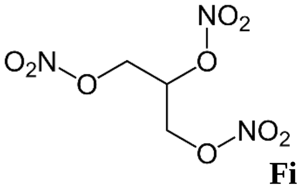
The Synthesis and Decomposition of Two 1,2,3,4-Thiatriazoles

Abstract

Two different 1,2,3,4-thiatriazoles were synthesized and characterized with IR and UV-Vis spectroscopy and a Mel-Temp apparatus to determine their decomposition temperatures. The products were obtained in poor yield and with possible impurities, but decomposed rapidly.

Introduction

Explosive reactions are exothermic reactions.[1] A commonly known explosive is dynamite, which is made from nitroglycerine.[2] The decomposition of nitroglycerine is shown in Figure 1.



(s) → $H_2O(g) + CO_2(g) + N_2(g) + O_2(g)$

Figure 1. The decomposition reaction of nitroglycerine

The decomposition of nitroglycerine is so favorable because forming dinitrogen and dioxygen is highly favorable. Another reason for its reactivity is due to fact that the carbons can react with the oxygens without the need for external oxygen.[3]

Alfred Nobel, the founder of the Nobel Prize, figured out how to mass produce dynamite in 1867, and also discovered a way to stabilize this reactive chemical. This discovery netted him enormous profits, and in his will he established the Nobel Prize which was to be awarded to people or organizations which promoted peace. Creating a prize committed to rewarding peace is in stark contrast to the destructive power of the chemical Nobel stabilized.[2] While the thiatriazoles are not dynamite, they are relatively similar, as they are nitrogen containing compounds. The difference between the two is that thiatriazoles are also sulfur containing compounds.

In this report, two different 1,2,3,4-thiatriazoles were synthesized through a diazotization reaction using 4-phenyl-3-thiosemicarbazide, thiosemicarbazide, hydrochloric acid, and sodium nitrite. Chemical equations are given in Figures 2 and 3.

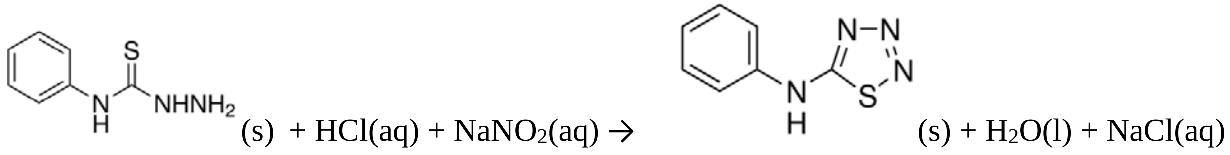


Figure 2. The diazotization reaction for 5-anilino-1,2,3,4-thiatriazole

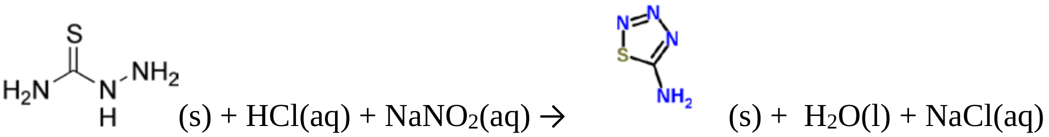


Figure 3. The diazotization reaction for 5-amino-1,2,3,4-thiatriazole

Thiatriazoles can be made to decompose when heated.[3] These two 1,2,3,4-thiatriazoles are expected to decompose violently and mimic the explosion of dynamite.

Methods

All reagents were used as received. The infrared spectra were collected on a FTIR spectrometer using an ATR apparatus. Decomposition temperatures were determined using a Mel-Temp melting point apparatus. A UV-Vis spectrum was measured for each product.

5-anilino-1,2,3,4-thiatriazole (**1**)- 0.469 grams of 4-phenyl-3-thiosemicarbazide was added to 2.5 mL of 15% HCL in a 25 mL Erlenmeyer flask. A small magnetic stir bar was added, and the suspension was cooled in an ice-bath with the temperature kept between 5℃ and 10℃. 0.210 grams of $NaNO_2$ were dissolved in 0.5 mL of water and 0.4 mL of this solution was added dropwise into the suspension of the 4-phenyl-3-thiosemicarbazide over 10 minutes, with the stir bar on medium. The product was then isolated in a Hirsch funnel, using suction filtration. The product was then rinsed with 0.5 mL of ice cold water, three times. A solution of 0.50 g of the 5-anilino-1,2,3,4-thiatriazole was used for the UV-Vis spectroscopy. Yield: 0.678g (33.7%) d.p. = 109°C. IR (cm^{-1}, ATR): 3397, 3328, 3244, 2935, 1614, 1601, 1566, 1455, 1293, 1197, 1095.

