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Trialkylsulfonium Thiocyanate Ionic Liquids: Investigation on Temperature-Dependent Ignition Behavior of Green Hypergolic Propellants

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ABSTRACT

Three trialkylsulfonium thiocyanate ionic liquids (ILs) are presented as fuel candidates for novel green hypergolic propellants. The physical and chemical properties such as density, viscosity, melting point and decomposition temperature as well as the enthalpy of formation of the ILs were determined. Further, the research focused on the potential of the ILs as fuel components for hypergolic propellants with highly concentrated hydrogen peroxide as oxidizer. For this, the theoretical maximum specific impulses of the propellants were calculated with NASA CEA. To evaluate the ignition delay times of the hypergolic propellants, drop tests were carried out. These were conducted not only at ambient conditions but also at lower levels of fuel temperature. It was found that all three propellant combinations still ignited reliably at temperature levels down to −25°C, however, the average ignition delay increased at lower temperatures. Overall, not only three promising hypergolic fuels were identified, but also important insights into the temperature-dependent ignition behavior of hypergolic ionic liquid-based propellants with thiocyanate anions were obtained.

1 | Introduction

In satellite orbit-control engines, hypergolic propellants are mainly used because they are storable and usually have high specific impulses [1]. In this type of space propellants, ignition of oxidizer and fuel components occurs spontaneously when they come into contact [2]. This offers several advantages such as reliable re-ignition capability and elimination of an additional ignition device [3]. In the last decades, hydrazine or derivatives such as MMH (monomethylhydrazine) or UDMH (unsymmetrical dimethylhydrazine) as fuels together with NTO (dinitrogen tetroxide) as oxidizer were standardly used [4]. These components are not only toxic, but in case of the hydrazines also carcinogenic and environmentally hazardous [5]. Thus, research on novel, so-called green propellants is ongoing to replace these conventional utilized substances [6].

Highly concentrated hydrogen peroxide is a suitable green oxidizer, offering very advantageous properties such as low toxicity, low vapor pressure, high density and non-hazardous decomposition products water and oxygen [7,8].

A promising class to consider in the exploration of new fuel components are ionic liquids (ILs) [9,10]. By definition, ILs are salts with melting points below 100°C or 150°C [11,12]. They feature negligible vapor pressures, high decomposition temperatures and high densities [13,14]. Furthermore, the cation and anion design can be adapted to adjust the properties of ILs to the requirements of the respective application. In the framework of propellant research, there has been plenty of work on ILs as fuels and WFNA (white fuming nitric acid) as oxidizer in recent years [15–17]. However, WFNA as oxidizer is considered as less green compared to highly concentrated

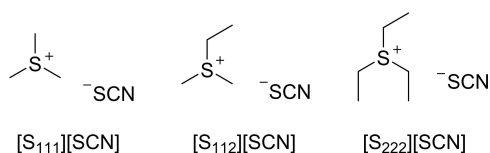hydrogen peroxide due to its high corrosivity and toxicity 18,[19].

Our research group has been working on hypergolic propellants consisting of ILs and hydrogen peroxide, also referred to as high test peroxide (HTP), for the last few years. Within the scope of previous work, ionic liquids with thiocyanate anions were identified as suitable fuels, because some of them exhibit hypergolicity with HTP without further additives. The first two thiocyanate ILs discovered to exhibit intrinsic hypergolicity with HTP were [BMIM][SCN] and [EMIM][SCN] with ignition delay times of 45.0 ms and 31.7 ms, respectively [20]. Further, pyridinium- and pyrrolidinium-based ILs as well as protic imidazolium-based ILs were investigated [21–22].

