760 [δ_s(N–H) and δ_{as}(N–H)], 1270–1490 [γ(N–H)], 1400–1510 cm^{-1} ν(C–N) and 730–860 cm^{-1} [ν(C–N) + ν(N–N)] [7,8,27,28].

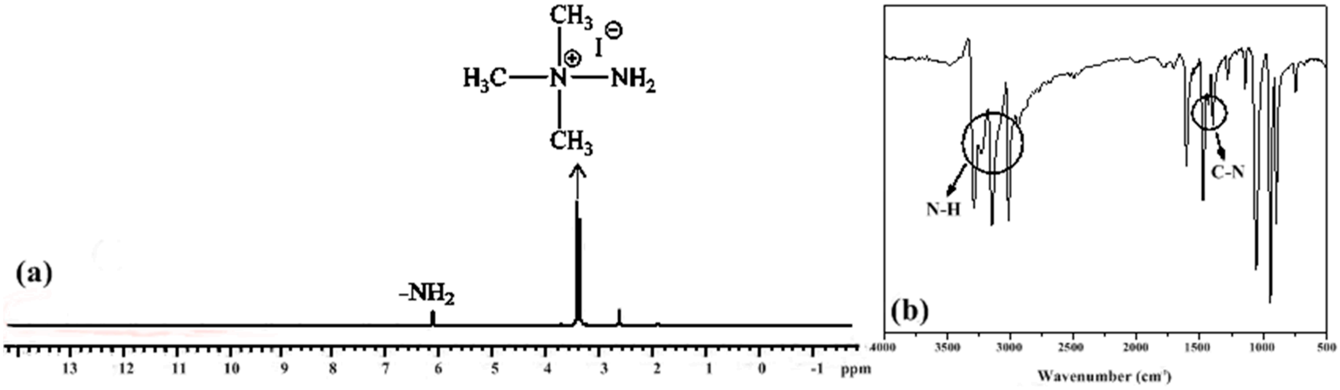

Figure 2. ^{1}H-NMR (**a**) and FT-IR spectrum (**b**) of the synthesized *N*,*N*,*N*-trimethylhydrazinium iodide, $[TMH]^+[I]^-$.

Figure 3 shows the ^{1}H NMR spectrum (**a**) and GC-mass data (**b**) of $[EMT]^+[I]^-$ as a hypergolic chemical. The ^{1}H NMR spectrum of $[EMT]^+[I]^-$ with $CDCl_3$ as solvent and TMS as an internal standard shows δ = 1.43, 4.4, 9.1, 10.0, and 3.9 ppm for the protons located at the (**a**–**e**) positions of $[EMT]^+[I]^-$ as shown in Figure 3a. The GC-mass spectrum of $[EMT]^+[I]^-$ in Figure 3b shows the ionic fragments having weight 30, 39, 41, 46, 56, 62, 69, 75, 82, 96, and 111, in which the biggest fragment (weight 111) is equivalent to the M^{+1} peak of $[EMT]^+[I]^-$ [29]. All prepared $[EMT]^+[I]^-$ is stable in air and can be stored for extended periods.

The obtained hypergolic chemicals, $[TMH]^+[X]^-$ ($X = CN^-, N_3^-, NO_3^-, NO_2^-, ClO_4^-, AlCl_4^-$) were in solid form. In order to prepare liquid hypergolic chemicals, we dissolved 0.15 g solid $[TMH]^+[X]^-$ in 0.85 mL of 2-hydroxyethylhydrazine. After that we measured the physical and chemical properties of the mixture of hypergolic chemicals with $[TMH]^+[X]^-$ and 2-hydroxyethylhydrazine. Table 1 shows the physical and chemical properties of the mixture. The mixture has a very high decomposition temperature (T_d) above 184 °C and minus (−) decomposition energy (ΔH_d). This means that the synthesized hypergolic chemicals with $[TMH]^+[X]^-$ and $HOCH_2CH_2NHNH_2$ have very good thermal stability.