5-amino-1,2,3,4-thiatriazole (**2**)- The procedure was repeated except with 0.275 grams of thiosemicarbazide being added to 1.0 mL of 3M HCl. 0.212grams of $NaNO_2$ were dissolved in 0.5 mL of water and 0.4 mL of the solution was added dropwise into the suspension of thiosemicarbazide. A solution of 0.10 g of the 5-amino-1,2,3,4-thiatriazole was used for the UV-Vis spectroscopy. Yield: 0.113 g (36.69%) d.p. = 110°C. IR (cm^{-1}, ATR): 3405, 3256, 3104, 1615, 1509, 1269, 1108, 684.

Results

The 5-anilino-1,2,3,4-thiatriazole was synthesized in poor yield. In the Mel-Temp apparatus, the 5-anilino-1,2,3,4-thiatriazole appeared to melt at 109°C and at 110°C it turned a lighter color and began bubbling at 112°C. The 5-amino-1,2,3,4-thiatriazole was also a relatively light brown color and was a powdery solid and similarly synthesized in poor yield (36.69%). In the Mel-Temp apparatus, the 5-amino-1,2,3,4-thiatriazole looked like it began to melt at 110°C. At 111°C, there was a soft pop and the 5-amino-1,2,3,4-thiatriazole began to bubble violently. The FTIR spectra and UV-Vis Spectra are shown below in Figures 4-7, with the key peak assignment in Table 1.