In the present study, three new trialkylsulfonium-based ILs with thiocyanate anions are introduced as fuel candidates. The focus of this work is on the temperature-dependent ignition behavior of oxidizer and fuel. Hereby it was investigated whether hypergolic ignition still occurs at low fuel temperatures and how the ignition delay evolves. This aspect is particularly important to ensure the reliable ignitability of the two fuel components even under fluctuating external conditions in a spacecraft.
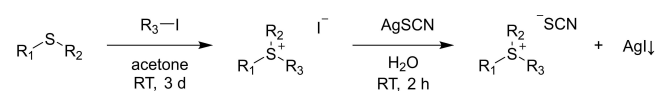
2 | Results and Discussion

2.1 | Synthesis and Characterization

Scheme 1 shows the structures of the three ILs that were designed and synthesized. Thiocyanate anions were chosen, as
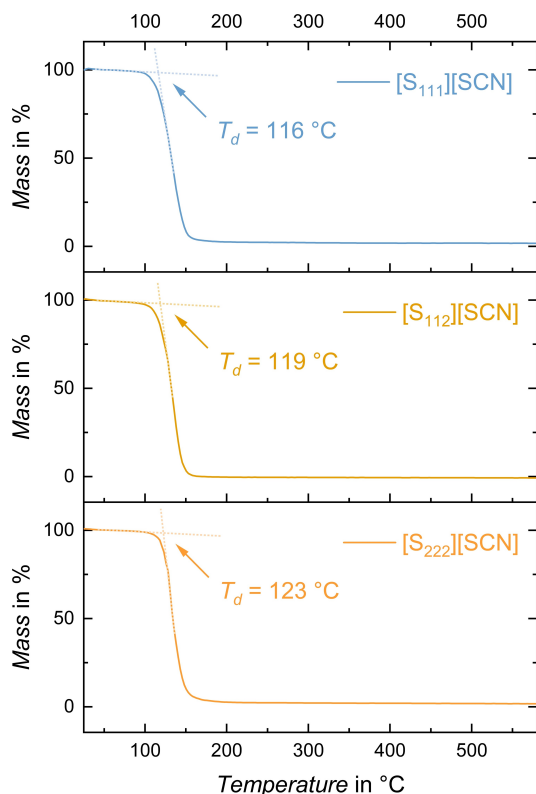
ILs with these anions showed hypergolic behavior with HTP before [20–22]. Trialkylsulfonium-based cations were selected because they exhibited very low viscosities with dicyanamide anions as described by Gerhard et al. [23]. Therefore, it was expected that ILs with these class of cations and thiocyanate anions would also provide relatively low viscosities compared to other SCN-based ILs, which is advantageous for short ignition delays as well as for pumping and spraying of the propellants [24,25]. The three selected substances are [S_{111}][SCN] (trimethlylsulfonium thiocyanate), [S_{112}][SCN] (ethyldimethylsulfonium thiocyanate) and [S_{222}][SCN] (triethylsulfonium thiocyanate).

An overview of the synthetic pathway of the three ILs is shown in Scheme 2, whereas the first step was performed only for [S_{112}][SCN]. The uniformly substituted iodide precursors were commercially available. Ethyldimethylsulfonium iodide was prepared by reaction with dimethyl sulfide and ethyl iodide in acetone. In a salt metathesis reaction with silver thiocyanate, which was obtained *in situ* by silver nitrate and potassium thiocyanate, the three desired trialkylsulfonium thiocyanate ILs were formed upon precipitation of silver iodide from the respective trialkylsulfonium iodide. After purification, the ILs were dried under reduced pressure. Characterization was performed by NMR and IR spectroscopy. Purity of the compounds was determined by ion chromatography and the water content was checked by volumetric Karl Fischer titration. Detailed information on the synthesis and characterization of the ILs can be found in the Supporting Information.

2.2 | Thermal and Physical Data

Table 1 shows that [S_{111}][SCN] is solid at room temperature with a melting point of 66°C, whereas [S_{112}][SCN] (0°C) and [S_{222}][SCN] (−13°C) have lower melting points due to extended alkyl chains of their cations. The decrease of the melting points with increase of the chain length is a typical phenomenon for ILs with short chain lengths [26]. Hereby, the melting temperature of [S_{112}][SCN] is located between [S_{111}][SCN] and [S_{222}][SCN] but is almost as low as that of the latter, as ILs with asymmetric cations generally tend to show lower melting points than ILs with comparable symmetric ones [27].