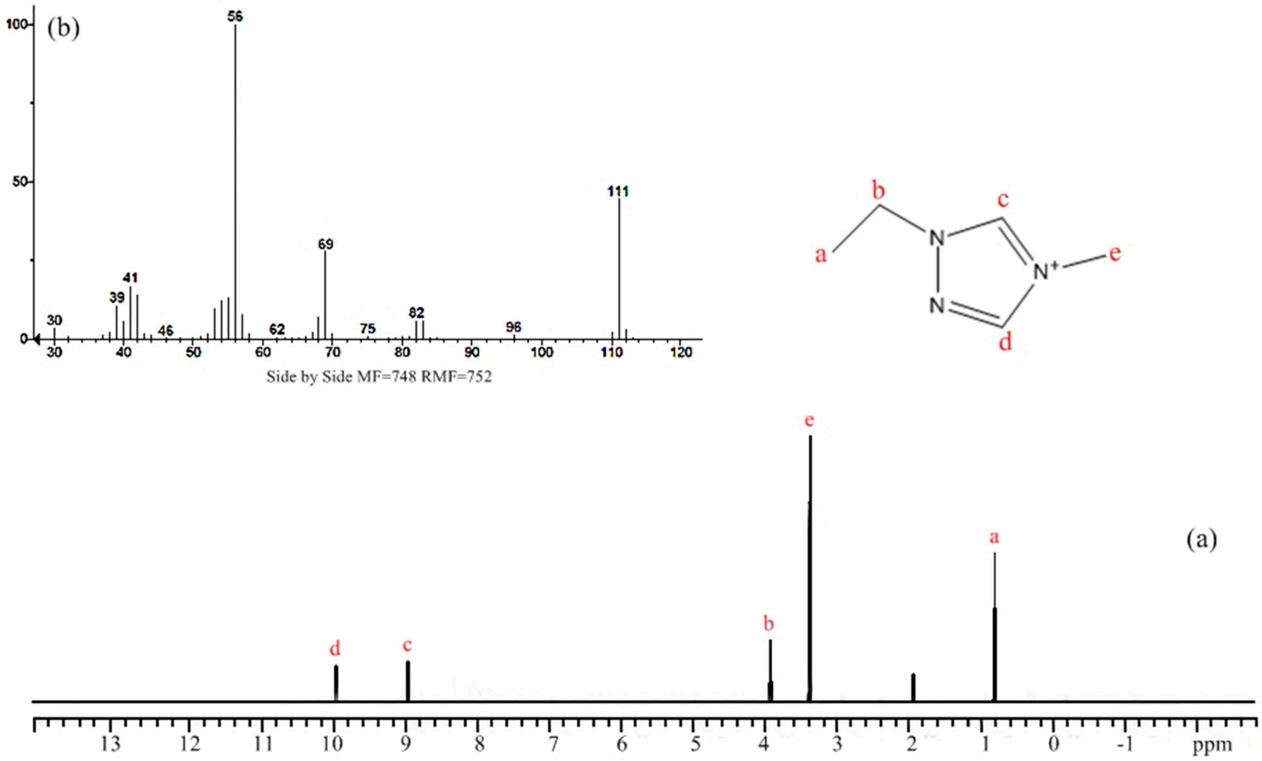

Figure 3. ^{1}H-NMR spectrum (**a**) and GC-mass data (**b**) of 1-ethyl-4-methyl-1,2,4-triazolium iodide, $[EMT]^+[I]^-$.

Table 1. Physical and chemical properties of the mixture solution with *N*,*N*,*N*-trimethylhydrazinium salts and 2-hydroxyethylhydrazine [a].

