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

Abstract

______Two different 1,2,3,4-thiatriazoles were synthesized from 4-phenyl-3-thiosemicarbazide and thiosemicarbazide 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

In this experiment two substances are synthesized that decompose rapidly, even explosively. Explosive reactions are exothermic reactions that release large amounts of heat and many moles of gas.[1] A commonly known explosive is dynamite, which is made from nitroglycerine.[1] The spontaneous decomposition reaction for nitroglycerine is shown in Figure 1.

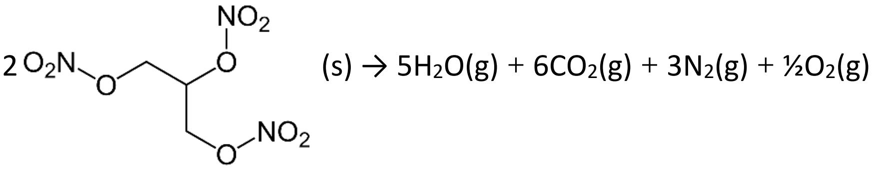

Figure 1. The decomposition reaction of nitroglycerine

Decomposition of nitroglycerine is so thermodynamically favorable because forming water, carbon dioxide, dinitrogen and dioxygen is highly exothermic due to their high bond enthalpies, and many moles of gas are formed. Another reason for dynamite's reactivity is that the carbon atoms can react with the oxygen atoms in the compound without the need for any external source of oxygen.[1]

Thiatriazoles are nitrogen and sulfur containing compounds, which form dinitrogen when decomposed. Because the nitrogen-nitrogen triple bond has a large bond enthalpy and dinitrogen is a gas, the decomposition reaction is explosive. Thiatriazoles may be synthesized using a diazotization reaction, which is shown below.[2] In this report, two different 1,2,3,4-thiatriazoles were synthesized using 4-phenyl-3-thiosemicarbazide, thiosemicarbazide, hydrochloric acid, and sodium nitrite. The reactions are shown below in Figures 2 and 3.

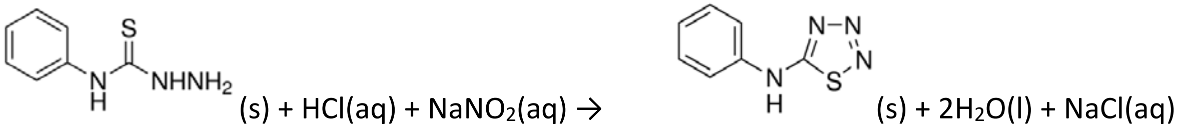

Figure 2. The diazotization reaction for formation of 5-anilino-1,2,3,4-thiatriazole

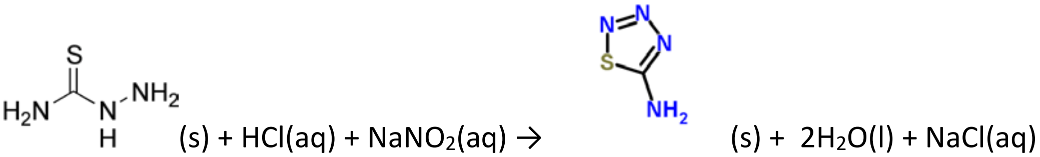

Figure 3. The diazotization reaction for formation of 5-amino-1,2,3,4-thiatriazole

Thiatriazoles decompose when heated.[3] These two 1,2,3,4-thiatriazoles are expected to decompose at high temperatures with release of heat and gas, mimicking the explosion of dynamite. The single and double bonds between the nitrogen atoms in the ring help to form dinitrogen, because the nitrogen atoms are already connected to one another.

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 done with the products in methanol.

5-anilino-1,2,3,4-thiatriazole (**1**)- Solid 4-phenyl-3-thiosemicarbazide (0.469 g, 2.79×10^{-3} mol) was added to HCl (2.5 mL of 15% HCl in water.) The suspension was stirred and cooled in an ice-bath, with the temperature kept between 5°C and 10°C. Solid $NaNO_2$ (0.210 g, 3.04×10^{-3} mol) was 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 moderate stirring, to avoid causing the temperature to rise above 10°C. The pasty brown product was isolated in a Hirsch funnel using suction filtration, and rinsed three times with 0.5 mL of ice cold water. A 1.0×10^{-4} M methanol solution of the resulting 5-anilino-1,2,3,4-thiatriazole was used for the UV-visible spectroscopy. Yield: 0.678g (3.8×10^{-3} mol, 33.7%) d.p. = 109°C. IR (cm^{-1}, ATR): 3397 (br, w), 3328 (w), 3244 (w), 2935 (m), 1614 (m), 1601 (m), 1566 (s), 1455 (s), 1293 (m), 1197 (m), 1095 (s).