The decomposition temperatures of the three ILs rise with increasing length of the alkyl moiety of the respective cation in the order [S_{111}][SCN] < [S_{112}][SCN] < [S_{222}][SCN], as shown in Figure 1. The viscosities determined for the two RTILs (room temperature ionic liquids) are 26.3 mPa·s for [S_{112}][SCN] and 34.2 mPa·s for [S_{222}][SCN]; both values are in a low range for ILs [23, 28]. The solid [S_{111}][SCN] has a density of 1.255 g cm^{-3}

SCHEME 1 | Overview of the structures of the ILs.

[S_{111}][SCN]: R$_1$,R$_2$,R$_3$ = CH$_3$

[S_{112}][SCN]: R$_1$,R$_2$ = CH$_3$, R$_3$ = C$_2$H$_5$

[S_{222}][SCN]: R$_1$,R$_2$,R$_3$ = C$_2$H$_5$

SCHEME 2 | Synthesis of trialkylsulfonium-based thiocyanate ionic liquids.

TABLE 1 | Thermal and physical data of sulfonium ionic liquids.

IL	Molecular formula	T_m[a] [°C]	T_d[b] [°C]	η[c] [mPa·s]	ρ[d] [g·cm^{-3}]
[S_{111}][SCN]	C$_4$H$_9$NS$_2$	66	116	-	1.255
[S_{112}][SCN]	C$_5$H$_{11}$NS$_2$	0	119	26.3	1.133
[S_{222}][SCN]	C$_7$H$_{15}$NS$_2$	−13	123	34.2	1.087

[a] Melting point. [b] Onset of decomposition temperature. [c] Viscosity at 25°C. [d] Density at 25°C.

FIGURE 1 | TG diagrams of [S_{111}][SCN] (blue), [S_{112}][SCN] (yellow), and [S_{222}][SCN] (orange).

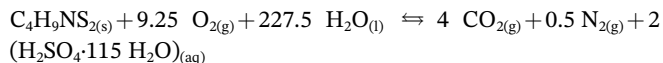at 25°C and is therefore higher compared to the values of the two RTILs.

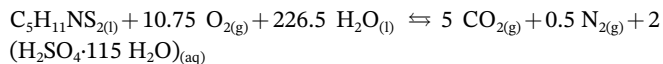## 2.3 | Performance Evaluation

2.3.1 | Enthalpy of Formation

For calculation of the combustion data, the enthalpies of formation of the ILs are required. These values were determined by calorimetry. Hereby, three measurements were performed per substance. Due to the sulfur and nitrogen atoms in the initial molecule, sulfuric acid and nitric acid were formed by dissolution of the combustion products in water. To specify a correction factor for this process, the total amount of acids formed was determined by titration with 0.1 M NaOH(aq). Using the standard molar enthalpies of formation

from literature, calculation of the enthalpies of formation was finally performed based on the following reaction equations, as described previously [21–22].
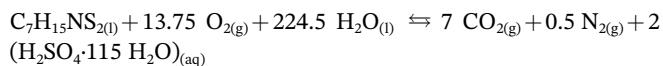
[S_{111}][SCN].

$C_4H_9NS_{2(s)} + 9.25\ O_{2(g)} + 227.5\ H_2O_{(l)} \leftrightarrows 4\ CO_{2(g)} + 0.5\ N_{2(g)} + 2\ (H_2SO_4 \cdot 115\ H_2O)_{(aq)}$

[S_{112}][SCN].

$C_5H_{11}NS_{2(l)} + 10.75\ O_{2(g)} + 226.5\ H_2O_{(l)} \leftrightarrows 5\ CO_{2(g)} + 0.5\ N_{2(g)} + 2\ (H_2SO_4 \cdot 115\ H_2O)_{(aq)}$

[S_{222}][SCN].

$C_7H_{15}NS_{2(l)} + 13.75\ O_{2(g)} + 224.5\ H_2O_{(l)} \leftrightarrows 7\ CO_{2(g)} + 0.5\ N_{2(g)} + 2\ (H_2SO_4 \cdot 115\ H_2O)_{(aq)}$

Detailed information on the experimental procedure and the values for the calculation can be found in the Supporting Information. The determined values for the standard enthalpies of formation are listed in Table 2.