Cation	Anion	T_d [b] (°C)	d [c] (g/cm^3)	ΔH_d [d] (kJ/mol)	η [e] (cP)	ID [f] (ms)
$C_3H_{11}N_2^+$	N_3^-	198.8	1.10	−18.31	216	55.6
	CN^-	192.0	1.09	−50.65	220	97.4
	NO_2^-	190.7	1.13	−41.19	243	175.0
	NO_3^-	195.2	1.15	−46.63	185	497.2
	ClO_4^-	191.0	1.13	−37.63	176	970.2
	$AlCl_4^-$	184.3	1.14	−80.06	162	341.0
	I^-	194.2	1.09	−64.52	203	190.3

[a] *N*,*N*,*N*-Trimethylhydrazinium salts (0.15 g) were dissolved in 2-hydroxyethylhydrazine (0.85 mL); [b] T_d was measured by DSC; [c] Density (at 25 °C); [d] ΔH_d was obtained from DSC; [e] Viscosity (at 27.7 °C); [f] Ignition delay time was detonated with H_2O_2.

The density (g/cm^3) and viscosity (cP) of the mixture was in the range of 1.09~1.15 and 162~216, respectively. Several energetic salts and ILs with considerably reduced ID times have already been designed [14,17,18]. In order to determine their applicability as rocket propellant liquid fuels, we determined the ID times by high-speed-camera for hypergolic chemical reactions between the synthesized hypergolic chemicals and H_2O_2 as oxidizer. The ID times of $[TMH]^+[N_3]^-$ and $[TMH]^+[CN]^-$ were 55.6 and 97.4 milliseconds (ms), respectively. This result indicates that a mixture of hypergolic chemicals such as $[TMH]^+[N_3]^-$ and $[TMH]^+[CN]^-$ can be used as rock propellant liquid fuels.

Figures 4–6 show the ID time photographs of the mixture of hypergolic chemicals with $[TMH]^+[N_3]^-$, $[TMH]^+[CN]^-$ and $[TMH]^+[I]^-$ and $HOCH_2CH_2NHNH_2$, respectively, using H_2O_2 as oxidizer. The ID times of mixtures with $[TMH]^+[N_3]^-$, $[TMH]^+[CN]^-$ and $[TMH]^+[I]^-$ and $HOCH_2CH_2NHNH_2$ was determined as 55.6, 97.4, and 109.3 milliseconds, respectively. As a result it is shown that the mixture of hypergolic chemicals with $[TMH]^+[N_3]^-$ could be used as rocket propellant liquid fuel.

In order to determine the presence of toxic chemicals, we measured the FT-IR spectrum of the explosion gas after ignition of the hypergolic chemicals with $[TMH]^+[CN]^-$ $HOCH_2CH_2NHNH_2$ using H_2O_2 as oxidizer and this showed the FT-IR spectrum in Figure 7. The characteristic peaks at 1111, 2230, around 3000, and around 3600 cm^{-1} due to the NN stretch of hydrazine, CO_2 stretch, NH_2, and NH stretch appeared. However, we could not observe the characteristic peaks of a nitro group in this experiment.

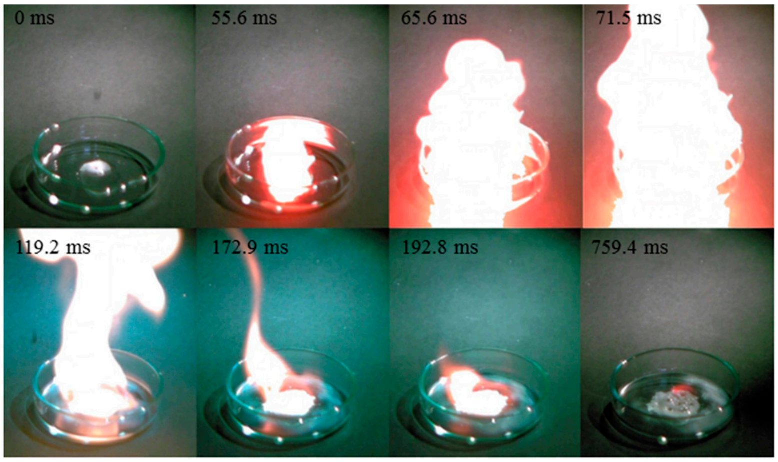

Figure 4. ID time photographs of the mixture hypergolic chemicals with $[TMH]^+[N_3]^-$ and $HOCH_2NHNH_2$ using H_2O_2.

