

THE INFLUENCE OF CHEMICAL DESCRIPTORS ON THE REACTIVITY OF POTENTIAL HYPERGOLIC FUELS WITH HYDROGEN PEROXIDE

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ABSTRACT

The state-of-the-art for storable hypergolic bipropellant systems is monomethylhydrazine (MMH) and mixed oxides of nitrogen (MON). While MMH and MON provide fast and highly reliable hypergolic ignition with excellent propulsive performance, they suffer from safety concerns impacting their production, cost, and supply to various test and launch facilities. In contrast, identifying and demonstrating low-toxicity fuels hypergolic with rocket grade hydrogen peroxide (H_2O_2) has been challenging with long ignition delay (IDT) and low propulsive performance affecting their deployment in flight systems. This work describes a preliminary observational study to assess the effects of molecular descriptors suspected to predict the reactivity and hypergolicity of compounds within the same chemical class (i.e., thioamide). The approach centered on evaluating functional groups, electrostatic potential, number of carbons, dipole moment, and adiabatic ionization energy. Thiourea is hypergolic with 89.2 wt.% H_2O_2 (minimum IDT of 21.9 ms) and was selected as a core fuel to study the reactivity of derived fuels with different functionalities. Additionally, the chemical properties were calculated with the Gaussian16 suite. The results showed that group substitution and generally increased number of carbons on thiourea increases IDT. It was observed that a more positively charged sulfur atom in the thioamide does not increase the reactivity towards H_2O_2 . The dipole moment analysis revealed an overall trend of decreasing IDT due to increasing dipole moment. Finally, a lower adiabatic ionization energy related to increased IDTs for most cases. Additional chemical classes comprising a wider range of functionalities and electrophilic attributes are being investigated in on-going work.

INTRODUCTION

Small spacecraft will play a key role in the next generation of deep space missions as they provide a means of growing science capabilities and maturing aerospace technologies through versatile and compact platforms that are affordable to build and launch. For example, the Artemis I vehicle launched nanosatellites for the BioSentinel, the Near-Earth Asteroid (NEA) Scout, and the Lunar Flashlight missions [1]. As these missions enable the demonstration of cutting-edge technologies, there is a major need for small spacecraft propulsion systems.

Multiple efforts in academia, government laboratories, and the private sector are underway to increase the capabilities and performance of small spacecraft with advanced propulsion systems. Many of these are based on monomethylhydrazine (MMH) and mixed oxides of nitrogen (MON). They have been the predominant selection for spacecraft propulsion systems due to their high performance, but safety concerns call for low-toxicity propellants to replace them. The drawbacks of hydrazine-based systems are the toxicity, corrosivity, and potential carcinogenic effects they pose [2]. In turn, NTO is toxic, highly corrosive, and has a high vapor pressure [2]. These properties impose the need for more rigorous handling procedures and safety precautions that incur higher costs associated with the lifecycle starting with the production and ending with the fueling stage [2]. For example, the use of Self-Contained Atmospheric Protective Ensemble (SCAPE) suits is required for these propellants due to high vapor pressure and health risks for humans.

Safety and supply concerns for hydrazine-based fuels have driven the interest in pursuing the growth of alternative propellants. This emerging field includes the development of green hypergolic

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propellants such as room temperature ionic liquids (ILs) [3], non-ionic liquids like amine-boranes [4], and less toxic oxidizers like rocket grade hydrogen peroxide (H_2O_2) [2, 3, 5, 6]. Rocket grade hydrogen peroxide is a highly concentrated solution (85 to 98 wt.%) of H_2O_2 that has been used since the 1960s [2]. Rocket grade H_2O_2 is less reactive than more commonly used oxidizers like NTO but it does not fume toxic vapors, it is highly environment-friendly (decomposes to oxygen and water upon heating) [7]. As with any novel development, this technology presents challenges that need to be overcome to increase its capabilities and meet the needs of small spacecraft. Most low-toxicity fuels have shortcomings like high IDTs (> 10 ms), low propulsive performance, and not meeting operational conditions (e.g., high freezing points). In addition, there is an interest in improving storability and reducing solid deposits on thruster assemblies.

To address these challenges, chemical design and/or tailoring of novel storable liquid green hypergolic propellants can be employed to enhance their performance with respect to the state-of-the-art (SOA) through the application of additives. Nonetheless, the hunt for new hypergolic fuels is typically based on “trial and error” methods, in which potential candidates are selected based on suspected reactivity, and then tested to confirm their chemical behavior [8]. We will present a literature review that reveals an evident gap of knowledge on fuel selection and the relationship between chemical descriptors and hypergolic behavior of pure or neat fuels with H_2O_2 . Therefore, there is a motivation to address this gap and establish a systematic approach that can assist and streamline the screening process and selection of possible hypergolic fuels (solid and liquid) with H_2O_2 . Correlational and predictive data is needed to better understand the impact of different chemical properties on reactivity and hypergolicity. Such a systematic approach should decrease the time invested in testing every possible fuel by selecting compounds with properties known to promote hypergolicity. The focus of this research was to conduct a simple exploratory and systematic study and to determine if the relationship between a small set of chosen molecular properties (physical, chemical, and structural) and reactivity and hypergolicity of fuels with H_2O_2 could build up predictions for fuel selection.

BACKGROUND

Previous investigations have employed systematic studies to understand the influence of chemical structure on the hypergolic behavior of liquid fuels with white fuming nitric acid (WFNA, highly concentrated HNO_3) [9] and NTO [10, 11]. In the case of WFNA, prior work focused on correlating the hypergolic behavior of aliphatic amines with their molecular structure [9]. The purpose was to determine the influence of amine class, carbon chain length, and substituents on the reactivity of multiple amines, and the relationship with IDT, if any. Some of the conclusions drawn from that work include: (1) the reactivity increases as chain length increases up to six carbons, (2) the reactivity of primary amines also increases when adding alkyl groups to the alpha-carbon, but decreases when added on the beta-carbon position, (3) tertiary amines are the most reactive, and (4) substituents enhance hypergolicity when added to the beta-carbon position. Further research found a generalized description of the ignition process [12] which helped to conclude that radical chain reactions are initiated after a high energy release obtain from an exothermic step that also decomposes the HNO_3 to nitrogen dioxide (NO_2) [11].

In comparison, an extensive summary of the reactivity of different organic and inorganic compounds with both NTO and NO_2 , in solvents as well as in gas phase were presented decades ago by Gray and Yoffe [10]. The authors studied unsaturated molecules, alkenes, and alkynes, and reported that the weaker the C–H bond, the more reactive the compounds were with NO_2 . Therefore, from a chemical structure standpoint, it was concluded that tertiary alkyls tend to be more reactive than secondary and primary due to the improved stability of tertiary radicals [10]. The authors also described that alcohol and amine functionalities exhibit similar reactivity with NTO producing alkyl nitrites (RONO) and nitrosamines (R–NO), respectively. Additional investigators conducted a mechanistic study to evaluate the possible reactive centers of N,N,N',N'-tetramethylethylenediamine (TMEDA) and N,N,N',N'-tetramethylethylenediamine (TMMDA) with NO_2 [11]. The fuel/oxidizer systems were assessed in gas phase using density functional theory (DFT) at the UB3LYP/6-311G** level [11]. The authors found that the strength of the N–H bond of the amine drove the reactivity of the free radical NO_2 just as seen

previously for alkanes. From this observation, it can be concluded that the N-H bond strength decreases by increasing the amine's level of substitution. This translates into increased reactivity due to the increased electron donor nature of nitrogen's lone pair [11].