5-amino-1,2,3,4-thiatriazole (**2**)- The procedure above was repeated with 0.275 grams of thiosemicarbazide being added to 1.0 mL of 3M HCl. Solid $NaNO_2$ (0.212g, 3.07×10^{-3} mol) was dissolved in 0.5 mL of water and 0.4 mL of the solution was added dropwise into the suspension of thiosemicarbazide. A 2.55×10^{-4} M methanol solution of the resulting 5-amino-1,2,3,4-thiatriazole was used for the UV-Vis spectroscopy. Yield: 0.113 g (1.1×10^{-3} mol, 36.69%) d.p. = 110°C. IR (cm^{-1}, ATR): 3405 (w), 3256 (w), 3104 (w), 1615 (m), 1509 (m), 1269 (w), 1108 (m), 684 (m).

Results

The 5-anilino-1,2,3,4-thiatriazole was synthesized in poor yield (33.7%) and was a beige colored clumpy solid. In the Mel-Temp apparatus, the 5-anilino-1,2,3,4-thiatriazole appeared to melt at 109°C. At 110°C it turned a lighter color and it 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 products both adhered to the sides of the Erlenmeyer flask, the stir bar, and the Hirsch funnel. Despite scraping the products off the equipment, a significant portion of the product was unable to be removed. The FTIR Spectra, UV-Visible Spectra, and key peak assignment can be found in Figures 4-7 and Table 1, respectively.

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 stretch	3256	weak	NH_2 stretch
1614	medium	C=N stretch	1615	medium	C=N stretch
1601	medium	Aromatic C=C stretch			

Table 1. Assignment of Peaks from Figures 4 and 5.