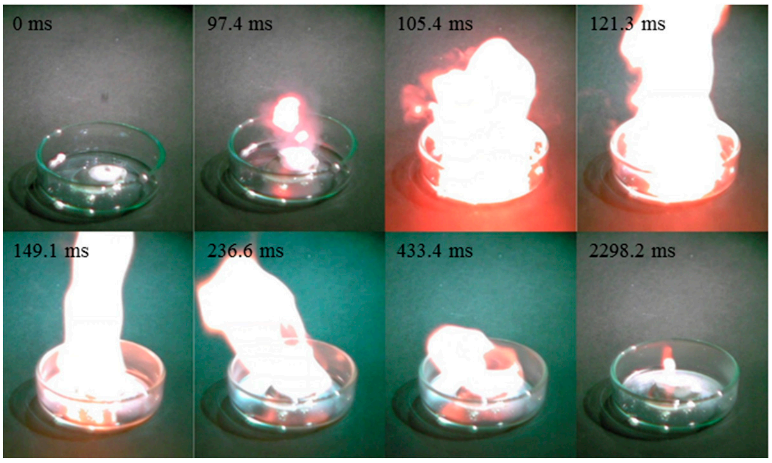

Figure 5. ID time photographs of the mixture hypergolic chemicals with $[TMH]^+[CN]^-$ and $HOCH_2CH_2NHNH_2$ using H_2O_2.

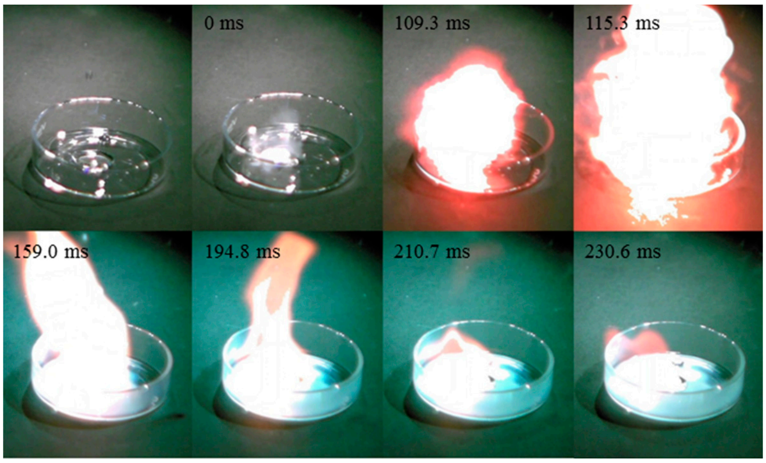

Figure 6. ID time photographs of the mixture hypergolic chemicals with $[TMH]^+[I]^-$ and $HOCH_2CH_2NHNH_2$ using H_2O_2.