Further literature review emphasized recognizing reactivity trends in fuels with H₂O₂ previously developed by the propulsion community. Focus was given to molecular or chemical descriptors suspected of promoting hypergolicity and/or reactivity with H₂O₂. Reactivity is characterized by evolution of gas, change in temperature, change in color, formation of precipitate and/or change in state. In comparison, hypergolicity is described by a reaction in which the substances combust spontaneously upon contact with each other emitting visible light.

One of the pioneering works was conducted during the late 1940's by Kelley and Kavanagh who explored reaction-driven fuels with 90 wt.% H₂O₂ [13]. Testing a variety of chemical classes and functional groups among more than 100 compounds, they found four hypergolic thioamides through qualitative observations (i.e., visual inspection of ignition without IDT reports). These were thiourea, thioacetamide, allylthiourea, and thiosemicarbazide (see **Figure 1**). All the fuels are solid at standard ambient conditions. A thioamide is a functional group with the general structure R₁-C(=S)-NH₂ where the hydrogens can be substituted by any functional group R₂ and R₃. Generally, the thioamides weaker carbonyl bond (130 kcal/mol) makes them more reactive with both nucleophiles and electrophiles than amides with a stronger carbonyl bond (170 kcal/mol) [14].

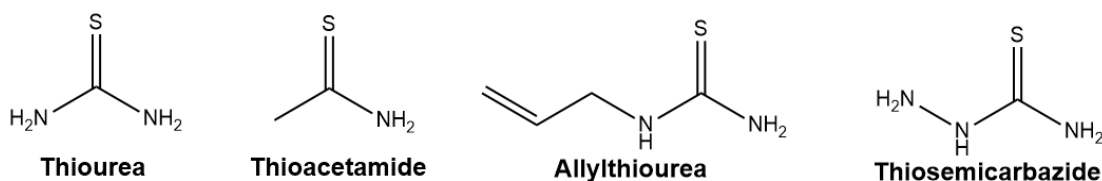


Figure 1. Thioamide hypergolic fuels studied by Kelley and Kavanagh [11].

The findings made by Kelley and Kavanagh motivated the screening of multiple amides and thioamides by Kamperschroer at Dr. Pourpoint's laboratory at Purdue University [15]. The purpose was to investigate the effects of molecular structure and different functionalities on ignition delay time. Emphasis was given to the reactions of chalcogen-amides (based on elements from group 16 of the periodic table) with rocket grade H₂O₂ [15]. Kamperschroer drop tested thiourea, thioacetamide, thioacetamide, among others with 95.0 wt.% H₂O₂. One of the most interesting results from the screening revealed distinct reactivity for two liquid amides, N,N-dimethylthioformamide and N,N-dimethylformamide, with H₂O₂ [15]. The first one, with a thiol functional group, is hypergolic (IDT of 28.8 ms) with 95.0 wt.% H₂O₂ while the latter, with a carbonyl group, is not. The tests also revealed that most of the oxygen-containing amides were non-reactive, or weakly reactive while all the examined sulfur-containing amides (i.e., thioamides) resulted in ignition. The observations indicate that the chalcogen element present in the double bond drastically affects reactivity. The results support the idea that the chalcogen element is the reactive center for the initial reactions of these compounds with rocket grade H₂O₂ [15]. Furthermore, Kamperschroer studied the electrostatic potential on the thioamides' sulfur atom and found it to be an important predictor of hypergolic behavior for the examined thioamide fuels [15].

To expand on the work previously conducted, a hypergolic fuel identified from Kelley and Kavanagh's research, thiourea, was selected as a core or base fuel in the present study. Thiourea is hypergolic with 95 wt.% H₂O₂ exhibiting a minimum IDT of 19.4 ms [15] but no IDT data is available for its ignition with 90 wt.% H₂O₂. The work strategy involved acquiring commercially available compounds derived from thiourea and substituting one of its amines with different functional groups while preserving the thioamide functional group (i.e., R₁-C(=S)-NH₂). The selection spanned seven different compounds chosen for their simple functionalities (seen in **Figure 2**). They all are solid in standard room conditions. Each compound was assigned a number seen in parenthesis in the next figure for identification purposes throughout the document.