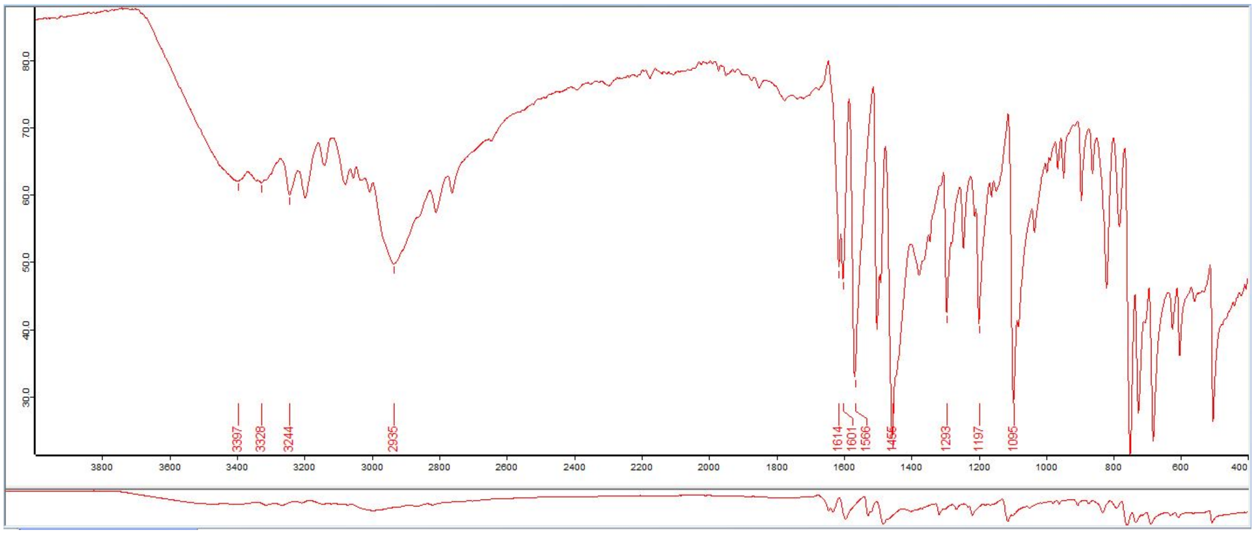


Figure 4. IR of 5-anilino-1,2,3,4-thiatriazole

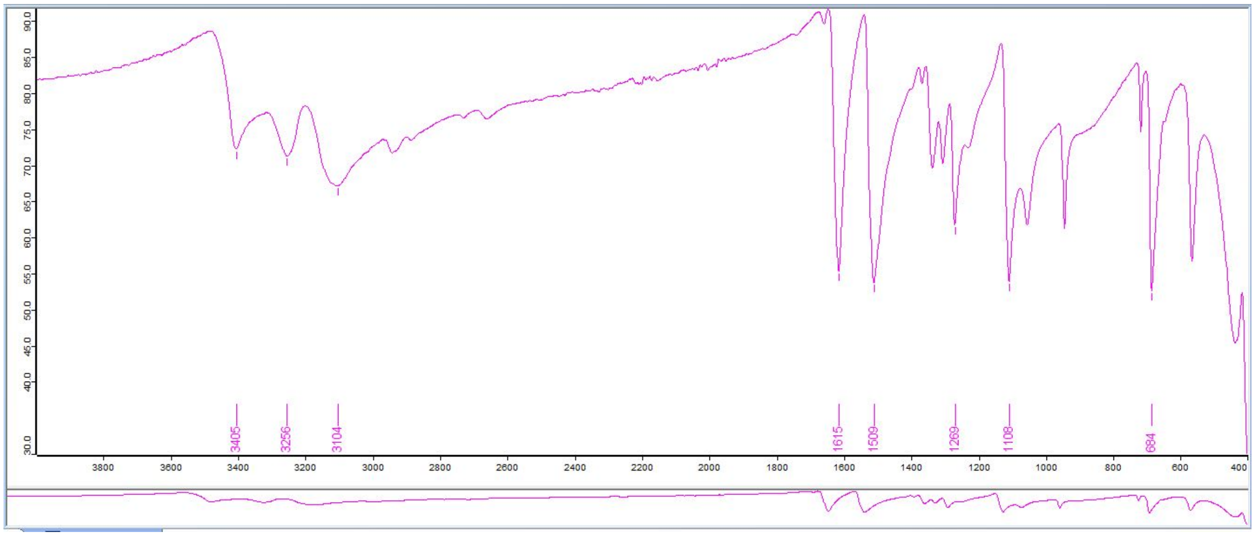


Figure 5. IR of 5-amino-1,2,3,4-thiatriazole

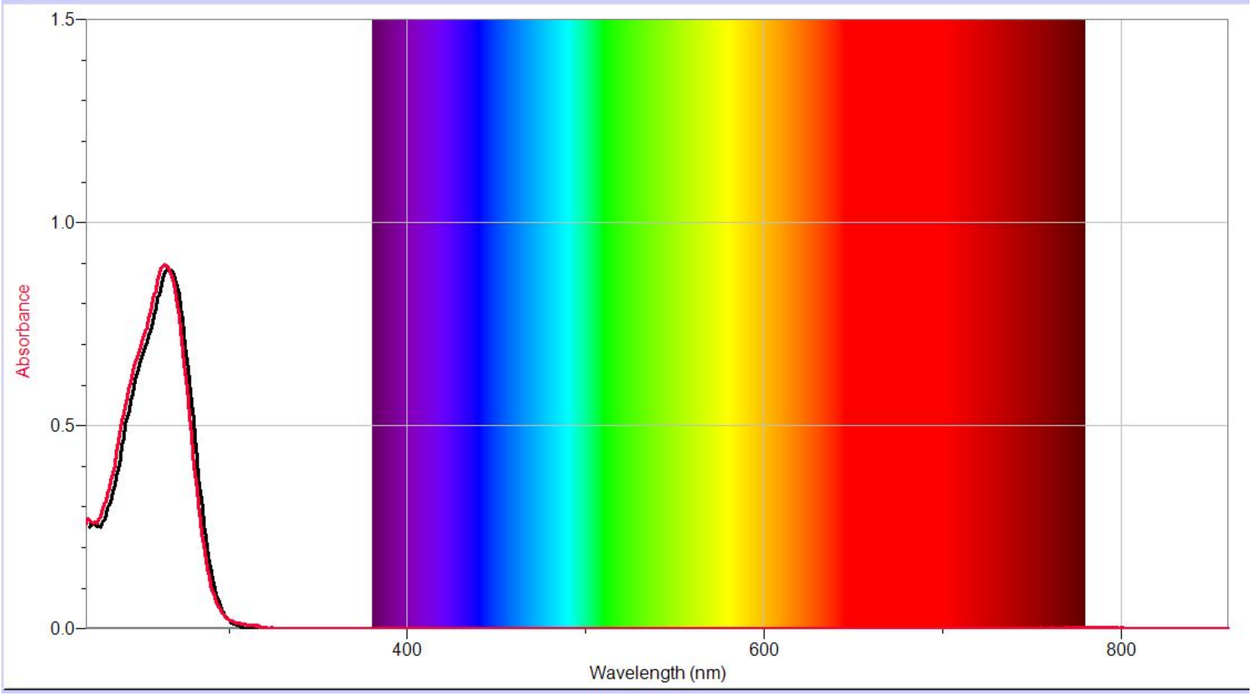


Figure 6. 5-amino-1,2,3,4-thiatriazole

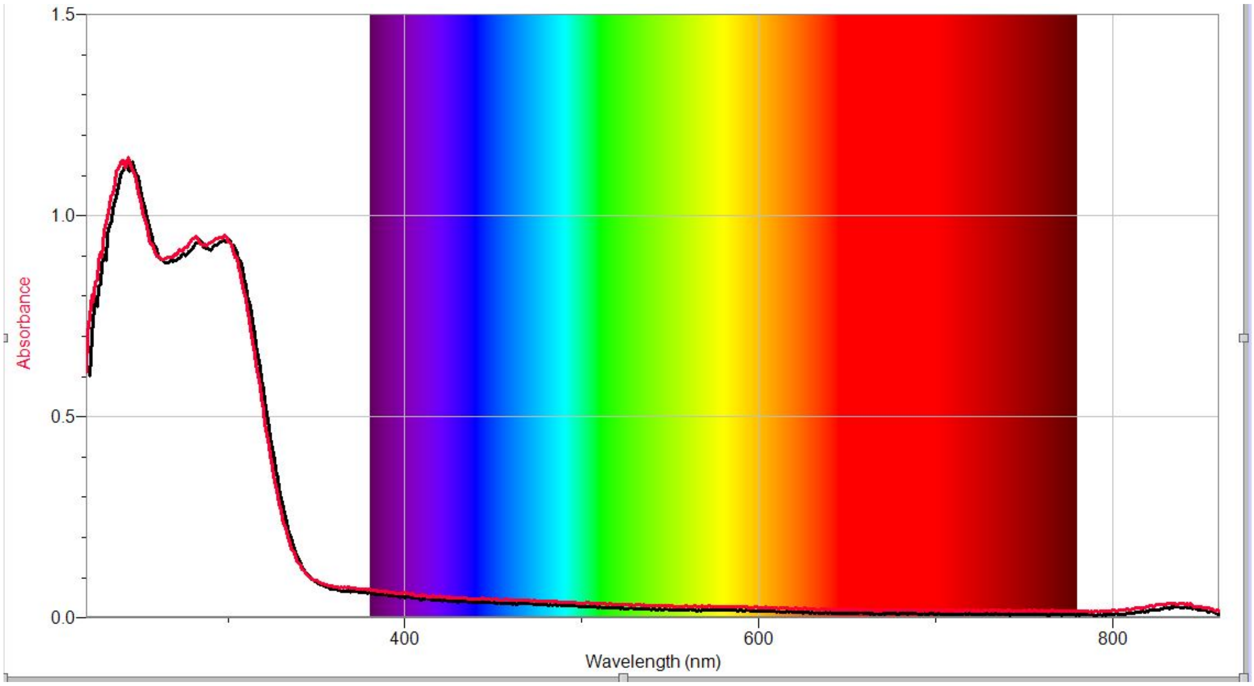


Figure 7. 5-anilino-1,2,3,4-thiatriazole

5-anilino-1,2,3,4-thiatriazole			5-amino-1,2,3,4-thiatriazole		
Band position (cm^{-1})	Intensity	Assignment	Band position (cm^{-1})	Intensity	Assignment
3397	weak	N-H	3256	weak	NH_2
1614	medium	C=N	1615	medium	C=N
1601	medium	Aromatic C=C			

Table 1. Assignment of Peaks from Figures 6 and 7.

Discussion

The temperature at which decomposition was expected to happen for both **1** and **2** was lower than the literature values. **1** was reported to begin decomposing at a lower temperature than found in literature (144℃).[4] **2** also began to decompose at a lower temperature than in literature (120℃-122℃).[5] The given λ_{max} of **1** was 302 nm and the given λ_{max} of **2** was 267 nm. The λ_{max} of both UV-Vis spectra, shown in Figures 6 and 7 are shifted from the expected values. It is difficult to suggest causes for the impurities, but it is possible that it could be from water, as there is a broad, weak peak that is characteristic for water in the 3400 cm^{-1} range in both IR spectra. The assignment of key peaks in Figures 4 and 5 are made in Table 1.