2.3.2 | Theoretical Combustion Data

Calculation of combustion data of the propellant combinations was performed using NASA CEA (Chemical Equilibrium with Applications) code [29]. All calculations were based on an *Ariane Group* 400 N thruster with a combustion chamber pressure of 1 MPa and an expansion ratio of 330 [30]. The calculations were performed assuming frozen supersonic expansion. For all calculations, an ideal HTP concentration of 98 wt% was assumed. The ratio of oxidizer to fuel (*ROF*) was calculated based on the mass flows of oxidizer ($\dot{m}_{oxidize}$) and fuel ($\dot{m}_{fuel}$):

$$ROF = \frac{\dot{m}_{oxidizer}}{\dot{m}_{fuel}}$$

The density of the combined propellant at the respective *ROF* was determined considering the densities of oxidizer ($\rho_{oxidizer}$) and fuel (ρ_{fuel}):

$$\rho_{propellant} = \frac{\rho_{oxidizer} \times \rho_{fuel} \times (ROF + 1)}{\rho_{oxidizer} + \rho_{fuel} \times (ROF)}$$

TABLE 2 | Calculated combustion data of sulfonium ionic liquids as fuels and HTP as oxidizer (assuming frozen supersonic expansion, $\varepsilon = 330$, $p_c = 1$ MPa).
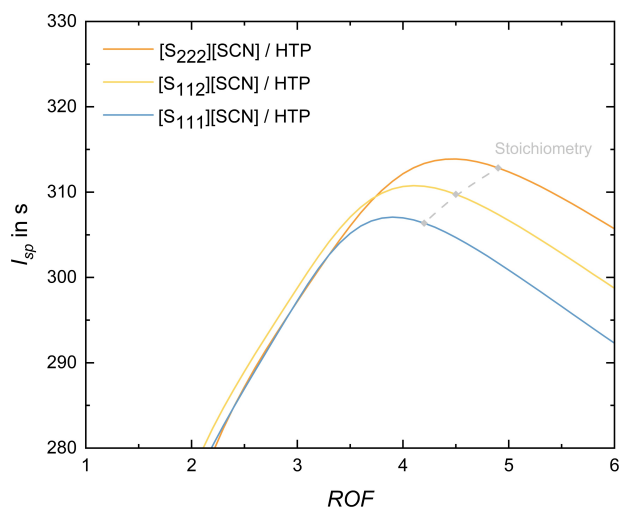
Fuel	ΔH_f[a] [kJ·mol^{-1}]	$I_{sp\ max}$[b] [s]	ROF[c]	$\rho I_{sp\ max}$[d] [s·g·cm^{-3}]	T_c at $I_{sp\ max}$[e] [K]	M[f] [g·mol^{-1}]	ROF_{sc}[g]	M_{sc}[h] [g·mol^{-1}]
[S_{111}][SCN]	−176 (s)	307	3.9	429	2759	24.3	4.2	24.4
[S_{112}][SCN]	−170 (l)	311	4.1	425	2778	23.8	4.5	24.0
[S_{222}][SCN]	−269 (l)	314	4.5	427	2780	23.4	4.9	23.6

[a] Heat of formation. [b] Maximum specific impulse at the nozzle. [c] Ratio of oxidizer to fuel at $I_{sp\ max}$. [d] Density specific impulse at $I_{sp\ max}$. [e] Adiabatic flame temperature. [f] Average molar mass of calculated combustion products. [g] *ROF* for stoichiometric combustion out of reaction equations. [h] Average molar mass of calculated combustion products for stoichiometric combustion.

Table 2 presents the relevant data obtained from the calculations. With longer alkyl chains, the maximum specific impulse $I_{sp\ max}$ increases, hence [S_{222}][SCN] offers the highest value of 314 s. In contrast, [S_{111}][SCN] shows the highest volumetric specific impulse $\rho I_{sp\ max}$ of 429 s g cm^{-3}, since the density of the fuel components at 25°C was used for the calculations (Table 1). Under these conditions, the calculated $I_{sp\ max}$ of MMH/NTO is 337 s at a ROF of 1.7 and therefore exceeds the $I_{sp\ max}$ values of the ILs with HTP. However, the volumetric specific impulse of the three presented propellants is significantly higher than that of the conventional hypergolic propellant MMH/NTO of 392 s g cm^{-3}. A high volumetric specific impulse is an important characteristic of a space propellant, as it allows the use of smaller tanks and leads therefore to a lower overall weight of structure, which is directly related with reduced cost [31]. Further, there are also systems which are volumetrically limited in terms of the tank size. Here, a high ρI_{sp} is particularly valuable. The adiabatic flame temperature rises with longer alkyl moieties, while the average molar mass of the combustion products decreases in this direction. The latter can be explained by the fact that with higher mass percentage of alkyl moieties, the percentage of heavier sulfur atoms is reduced.