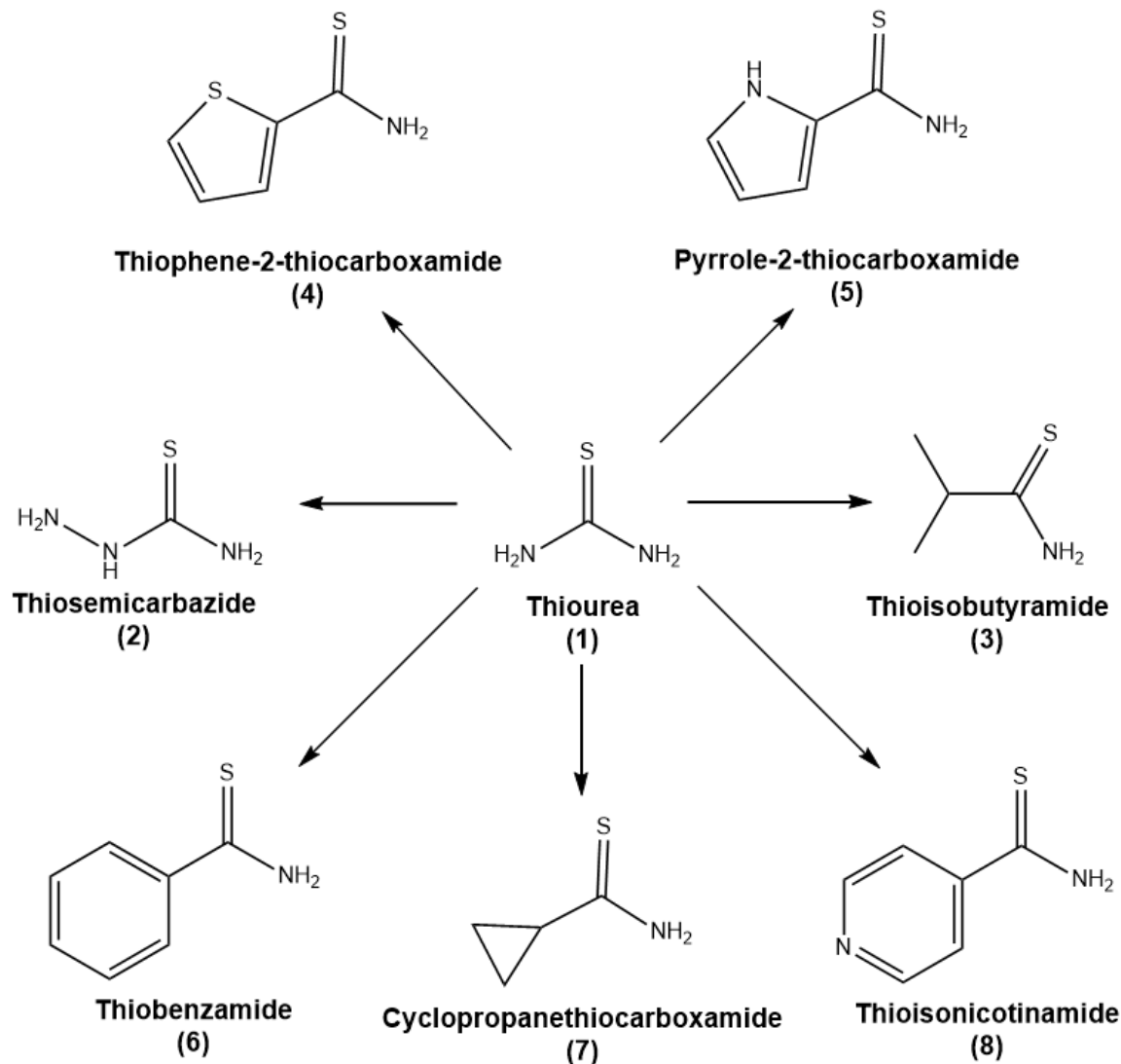


Figure 2. Thioamide-based compounds used in the present study.

In the present study, a small set of chemical properties were chosen based on suspected influence on reactivity and hypergolicity. The molecular descriptors of interest were chemical structure, steric (nonbonding interactions and arrangements in a compound), and electronic (charge distribution). The chosen properties include chemical structure-based parameters such as functional groups and number of carbons. Chemical descriptors, including electrostatic potential, dipole moment, and adiabatic ionization energy, were investigated computationally. By establishing some of these properties, relationships between the fuels' hypergolicity and reactivity with H_2O_2 can be established to set the basis for developing a systematic approach for fuel selection.

Functional groups were of interest because we intended to evaluate the impact of different functionalities on hypergolic reactions with H_2O_2 . Moreover, assessing if group substitution affected chemical behavior due to steric effects was important. In contrast, electrostatic potential is defined as the energy required to move a charge opposed to an electric field. Electrostatic potential can give information about electron-deficient areas in molecules which can be related to the groups' reactivity. Another charge-based property assessed in the study was dipole moment. It was of interest because typically, the greater

the dipole moment, the greater the reactivity due to increased instability that influences and enhances reaction mechanisms [16]. The dipole moment is defined as the measure of the electrical polarity of a system of charges. Additionally, adiabatic ionization energy is defined as the lowest energy required to eject an electron from a molecule or atom. It is the transition of the isolated molecule from the ground electronic, vibrational, and rotational level to the lowest electronic, vibrational, and rotational level of the isolated cation [17]. In other words, it is the energy difference between the optimized cationic state and the optimized neutral molecule [18]. Adiabatic ionization energy was of interest because it is an important parameter used to assess how likely is a compound to participate in an electron transfer mechanism. Discussions with Dr. Kentämaa from the Chemistry Department at Purdue University motivated the idea of studying adiabatic ionization energy to observe its relationship with reactivity. This was an exploratory assessment that do not imply that electron transfer mechanisms drive the hypergolic reactions of pure fuels with H_2O_2 .

EXPERIMENTAL METHODOLOGY

The selected thioamides were drop tested to study reactivity and hypergolic ignition. Drop tests are simple, bench-scale experiments that provide information about the chemical interaction and ignition (when applicable) of different fuel and oxidizer combinations. In the present work, drop tests were performed in open air at atmospheric pressure and temperature. The fuel was placed inside a 12-mm diameter glass vial (Fisher Scientific, catalog number 03-339-26A) and located on a two-axis translation stage for alignment. H_2O_2 concentration was 89.2 ± 1 wt.% and was determined via a refractometer (Fisher Scientific, model 334620). The oxidizer was placed in a syringe (Hamilton, part number 81000) and dropped into a pool of fuel from an approximate height of 6 inches (see **Figure 3**). A Phantom V7.3 high-speed camera was used with a Nikon 300 mm lens to capture the evolution of the chemical interaction and identify the reaction delay time (RDT) and IDT if warranted. The reaction between the fuel and oxidizer was captured between 9,000 and 16,000 fps with an acquired resolution of 256 x 512.

The RDT is defined as the time interval between the first contact of the propellants and the first visual indication of reaction. In our case the reaction indication was established by gas formation. In comparison, the IDT is defined as the time interval between the first contact of the propellants and the first emission of light. It is important to mention that there could have been variability in IDT that was not accounted for since the environment (e.g., temperature, relative humidity) is not controlled in open air conditions. Occasionally, minimum IDTs are preferred over average values, since they correspond to the fastest reaction kinetics between the propellants which gives the closest value to an ideal IDT [8]. For comprehensiveness, both minimum and average RDTs and IDTs as well as probability of ignition are reported below.

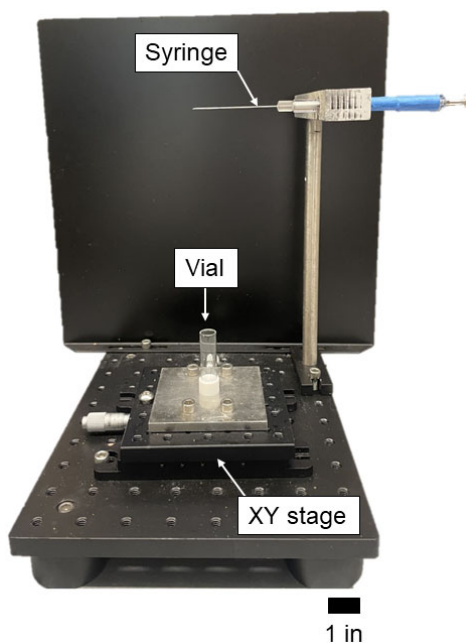


Figure 3. Drop test setup with syringe, fuel vial, and XY stage for experimental observations of reactivity and ignition. High-speed camera is omitted for clarity.