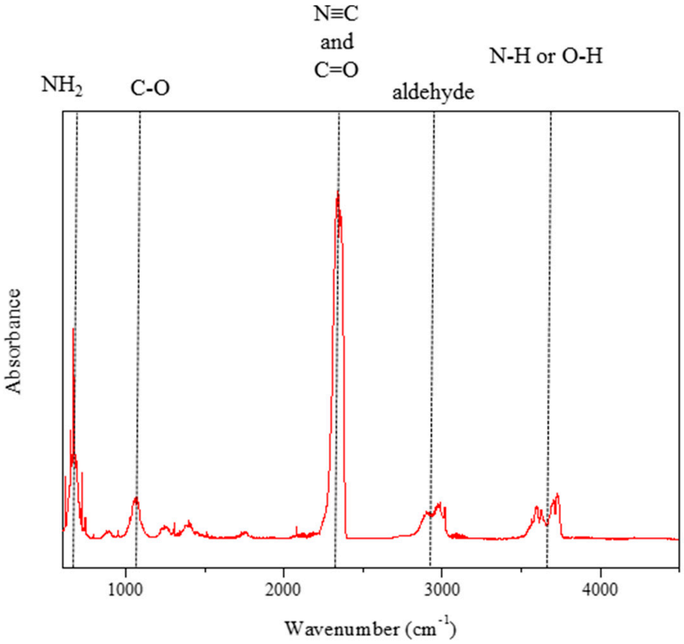

Figure 7. FT-IR spectrum of explosion gas of an mixture hypergolic chemicals with $[TMH]^+[CN]^-$ and $HOCH_2CH_2NHNH_2$ using H_2O_2.

Table 2 shows the physical and chemical properties of the mixture of hypergolic chemicals with $[EMT]^+[X]^-$ (X = CN^-, N_3^-, NO_3^-, NO_2^-, ClO_4^-, $AlCl_4^-$) and $HOCH_2CH_2NHNH_2$. The mixture has a very high decomposition temperature (T_d) above 117 ° C and minus (−) decomposition energy (ΔH_d). This means that the synthesized hypergolic chemicals with $[EMT]^+[X]^-$ and $HOCH_2CH_2NHNH_2$ have very good thermal stability. The density (g/cm^3) and viscosity (cP) of the mixture was in the range of 1.15~1.25 and 115~938, respectively.

We also determined the ID times using a high-speed camera for the reaction between the synthesized hypergolic chemicals and H_2O_2 as oxidizer. The ID times of $[EMT]^+[N_3]^-$, $[EMT]^+[CN]^-$, $[EMT]^+[AlCl_4]^-$, and $[EMT]^+[I]^-$ were 18.0, 32.6, 27.6, and 7.97 milliseconds (ms), respectively. This result indicated that the mixture hypergolic chemicals could be used as rocket propellant liquid fuel. The other mixture could be applied as a rocket propellant liquid fuel based on the ID time test.

Table 2. Physical and chemical properties of the synthesized 1-ethyl-4-methyl-1,2,4-triazolium salts dissolved at 2-hydroxyethylhydrazine [a].

Cation	Anion	T_d [b] (°C)	d [c] (g/cm^3)	ΔH_d [d] (kJ/mol)	η [e] (cP)	ID [f] (ms)
$C_5H_{10}N_3^+$	N_3^-	121	1.15	−36.5	201	18.0
	CN^-	175	1.19	−37.8	250	32.6
	NO_2^-	119	1.29	−53.2	248	489.0
	NO_3^-	117	1.11	−22.2	115	426.0
	ClO_4^-	207	1.21	−105.3	165	524.0
	$AlCl_4^-$	232	1.21	−32.9	191	27.6
	I^-	136	1.22	−82.4	938	7.97

[a] 1-Ethyl-4-methyl-1,2,4-triazolium salts (0.3 mL) were dissolved in 2-hydroxyethylhydrazine (0.7 mL); [b] T_d was measured by DSC; [c] Density (at 25 °C); [d] ΔH_d was obtained from DSC; [e] Viscosity (at 27.7 °C); [f] Ignition delay time was determined by detonation with H_2O_2.

Figures 8–10 show the ID time photographs of the mixture with $[EMT]^+[N_3]^-$, $[EMT]^+[CN]^-$ and $[EMT]^+[I]^-$, and $HOCH_2CH_2NHNH_2$, respectively, using H_2O_2 as oxidizer. The ID time of the mixture was determined as 18.0, 32.6, and 7.97 milliseconds, respectively. As a result, the mixture with $[EMT]^+[X]^-$ ($X = N_3^-$, CN^-, and I^-) could be used as a rocket propellant liquid fuel based on the ignition delay time.