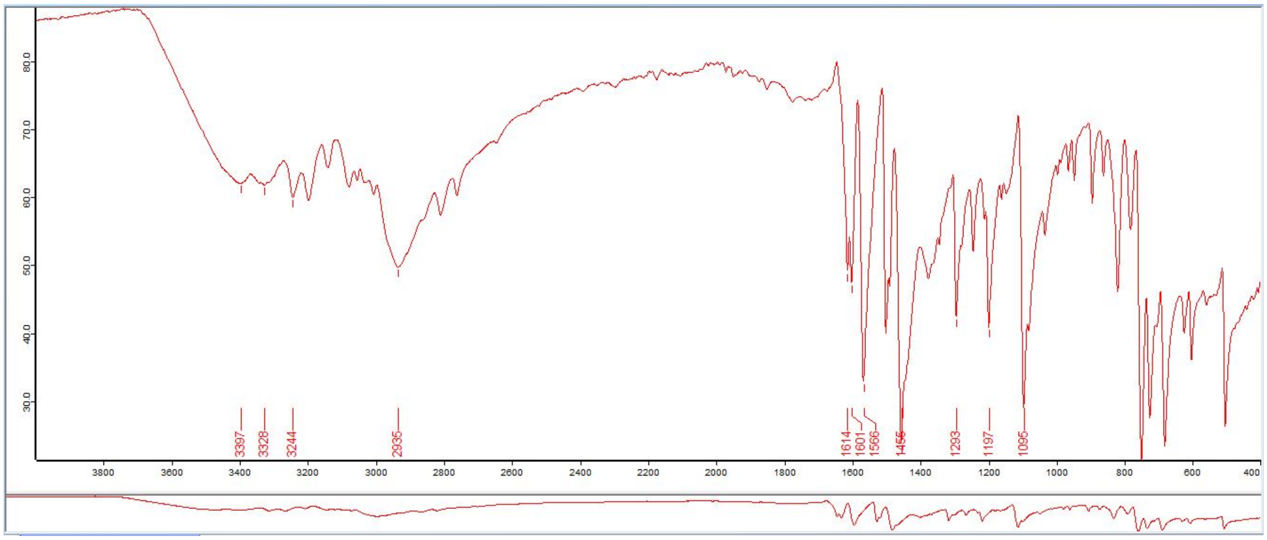

Figure 4. Infrared Spectrum of 5-anilino-1,2,3,4-thiatriazole

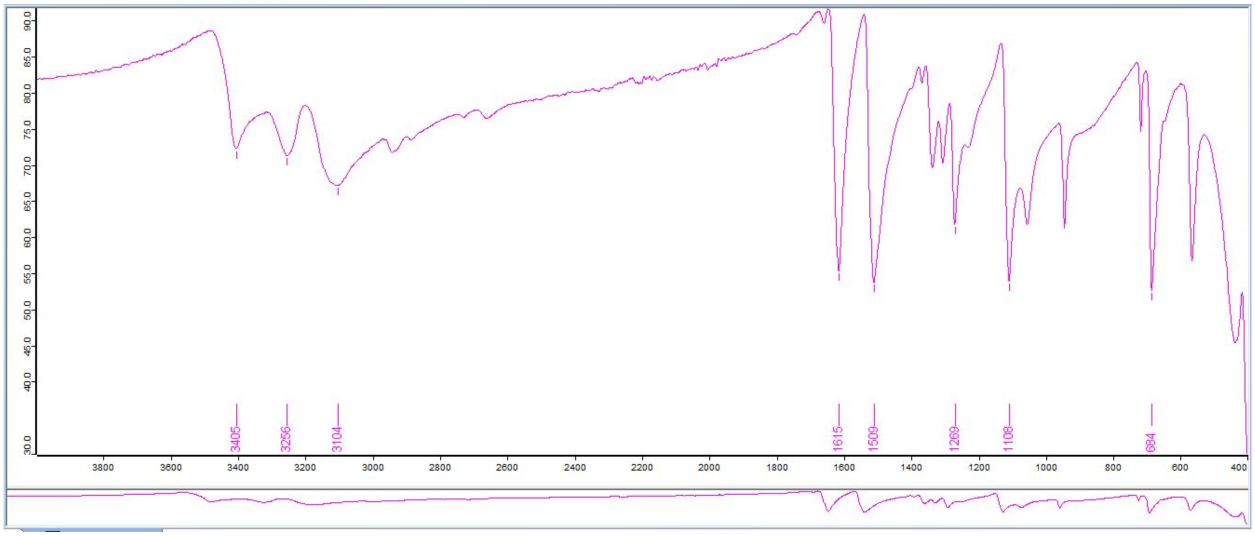

Figure 5. Infrared Spectrum of 5-amino-1,2,3,4-thiatriazole

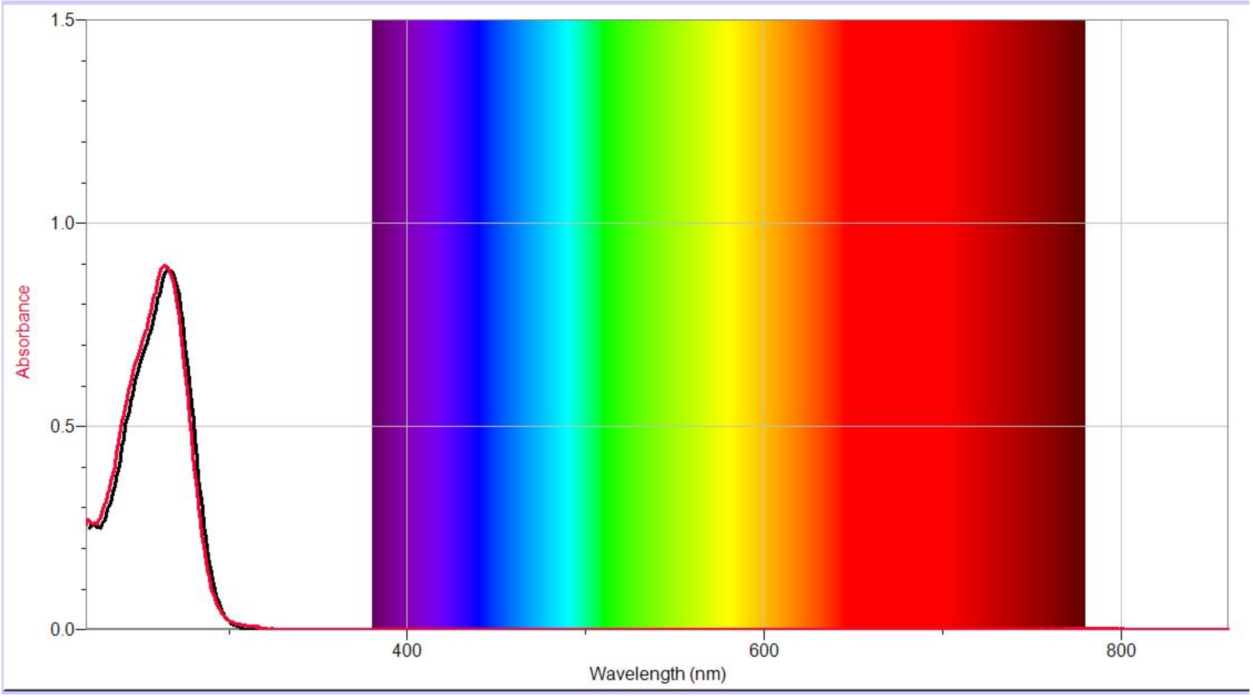

Figure 6. UV-Vis Spectrum of 5-amino-1,2,3,4-thiatriazole

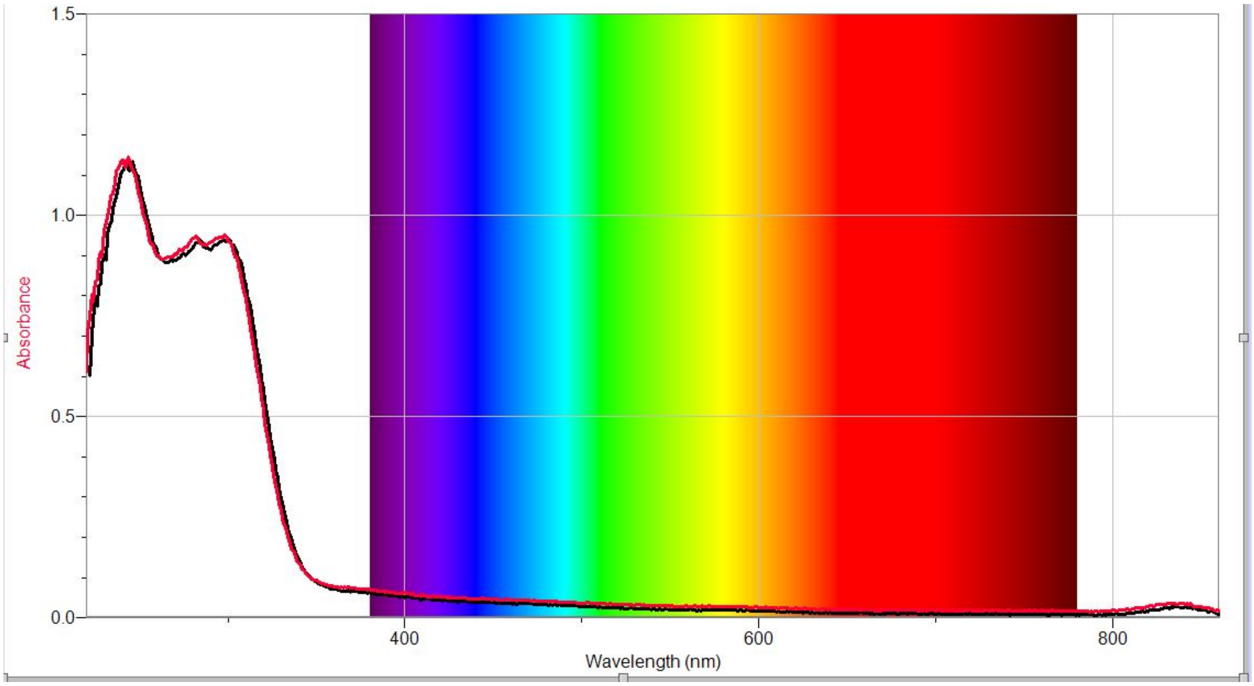

Figure 7. UV-Vis Spectrum of 5-anilino-1,2,3,4-thiatriazole

Discussion

The temperature at which decomposition occurred for both **1** and **2** was lower than the literature values, with **1** beginning at 112°C, a lower temperature than found in literature (144°C), and **2** bubbling at 111°C (literature value: 120-122°C).[4,5] The lower decomposition points suggest that both products were impure, and the UV-Vis spectroscopy and FTIR spectrum support this. 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 which could be the result of impurities which could have arisen from unclean glassware. Another possibility for the lower decomposition points is that the samples were not completely dry. A broad, weak peak that is characteristic for water can be seen in the 3400 cm^{-1} range in both IR spectra, which are shown in Figures 4 and 5 with their key peak assignments 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 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**. Although neither product was formed in good yield, this is likely due to the loss of a significant amount of both products on the stir bars, inside the Erlenmeyer flasks, and on the Hirsch funnel.

Conclusion

The two different 1,2,3,4-thiatriazoles were synthesized, characterized by UV-Vis and IR spectroscopy, and decomposed under heat; however, yields were low and the products appeared to be impure. The two products decomposed in a much more controlled manner than that of dynamite. The purity of the products could be checked further using mass spectrometry. Repeating the experiment several times might produce higher purity products that could be compared with those obtained in this report. The lower reactivity of the thiatriazoles means that they could be used in car airbags due to the controllable nature of the decomposition.

References

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