Complementing the experimental aspect, some of the fuel chemical properties were investigated with quantum chemical calculations using the Gaussian16 suite. Three properties were examined: the electrostatic potential of the sulfur atom on the thioamide, dipole moment, and the adiabatic ionization energy. The electrostatic potential (ESP) derived charges were calculated for each fuel with the electrostatic potentials using a grid-based method (CHELPG) scheme. This scheme fits atomic charges to reproduce the molecular ESP at several points around the molecule in a regularly spaced cubic grid [19]. In comparison, the dipole moment was a simple output computed at the M06-2x/6-311++G(d,p) level of theory and was examined for neutral molecules. Finally, the adiabatic ionization energy was obtained as the difference between the free enthalpy energies of the cation and neutral molecule of each compound. The cation and neutral molecules geometries were optimized for the gas phase and computed at the M06-2x/6-311++G(d,p) level of theory. This level of theory has demonstrated adequate performance in terms of predicting the general trends in the conformer relative energies and identifying the global minimum conformer [20]. The results were used to generate plots of the relationship between ignition delay time and the calculated chemical descriptors.

RESULTS AND DISCUSSION

This section is dedicated to the results from the exploratory study in which the influence of chemical structure and descriptors on the reactivity and hypergolicity of selected thioamide-based compounds with rocket grade H_2O_2 was examined. We present the results and discussion associated with the open-air drop tests followed by the evaluation of structural properties and calculated chemical properties. The results provide supporting information to build relationships between the reactivity and hypergolicity of potential fuels with H_2O_2 and chemical descriptors.

DROP TESTS

The reactivity and hypergolicity were assessed for the eight thioamide-based compounds. The minimum and average RDT and IDT as well as the probability of ignition over five tests were reported for each compound. The probability of ignition was defined as the number of drop tests where ignition occurred over the total number of drop tests performed. This quantity was reported to consider the variability in reactivity associated with factors other than environmental inconsistencies.

Table 1 summarizes the results of the drop tests performed for the selected compounds with 89.2 wt.% H₂O₂ in open air. Spontaneous ignitions were observed for all the thioamide-based fuels. Most of the fuels reacted vigorously with the oxidizer, forming gas and creating a cloud of vapor that turned into an intense reddish flame.

Table 1. Drop test results for thioamide-based fuels with 89.2 wt.% H₂O₂.

Fuel Name	Minimum reaction delay time (ms)	Average reaction delay time (ms)	Minimum ignition delay time (ms)	Average ignition delay time (ms)	Probability of ignition (%)
Thiourea (1)	13.1	14.7	21.9	23.2	100
Thiosemicarbazide (2)	39.5	42.7	64.3	63.2	80
Thioisobutyramide (3)	14.4	15.2	52.9	72.2	100
Thiophene-2-thiocarboxamide (4)	90.4	104.8	123.7	130.8	100
Pyrrole-2-thiocarboxamide (5)	274.5	291.8	285.9	319.4	100
Thiobenzamide (6)	32.4	39.9	67.9	77.6	60
Cyclopropane-thiocarboxamide (7)	13.4	17.7	31.7	39.3	100
Thioisonicotinamide (8)	52.2	55.2	91.2	116.4	100

Thiourea (1), the core fuel, exhibited the shortest minimum and average RDT and IDT from all fuels. It was a very consistent and reliable hypergolic fuel with low deviations in between tests. Thiourea reacted hypergolically with H₂O₂ and created a very dim combustion flame (see **Figure 4**) that was short lived in all the drop tests. In comparison, cyclopropanethiocarboxamide (7) is the second hypergolic fuel with the shortest average IDT, surpassing thiourea by 16.1 ms. As expected, cyclopropanethiocarboxamide's combustion flame is very bright and intense (as seen in **Figure 5**) due to the higher carbon content added by the propane group in the molecule. In contrast, pyrrole-2-thiocarboxamide exhibited the longest average RDT and IDT from all fuels. The hypergolic reaction of pyrrole-2-thiocarboxamide with H₂O₂ also creates a combustion flame that burns very intensely (see **Figure 6**) which lasts for the longest time of all flames. From the results, it is evident that all the tested solid hypergols have IDTs that are longer than the ideal requirement for a liquid propulsion system (i.e., < 10 ms). The long IDTs decrease the potential of using the examined fuels as additives for hypergolic fuel mixtures.

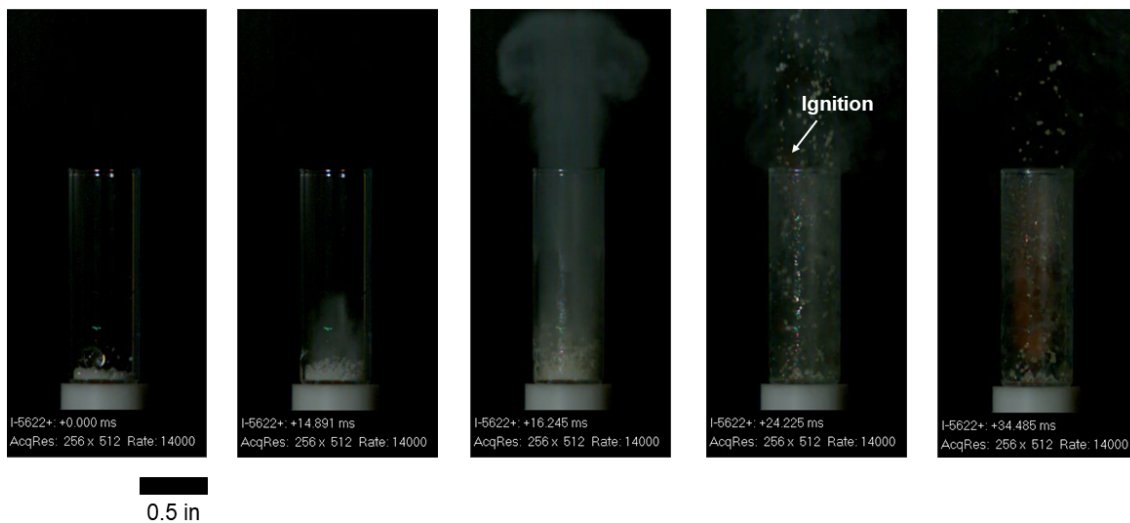


Figure 4. Hypergolic reaction of thiourea (1) with 89.2 wt.% H₂O₂.