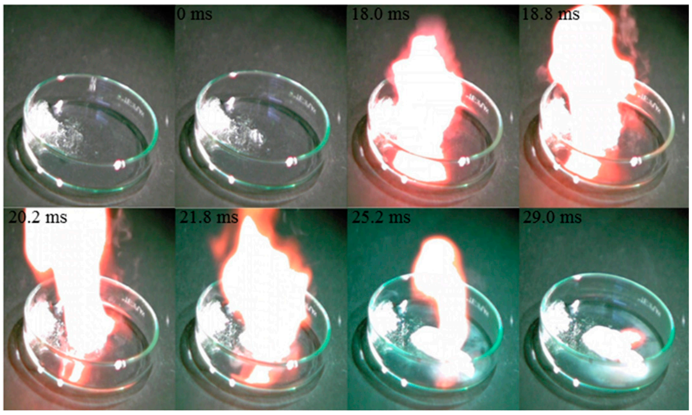

Figure 8. ID time photographs of the mixture hypergolic chemicals with $[EMT]^+[N_3]^-$ and $HOCH_2CH_2NHNH_2$ using H_2O_2.

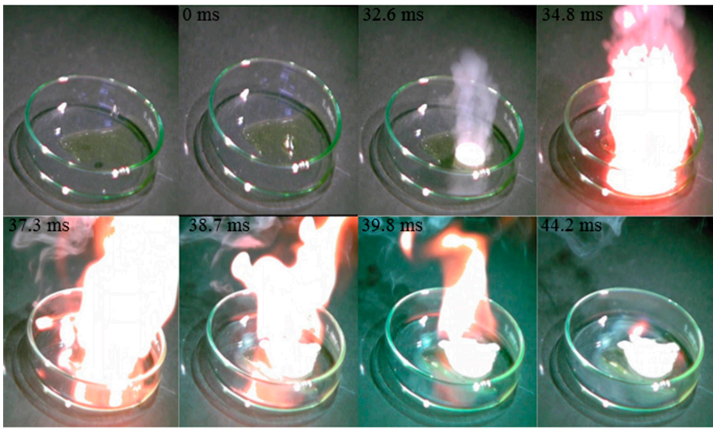

Figure 9. ID time photographs of the mixture hypergolic chemicals with $[EMT]^+[CN]^-$ and $HOCH_2CH_2NHNH_2$ using H_2O_2.

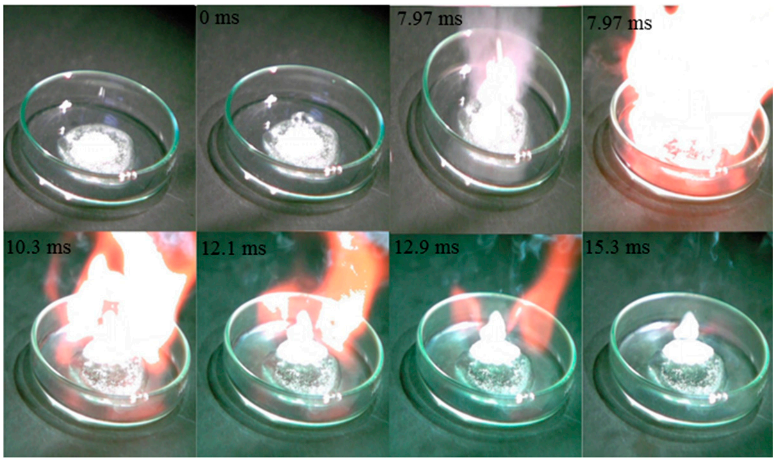

Figure 10. ID time photographs of the mixture hypergolic chemicals with $[EMT]^+[I]^-$ and $HOCH_2CH_2NHNH_2$ using H_2O_2. Figure 11 shows the FT-IR spectrum of the explosion gas of a mixture with $[EMT]^+[CN]^-$ and $HOCH_2CH_2NHNH_2$ using H_2O_2. The characteristic peaks were assigned as shown in Figure 10. However, nitro group peak indicating toxic chemicals were not observed in this experiment.