While both products did decompose at high temperatures, **2** decomposed with an audible pop, whereas **1** did not. A reason for this could be due to the aromatic benzene ring on **1**. Aromatic benzene rings are particularly unreactive, which could have lowered the reactivity of the molecule. Despite the slight difference in reactivity, the two products decomposed violently and produced gas which was evident by the bubbling observed from the decomposition of **1** and bubbling and popping noise observed from the decomposition of **2**. Neither product was formed in good yield. This is likely because both products adhered to the beakers and filtration systems.

Conclusion

The two different 1,2,3,4-thiatriazoles were successfully synthesized, characterized by UV-Vis and IR spectroscopy, and decomposed. The two products decomposed in a less violent manner than dynamite. The purity of the products could be checked using Mass Spectrometry and by repeating the experiment multiple times.

References

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[1] Akhavan, J. The Chemistry of Explosives, 2011.

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[3] Holm, A.; Carlsen L.; Larsen E. J. Org. Chem., **1978**, *43* (25), 4816–4822

[4] 5-Anilino-1,2,3,4-thiatriazole 152404 http://www.sigmaaldrich.com/catalog/product/aldrich/152404?lang=en®ion=US (accessed 2/15/2017).

[5] 1,2,3,4-Thiatriazol-5-amine http://www.chemspider.com/Chemical-Structure.214029.html (accessed 2/15/2017).