Furthermore, the ROF_{sc} (ROF for the stoichiometric combustion) values were calculated. These values are slightly higher compared to the values for the ROF values calculated with NASA CEA, where the specific impulse reaches its respective maximum. This is because the mass of combustion products in stoichiometric combustion (M_{sc}) is higher than that of fuel rich combustion mixtures (e.g. higher fraction of CO compared to CO_2). Lighter combustion products are advantageous for the specific impulse; hence it reaches its maximum value at smaller $ROFs$.

Figure 2 shows the variation of the specific impulse of the different fuel combinations over the ROF between 1 and 6. The dashed gray line indicates the position of the respective points of the ROF_{sc} for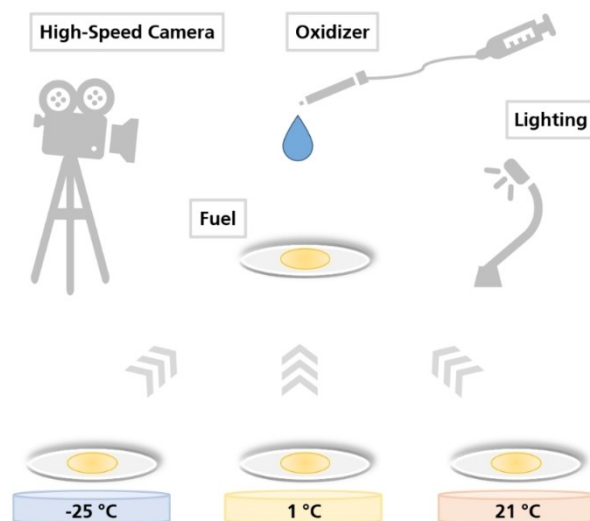 stoichiometric combustion, which, as explained above, are shifted toward higher values compared to ROF values of the maxima of the three plotted I_{sp} curves.

2.4 | Temperature Dependent Ignition Behavior

A schematic drop test setup for the hypergolic ignition tests is shown in Figure 3. All drop tests were carried out under air atmosphere. The unique aspect of this setup is that the fuel was pre-tempered to three different temperature levels prior to the start of the test, namely −25°C, 1°C and 21°C. In this way, the change of the ignition behavior at lower fuel temperatures was evaluated. A digital thermometer was used to measure the temperature of the fuel immediately before each test. To carry out the droplet experiments, the pre-tempered fuel was placed into position and the oxidizer drop was applied from above by a glass pipette, which was remotely controlled by a syringe. The distance between the tip of the oxidizer pipette and the fuel pool was 8.7 cm. The average volume of oxidizer drops was 32 µl. The fuel was applied with a piston pipette for liquid fuels and a spatula for solid fuels. The fuel volume was set at 150 µl to ensure reliable collision of the two components. The experiments were filmed by a *Photron fastcam SA-X2* color high-speed camera with a recording speed of 3000 fps (frames per second). Additional lighting has been installed laterally. For determination of the HTP concentration, its density was determined prior to the experiments and converted to a value of 97 wt% [32].

Three tests were conducted at each fuel temperature per IL and the average ignition delays were determined (Table 3). The ignition delay time (IDT) is defined as the time span between first contact of oxidizer and fuel and first flame observation.

Figure 4 shows that for all three compounds, the ignition delay decreases with increasing fuel temperature. The average IDTs of [S_{112}][SCN] are significantly shorter compared to the other two ILs for all temperatures. In contrast to [S_{222}][SCN], the IL [S_{112}][SCN] exhibits a significantly lower viscosity, which may

FIGURE 2 | Comparison of I_{sp} over ROF of [S_{111}][SCN] (blue), [S_{112}][SCN] (yellow) and [S_{222}][SCN] (orange) with HTP as oxidizer.