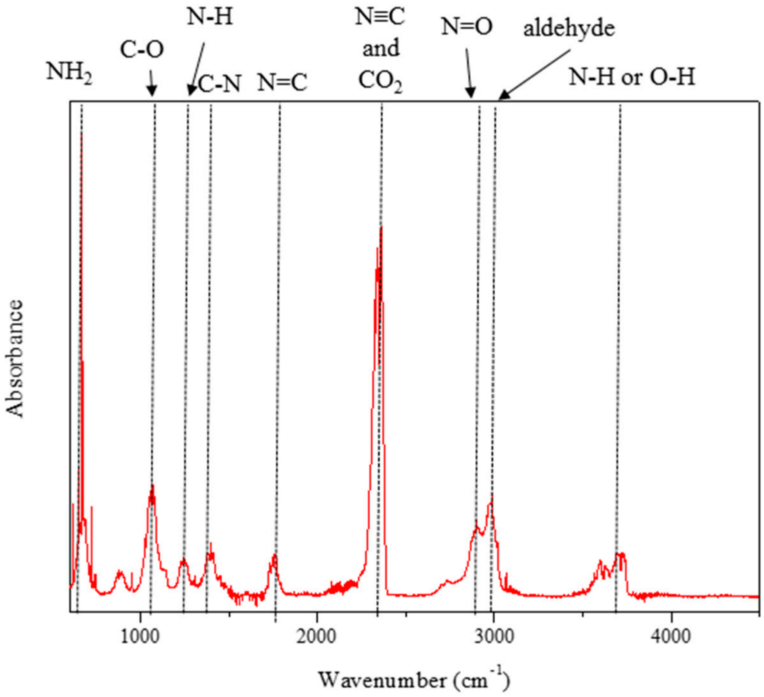

Figure 11. FT-IR spectrum of explosion gas of an mixture hypergolic chemicals with $[EMT]^+[CN]^-$ and $HOCH_2CH_2NHNH_2$ using H_2O_2.

4. Conclusions

We successfully synthesized the advanced hypergolic chemicals $[TMH]^+[X]^-$ and $[EMT]^+[X]^-$ ($X = I^-$, CN^-, N_3^-, NO_3^-, NO_2^-, ClO_4^-, and $AlCl_4^-$) by ion-exchange reaction following an S_N2 reaction. The physical and chemical properties of the synthesized mixture of hypergolic chemicals with $[TMH]^+[X]^-$ and $[EMT]^+[X]^-$ were evaluated. We were able to conclude the following:

(1) The synthesized hypergolic chemicals with $[TMH]^+[X]^-$ and $[EMT]^+[X]^-$ have good thermal stability.
(2) The mixture of hypergolic chemicals with $[TMH]^+[N_3]^-$ have a low ID time of 55.6 ms.
(3) The mixture of hypergolic chemicals with $[EMT]^+[N_3]^-$, $[EMT]^+[CN]^-$, and $[EMT]^+[I]^-$ have very short ID times (18.0, 32.6, and 7.97 ms, respectively).
(4) Toxic nitro group-contained chemicals were not detected after detonation between hypergolic chemicals and H_2O_2 as oxidizer.
(5) A synthesized mixture hypergolic chemicals such as $[TMH]^+[N_3]^-$, $[EMT]^+[N_3]^-$, $[EMT]^+[CN]^-$, and $[EMT]^+[I]^-$ could be used as rocket propellant liquid fuel.

Acknowledgments

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Author Contributions

S.-H.C. conceived the underlying idea of the paper. S.-H.C. and Y.-S.K. designed the experiment. Y.-S.K., G.-H.S. and T.-K.N. performed the experiment. S.-H.C. and Y.-S.K. analyzed the data and wrote the paper. S.-H.C. and Y.-S.K. revised the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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