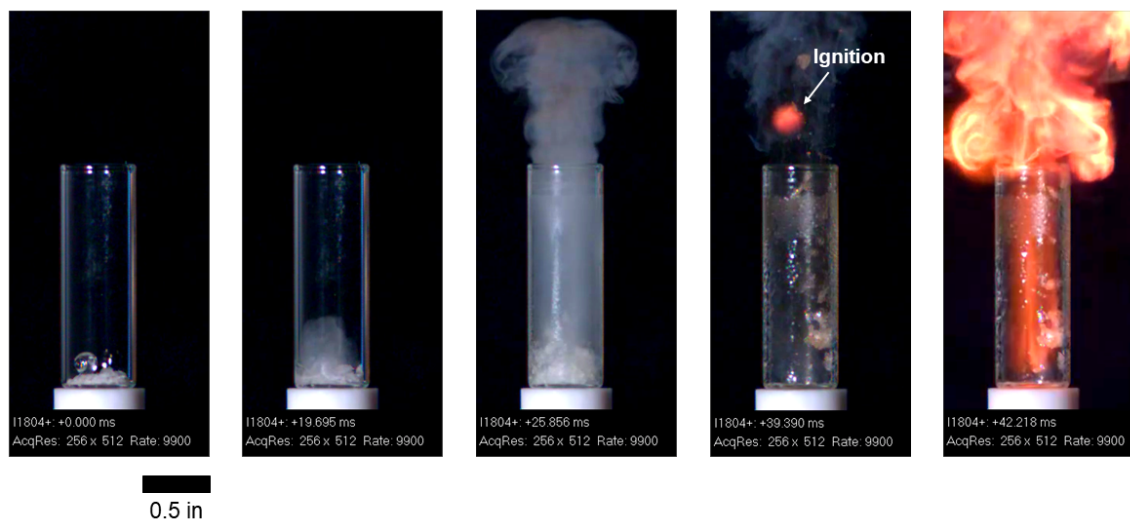


Figure 5. Hypergolic reaction of cyclopropanethiocarbamide (7) with 89.2 wt.% H₂O₂.

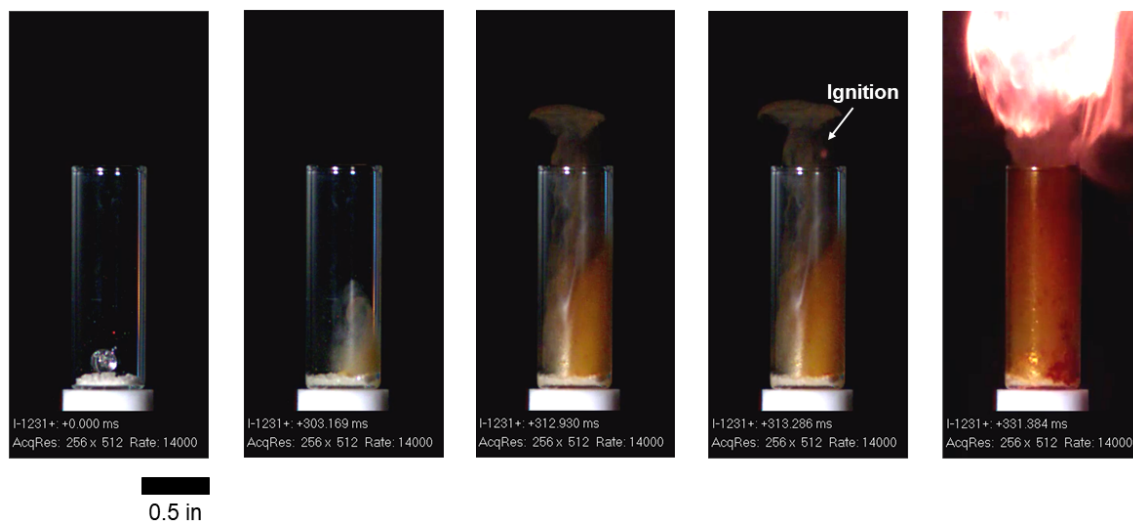


Figure 6. Hypergolic reaction of pyrrole-2-thiocarboxamide (**5**) with 89.2 wt.% H₂O₂.

An additional comparison is presented to examine the effect of the oxidizer concentration on the minimum RDT and IDT. **Table 2** shows the minimum RDT and IDT for thiourea (**1**) and thiobenzamide (**6**). The results presented for 89.2 wt.% H₂O₂ are a contribution from the present study while the data reported for 95.0 wt.% H₂O₂ is a contribution from Kamperschroer studies [15]. As expected, a higher oxidizer concentration decreases the time required for mixing and combustion which translates into shorter RDTs and IDTs. Curiously, the difference in H₂O₂ concentration should be significant in terms of the expected reactivity, however, the results for thiourea (**1**) do not deviate significantly for 89.2 and 95.0 wt.% H₂O₂.

Table 2. Comparison of minimum reaction delay time and minimum ignition delay time for thiourea and thiobenzamide with rocket grade H₂O₂.

Compound	H ₂ O ₂ concentration (wt.%)			
	89.2		95.0	
Metric	Minimum reaction delay time (ms)	Minimum ignition delay time (ms)	Minimum reaction delay time (ms)	Minimum ignition delay time (ms)
Thiourea (1)	13.1	21.9	9.5 [15]	19.4 [15]
Thiobenzamide (6)	32.4	67.9	23.5 [15]	25.2 [15]

The hypergolicity of the selected thioamide-based fuels supports Kelley and Kavanagh's [13] findings as well as Kamperschroer's studies [15] on thioamides igniting spontaneously with H₂O₂. The results permit us to hypothesize that thioamide-based compounds are persistently hypergols with H₂O₂. The observations provide insight into the influence of group substitution and electronic effects that will be discussed in the next subsection.

EFFECTS OF FUNCTIONAL GROUPS

Complementary to the effect of functional groups on the core fuel, the electrostatic potential is shown and also discussed in this section to support the observations. **Figure 7** shows the electrostatic potential of the sulfur atom (depicted as the yellow atom in each molecule) of the thioamide-based fuels based on the CHELPG scheme.

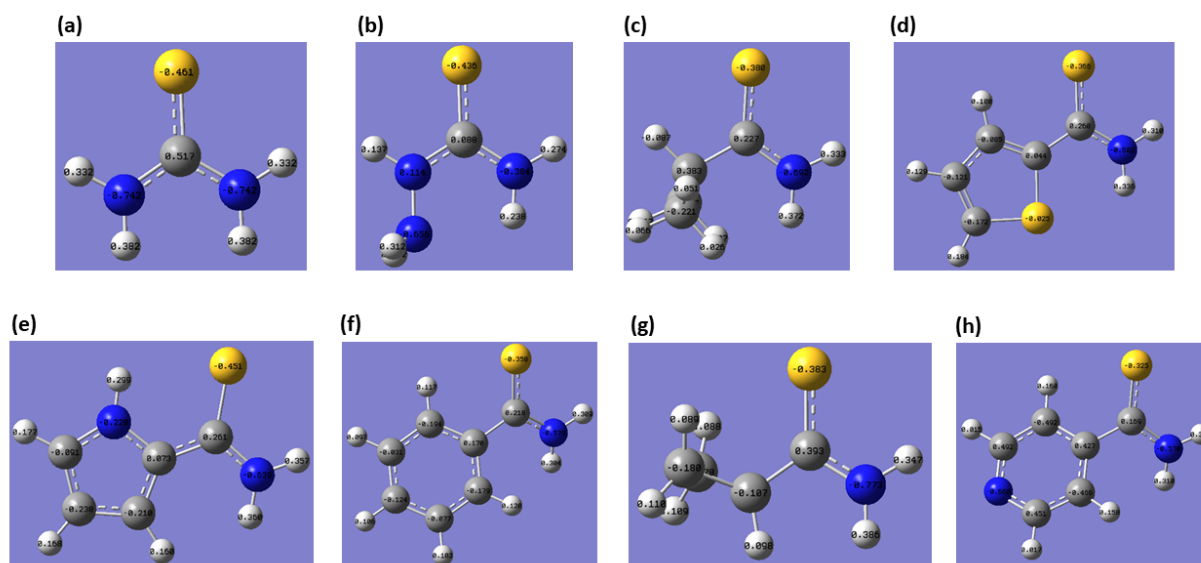


Figure 7. Electrostatic potential for (a) thiourea (b) thiosemicarbazide (c) thioisobutyramide (d) thiophene-2-thiocarboxamide (e) pyrrole-2-thiocarboxamide (f) thiobenzamide (g) cyclopropanethiocarboxamide (h) thioisonicotinamide.