FIGURE 3 | Drop test set-up for investigation of the hypergolic ignition behavior at different fuel temperatures.

TABLE 3 | Results of drop tests sulfonium-based thiocyanate ionic liquids as fuels and HTP as oxidizer at three different fuel temperatures.
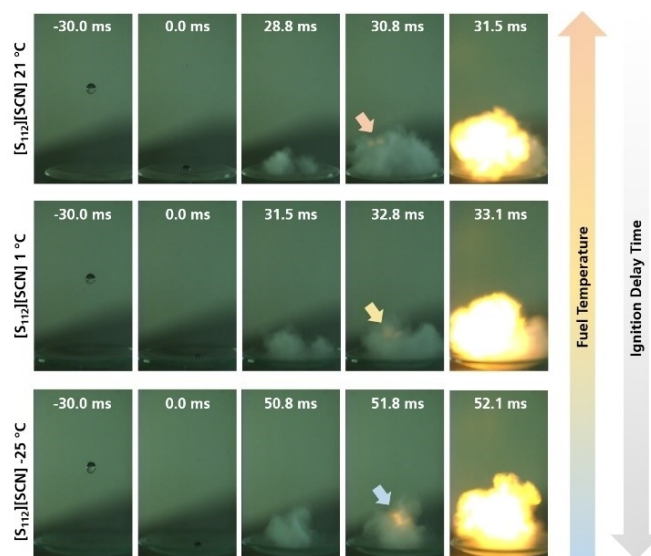
IL	−25°C		1°C		21°C	
	IDT[a] [ms]	SD[b] [ms]	IDT[a] [ms]	SD[b] [ms]	IDT[a] [ms]	SD[b] [ms]
$[S_{111}][SCN]$	83.6	3.7	65.1	1.2	55.1	5.1
$[S_{112}][SCN]$	51.8	4.9	32.8	1.9	30.8	0.6
$[S_{222}][SCN]$	79.2	4.6	69.2	3.2	61.8	4.7

[a] Average ignition delay time out of three drop tests. [b] Standard deviation of the ignition delay time.
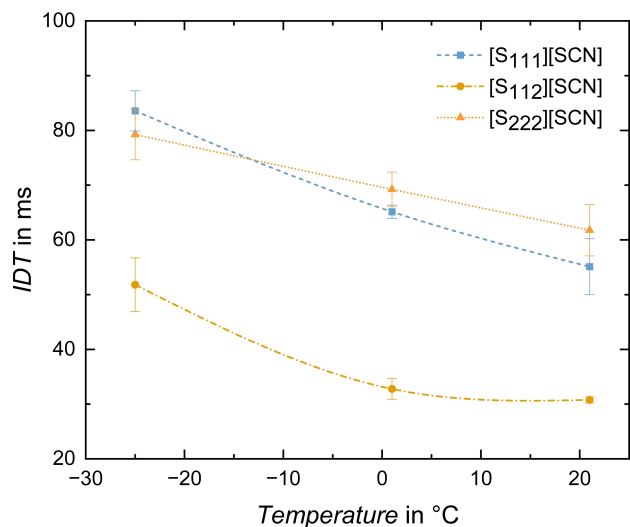
FIGURE 4 | Ignition delay times of sulfonium based ILs as fuels and HTP as oxidizer in dependence of the fuel temperature.

FIGURE 5 | Single high-speed video frames of hypergolic drop tests of $[S_{112}][SCN]$ at −25°C (top), 1°C (middle) and 21°C (bottom).

be an explanation for the improved ignition performance. However, in the case of $[S_{111}][SCN]$ which a solid up to 66°C, this explanation is not feasible. From a previous study, however, it is known that the solid state of the fuel is not detrimental to the ignition delay - rather the opposite was found [22]. The steric shielding by the differently demanding alkyl substituents (ethyl > methyl) cannot have a relevant influence here, since $[S_{112}][SCN]$ can be arranged between the other two ILs in this respect. An explanatory approach for the shorter ignition delay could be provided by the lower symmetry of the cation of $[S_{112}][SCN]$ compared to the other two; this aspect has also already been discussed in terms of the melting temperature. Whether the cation symmetry does have an impact on the ignition delay will be investigated in further work, for example by substituting sulphur by other suitable heteroatoms.