From the examined fuels, we can observe that thiourea (**1**) has the shortest average RDT and IDT. Replacing one of the amine groups present in thiourea with propane (i.e., cyclopropanethiocarboxamide (**7**)) increases the RDT and IDT. This physically makes sense since propane adds bulkiness to the core fuel which sterically shields the reactive sulfur atom on the thiourea moiety from reaction. In comparison, making an amine substitution in one of thiourea's available hydrogens, yields thiosemicarbazide (**2**). This substitution increases the average IDT with respect to thiourea (**1**) by almost 300%. In general, the nitrogen atom is more electronegative than the sulfur atom. This should translate to the additional nitrogen withdrawing electron density toward itself leaving sulfur even more electron-deficient and more reactive to H_2O_2 . This was observed in the partial charge of the sulfur atom on thiosemicarbazide (**2**) seen in **Figure 7(b)**. Despite the partial charge becoming less negative, the IDT did not increase. Apparently, the contribution of the amine substitution is to slow the reaction kinetics due to steric effects shielding the sulfur atom from reacting with H_2O_2 . Also, the amine could be competing with the sulfur for the reaction center due to its positive charge seen in **Figure 7(b)**.

When substituting thiourea with the alkyl groups seen in thioisobutyramide (**3**), the RDT and IDT also increase. This behavior was expected as methyl groups add bulkiness to the core fuel which sterically hind reactions at the expected reactive sulfur atom. This steric effect does not seem to be overruled by the increase in partial charge of the sulfur atom (see **Figure 7(c)**) in thioisobutyramide (**3**). Moreover, placing a benzyl group in thiourea yields thiobenzamide (**6**). This substitution also increases the time for reaction and ignition. Benzyl can act as an electron withdrawing or electron-donating group. In this case, it appears to be acting as an electron-withdrawing group since the partial charge on the sulfur atom of thiobenzamide (**6**) seen in **Figure 7(f)** increased. This means that the sulfur atom should be more electron-deficient and reactive. However, steric effects might be playing a more dominant role in the reactivity of thiobenzamide (**6**) increasing the time it takes to react.

Furthermore, substitution of thiourea with pyridine yields thioisonicotinamide (**8**). Pyridine should be more reactive than benzene because the nitrogen atom is more electronegative than carbon and should increase the reactivity with respect to thiobenzamide (**6**) due to higher electron withdrawing

effects. The partial charge on the sulfur atom of thioisonicotinamide (**8**) seen in **Figure 7(h)** is more positive than the partial charge for thiourea (**1**) (seen in **Figure 7(a)**) and thiobenzamide (**6**) (seen in **Figure 7(f)**). Despite the higher partial charge on the sulfur atom, the pyridine substitution substantially increased the RDT and IDT. Moreover, extending the range of substitution, thiophene-2-thiocarboxamide (**4**) incorporates a second sulfur atom in the ring which seems to increase the RDT and IDT. Since the sulfur atom in the ring is less negatively charged than the sulfur atom in the thioamide (see **Figure 7(d)**), it can be theorized that the ring's sulfur atom could be competing as a reaction center. Finally, pyrrole-2-thiocarboxamide (**5**) incorporates a nitrogen atom in the ring which also increases the RDT and IDT. The partial charge of the ring's nitrogen atom (see **Figure 7(e)**) is less negative than the partial charge of the sulfur atom. It seems that the added nitrogen atom might be competing with the thioamide's sulfur atom and increasing the reaction rates, delaying the ignition of the core fuel to approximately 320 ms on average.

An additional comparison can be made for pairs of fuels that share similar bulkiness (i.e., number of carbons). When examining fuels with one carbon like thiourea (**1**) and thiosemicarbazide (**2**), we see that the partial charge of the sulfur atom on fuel (**2**) is less negatively charged than in fuel (**1**). However, thiosemicarbazide (**2**) exhibits higher IDTs. Moreover, when comparing thioisobutyramide (**3**) and cyclopropanethiocarboxamide (**7**), we observe that fuel (**3**) also has a less negatively charged sulfur atom and higher IDTs than fuel (**7**). In contrast, when examining fuels with five carbons like thiophene-2-thiocarboxamide (**4**) and pyrrole-2-thiocarboxamide (**5**) we see an exception. Fuel (**4**) has a less negative charge on the sulfur atom and does exhibit a lower IDT as expected based on Kamperschroer observations [15].

The examination of functional groups' effects shows that the electronegativity and electron-withdrawing nature of chemical groups do not affect the reactivity and hypergolicity as expected. In general, a less negative partial charge on the thioamides' sulfur atom should increase the reactivity towards H_2O_2 and lower RDTs and IDTs. Nonetheless, this was not observed for any of the derived thioamide fuels with respect to thiourea (**1**) except for fuels (**4**) and (**5**). It appears that shielding of the sulfur atom due to the group substitutions can drastically affect the expected reactivity, perhaps overruling electron-withdrawing effects. The results provide insight into how the role of the sulfur atom can be affected in the hypergolic behavior of the fuels with H_2O_2 .

EFFECTS OF ELECTROSTATIC POTENTIAL

Based on the results from **Figure 7**, a plot shown in **Figure 8** was generated to evaluate if a correlation exists between minimum IDT and electrostatic potential on the thioamide's sulfur atom of each hypergolic fuel.

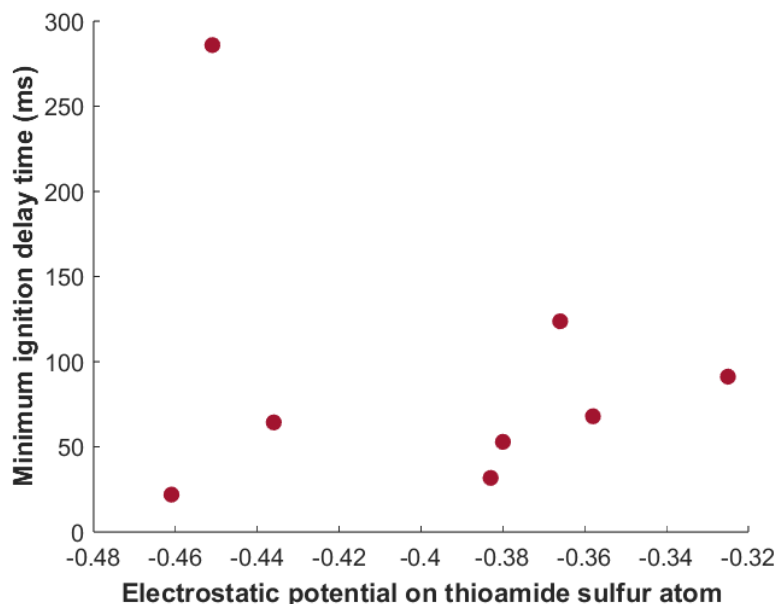


Figure 8. Minimum ignition delay time as a function of electrostatic potential on each thioamide's sulfur atom.

From **Figure 8**, we see a trend of increasing minimum ignition delay with less negative or more positive electrostatic potential, except for pyrrole-2-thiocarboxamide (**5**). In general, it was expected to observe a less negative charge on the sulfur atom for the hypergolic fuels with lower IDTs. This idea was supported by Kamperschroer who showed that a less negative charge on the thioamide's sulfur atom lowers the electron density which increases the reactivity toward nucleophiles such as H_2O_2 [15]. However, this is the opposite behavior of what we observe in **Figure 8**. Thiourea (**1**) has the most negative partial charge on the sulfur atom and the lowest minimum IDT. To contrast, pyrrole-2-thiocarboxamide (**5**) has the second most negative partial charge on the thioamide's sulfur atom and the highest minimum IDT. This in fact agrees with Kamperschroer's observations of lower reactivity due to more negative partial charge on the sulfur atom.

The results evidence that electrostatic potential on the thioamides' sulfur atom alone cannot predict how reactive compounds within the thioamide chemical class will be with H_2O_2 . It appears that the effects of electron-withdrawing groups and electronegative atoms are being overruled by chemical descriptors associated to molecule arrangement such as steric hindrance.

EFFECTS OF NUMBER OF CARBONS

There was interest in observing if there was a relationship or correlation between the number of carbons present in each thioamide-based fuel and minimum IDT. **Figure 10** was generated to explore this relationship.

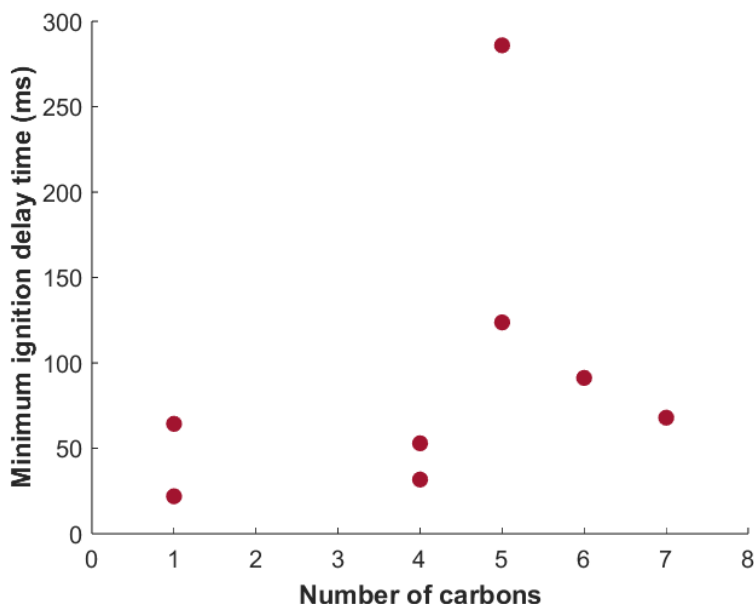


Figure 10. Minimum ignition delay time as a function of number of carbons present in each thioamide-based fuel.

On the left side of the plot, it seems that decreasing the number of carbons decreases the minimum IDT. This agrees with the fact that thiourea (**1**) exhibits the lowest minimum IDT with the lowest number of carbons. In general, an overall trend from **Figure 10** demonstrates that the highest minimum IDTs occur for compounds with more than four carbons, likely due to increased steric hindrance. However, other factors are at play here like the electron-withdrawing nature of some of the substitution groups. The previous plot only relates the properties for eight thioamide-based hypergolic fuels and no conclusions can be made for this subset nor for a wider range of compounds and reactivity based solely on the number of carbons.

EFFECTS OF DIPOLE MOMENT

The dipole moment calculated for the neutral molecules of the hypergolic fuels. **Figure 9** was generated to evaluate if a correlation exists between minimum IDT and dipole moment for the hypergolic fuels.

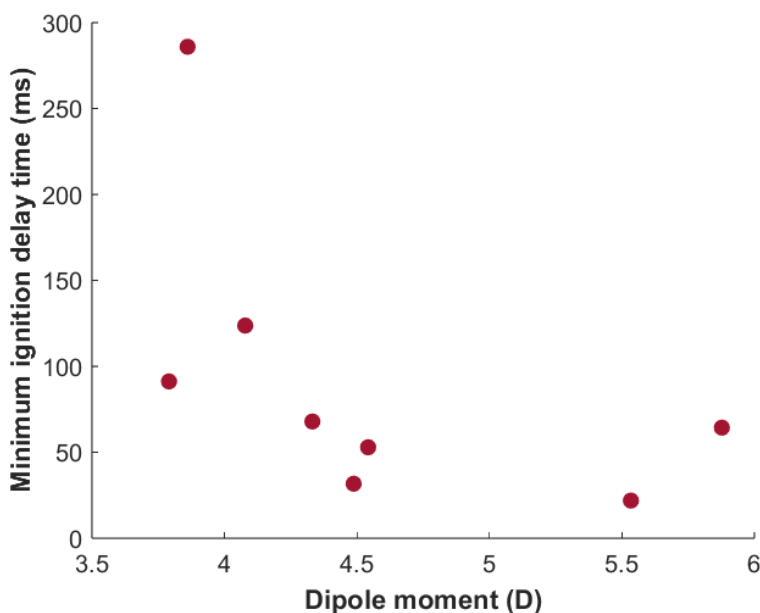


Figure 9. Minimum ignition delay time as a function of dipole moment.

In general, it would be expected that a higher dipole moment would relate to higher reactivity due to the separated charge increasing instability and chemical reaction rates. From **Figure 9**, most of the data points seem to follow an exponential decay or even a quadratic relationship. A quadratic relationship would make sense from a mixing consideration. This would mean that when the dipole moment is close to that of H_2O_2 (2.2 D [21]), mixing would be promoted, allowing faster reactions. When observing the left side of the plot, it might appear that for some hypergolic fuels, lower dipole moment increases the minimum IDT. As seen in **Figure 9**, pyrrole-2-thiocarboxamide (**5**) has the second lowest and closest dipole moment to H_2O_2 but the highest minimum IDT which does not agree with the mixing consideration. Moreover, when evaluating the hypergolic fuel with the lowest minimum IDT, thiourea (**1**), it is observed that it has the second highest dipole moment. This behavior also disagrees with the idea that closer dipole moment to that of H_2O_2 accelerates chemical reactions. From the observations, we cannot state that increasing dipole moment will always increase IDT nor that dipole moment closer to that of H_2O_2 will increase reaction rates due to enhanced mixing between bipropellants. Therefore, the plot does not provide conclusive information about how the reactivity of the examined set of fuels can be predicted by the dipole moment nor how an extended group of thioamides could react. Drop test experiments for additional thioamide-based fuels or other pure fuels should be considered to assess the validity of an exponential decay or quadratic relationship for minimum IDT and dipole moment.