Another notable observation in Figure 4 is the intersection of the curves of $[S_{111}][SCN]$ and $[S_{222}][SCN]$. Although the melting point of $[S_{222}][SCN]$ of −13°C is in the relevant area, it can be assumed that crystallization of the fuel has not yet occurred since ILs show a strong tendency for supercooling and thus crystallize at rather lower temperatures as their respective melting temperature [33]. The samples were visually inspected immediately before the tests, whereby both $[S_{222}][SCN]$ and $[S_{112}][SCN]$ were optically liquid at all temperatures. Besides, with a view on the standard deviations of the ignition delay

times of the two substances at −25°C and 1°C, an interpretation of this anomaly should be made with caution.

Individual sequences of hypergolic drop tests of $[S_{112}][SCN]$ as fuel at the three temperatures are shown in Figure 5 plotted among each other. Considering the temperature, which increases from top to bottom, a clear trend can be observed that the ignition delay decreases as the higher temperatures.

3 | Conclusion

In this work, three ionic liquids containing trialkylsulfonium cations and thiocyanate anions were synthesized and characterized. The physical properties of the new substances were determined, highlighting the low viscosity in case of $[S_{112}][SCN]$ ($\eta = 26.3$ mPa·s) at 25°C.

The theoretical combustion data of the ILs as fuels with highly concentrated hydrogen peroxide as oxidizer was calculated using NASA CEA. It was found that $[S_{222}][SCN]$ exhibits the highest specific impulse of 314 s at $ROF = 4.5$; whereas $[S_{111}][SCN]$ shows the highest volumetric specific impulse of 429 s g cm^{-3} at $ROF = 3.9$ due to its high density. Monomethyl hydrazine and dinitrogen tetroxide offer a calculated volumetric specific impulse of 392 s g cm^{-3} under these conditions. This

value is clearly exceeded by all three presented combinations. Thus, smaller propellant tanks are required, which is not only advantageous for volumetric limited systems but results also in a lower structure mass of the tanks and is therefore correlated with lower overall costs of a mission.

To investigate the hypergolic ignition behavior, drop tests were conducted at three different fuel temperatures (21°C, 1°C and −25°C). All three fuels showed reliable hypergolic ignition at all temperatures with highly concentrated hydrogen peroxide as oxidizer. It was also found that the ignition delay decreased at higher temperatures. $[S_{112}][SCN]$ featured the shortest ignition delay among the three ionic liquids studied with an average value of 30.8 ms at ambient conditions, increasing to 32.8 ms at 1°C and to 51.8 ms at a fuel temperature of −25°C. Future research will investigate whether the lower symmetry of $[S_{112}][SCN]$ might be responsible for the short ignition delay of this substance. Moreover, the oxidizer temperature will be varied in order to evaluate its influence on the hypergolicity as well and experiments in an inert atmosphere will be performed to further investigate the hypergolic ignition.

Symbols and Abbreviations

DLR	German Aerospace Center
DSC	Differential scanning calorimetry
Equiv.	Equivalent(s)
IDT	ignition delay time
IL(s)	Ionic liquid(s)
IR	infrared
MMH	Monomethylhydrazine
NTO	Nitrogen tetroxide
ROF	Ratio of oxidizer to fuel
RTIL(s)	Room temperature ionic liquid(s)
sc	Stoichiometric combustion
SD	Standard deviation
TGA	Thermogravimetric analysis
UDMH	Unsymmetrical dimethylhydrazine
WFNA	White fuming nitric acid
$[S_{111}][SCN]$	Trimethlylsulfonium thiocyanate
$[S_{112}][SCN]$	Ethyldimethylsulfonium thiocyanate
$[S_{222}][SCN]$	Triethylsulfonium thiocyanate

Acknowledgments

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.