EFFECTS OF ADIABATIC IONIZATION ENERGY

The calculated adiabatic ionization energies were used to generate **Figure 11** which shows the relationship between minimum IDT and adiabatic ionization energy.

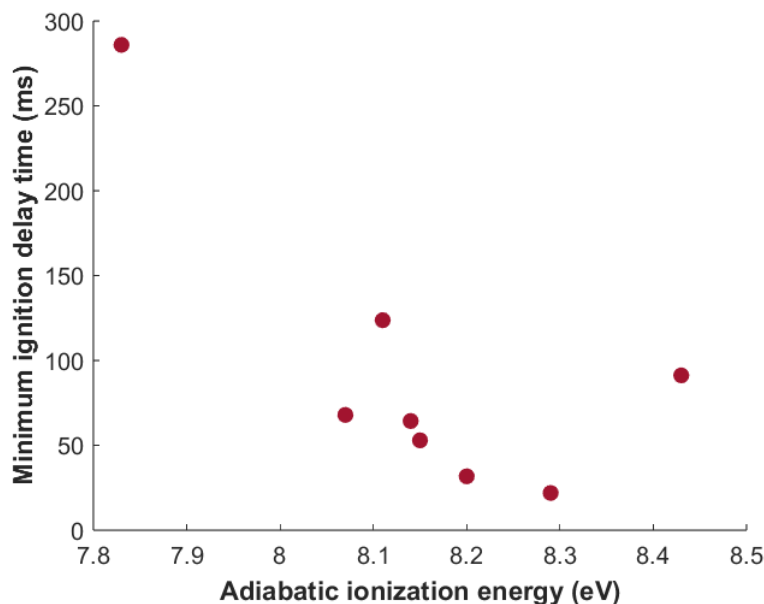


Figure 11. Minimum ignition delay time as a function of adiabatic ionization energy.

From the previous plot, an exponential decay, quadratic or even linear relationship could be drawn between minimum IDT and adiabatic ionization energy. If the hypergolic reactions with H_2O_2 were dominated by electron transfer mechanisms, the expectation would be to observe lower minimum IDTs for fuels with lower adiabatic ionization energy. This means that it would be easier to remove an electron from compounds with lower adiabatic ionization energy accelerating the reaction kinetics and decreasing the IDTs. Interestingly, thiourea (**1**) exhibits one of the highest adiabatic ionization energies while attaining the lowest minimum IDT. In the other extreme, pyrrole-2-thiocarboxamide (**5**) has the lowest adiabatic ionization energy and highest minimum IDT. These observations contradict the expected behavior for electron transfer driven mechanisms. Further testing should be conducted to examine a wider range of fuels and chemical classes with variable reactivity to observe the differences in adiabatic ionization energies.

SUMMARY AND CONCLUSIONS

The present work intended to assess the influence of five chemical descriptors (i.e., functional groups, electrostatic potential, dipole moment, number of carbons, and adiabatic ionization energy) on the hypergolicity and/or reactivity of thioamide-based fuels with rocket grade H_2O_2 . The objective was to establish relationships between reactivity and hypergolicity and chemical descriptors to aid in the foundation of a more simple and systematic approach to select potential hypergolic fuels. This would bypass the “trial and error” approach previously implemented in the propulsion community. To study the chemical descriptors, a consistent hypergolic functional group, thioamide, was substituted with additional functional groups to assess the effect of this addition on steric interactions, RDTs, and IDTs. The fuels were drop tested in air to obtain information about reactivity and hypergolic ignition. The drop tests showed that all the thioamide-based fuels were hypergolic with 89.2 wt.% H_2O_2 . From these fuels, thiourea (i.e., the core fuel), exhibited reliable ignition with 23.2 ms of IDT in average.

In general, group substitutions increased RDTs and IDTs due to probable increased steric effects (i.e., increased number of carbons) which translated into lower reactivity. This was evidenced by thiourea (**1**) which exhibits the lowest IDTs and minimum count of carbons. Steric effects could be decreasing the

reactivity by hindering access to the reactive center at the thioamide's sulfur atom. Steric effects and electron-withdrawing nature of chemical groups simultaneously affect the reactivity of the examined hypergolic fuels. When assessing the electrostatic potential on the thioamides' sulfur atom, a relationship between a more positively charged sulfur atom and a lower IDT was not observed as previously shown by Kamperschroer [15]. In terms of dipole moment, a general trend of decreasing IDT with increasing dipole moment was observed. Particularly, thiourea (**1**) exhibited the second largest dipole moment and lowest IDT while pyrrole-2-thiocarboxamide (**5**) exhibited the second smallest dipole moment with the highest IDT. Finally, lower adiabatic ionization energy seemed to increase the IDTs where the least reactive hypergolic fuel (pyrrole-2-thiocarboxamide (**5**)) exhibited the lowest adiabatic ionization energy.

The results drive the recommendation of examining additional chemical classes (focusing on compounds with sulfur atoms), shapes, functionalities, and electrophilic and nucleophilic attributes to expand the range of reactivity and hypergolicity to validate the observations made in this work. It is anticipated that the work presented will help optimize fuel selection for green oxidizers like rocket grade H₂O₂ to later improve them to meet the practical considerations of space propulsion systems.

FUTURE WORK

The presented work will be continued by exploring additional chemical classes and molecular descriptors to complete a more comprehensive model to fully describe a systematic approach for the selection of potential hypergolic fuels with H₂O₂. The requirements for potential new fuels would include low ignition delay, high performance, low freezing point, high density, and high boiling point.

It is also intended to down-select liquid fuels for further characterization (determine the physicochemical properties) and, if required, chemically tailor them with additives to improve one or more desirable properties based on space propulsion requirements. To accomplish the latter, an extensive review will be made to identify additives that can possibly impart hypergolicity in fuels with low reactivity and improve physical, chemical, and performance properties. This will aid in the creation of a more robust database with properties and characterization parameters of the selected fuels. Moreover, the research efforts will be supported by studying the likely early-stage reactions and identifying key intermediate species using mass spectrometry. Additionally, Nuclear Magnetic Resonance (NMR) will be used to elucidate the structure of the reactions' products. These analytical chemistry techniques will provide fundamental knowledge needed to explore and confirm the reaction mechanisms of hypergolic fuels with H₂O₂.

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