

Study on synthesis and properties of ammonium salts of 1,2,4-triazole-3-one and 1,2,4-triazolidine-3,5-dione

Mieko Kumasaki^{*†}, Mikito Nakano^{*}, Kohei Sasahara^{*}, Shingo Date^{**},
and Takaaki Mizutani^{***}

^{*}Graduate School of Yokohama National University
79-5 Tokiwadai, Hodogaya, Yokohama, Kanagawa, 240-8501, JAPAN
Phone +81-45-339-3994

[†]Corresponding author : kumasaki@ynu.ac.jp

^{**}National Defense Academy 1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, JAPAN

^{***}National Institute of Occupational Safety and Health, Japan 1-4-6 Umezono, Kiyose, Tokyo, 204-0024, JAPAN

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Abstract

Ammonium salts of 1,2,4-triazole-3-one and 1,2,4-triazolidine-3,5-dione were synthesised and their properties were evaluated. The boiling point of 1,2,4-triazole-3-one allowed direct reaction with liquid ammonia.

Elemental analysis showed that nitrogen content of the ammonium salts increased, as expected, which is favourable for gas generating agents. FT-IR spectra indicated that the framework structures were conserved during the reaction. However, ammonia gas was released from 1,2,4-triazole-3-one salts at room temperature, while 1,2,4-triazolidine-3,5-dione maintained its composition.

The thermal decomposition behaviour of 1,2,4-triazolidine-3,5-dione salt showed that ammonium gases evolved at 85°C. Sensitivity tests were carried out and burning rates of the mixtures with ammonium nitrate and CuO were measured to understand the properties of azole-ammonium salts.

Keywords : 1,2,4-triazole-3-one and 1,2,4-triazolidine-3,5-dione, ammonium salts, pyrolysis behaviour, sensitivity, combustion behaviour

1. Introduction

Pyrotechnic substances can release enormous amounts of energy when stimulated by an external energy, such as heat, friction, impact, and so forth. Considerable effort has been devoted to analysing the energy release mechanisms of pyrotechnics so as to develop new applications^{1),2)} and prevent accidents³⁾. The properties of pyrotechnics have been examined extensively, and they are now used in a variety of applications. Perhaps the best known pyrotechnics are fireworks⁴⁾, however, life saving devices, such as airbag inflators⁵⁾ also harness the energy of pyrotechnics by using the rapidly expanding gasses to inflate an airbag during a collision. This rapid release of gas has also been used to develop rockets⁶⁾.

As the demand for pyrotechnics has increased, pollution from by-products has become an issue⁷⁾. Of particular concern are heavy metals and chlorine species, which are often added to pyrotechnics to enhance the rate of combustion⁸⁾. Incomplete decomposition can also cause pollution by creating smoke or particulate matter. These substances are harmful not only to humans but also to the environment. The widespread use of pyrotechnic substance inevitably poses a significant risk of exposure to harmful decomposition pollutants, which has spurred demand for so-called 'green' pyrotechnics.

One promising avenue for directions pollutants is high nitrogen content materials⁷⁾. Pyrotechnics with high nitrogen content are desirable as they reduce the amount

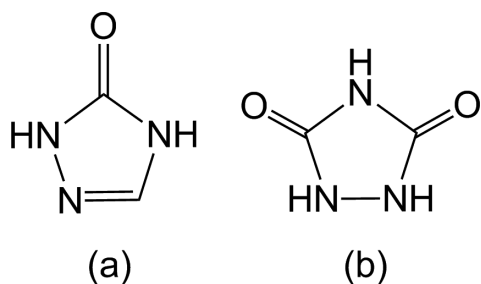


Figure 1 The chemical structures in this study (a) TO, (b) UR.

of smoke, particulate matter, and decomposition residue because the reaction products are expected to be nitrogen and small molecules. Unfortunately, high nitrogen content molecules are often unstable, which makes them difficult to handle and increases the risk of an accidental explosion or fire. However, the high energy content does make them suitable pyrotechnics and decrease the need for additional materials that enhance the decomposition rate, which often go on to become harmful pollutants.

Therefore, there is as strong demand for pyrotechnic substances that exhibit good stability and good energy release, even though these requirements seem mutually exclusive. To achieve high nitrogen content and reasonable stability, many of the most common materials in modern pyrotechnics utilise conjugated systems such as azoles, guanidine, and tetrazine, and so forth⁹.

Conjugated systems, in the context of pyrotechnics, comprise a framework of unsaturated bonds and nitrogen or oxygen lone pairs, which are resilient to electronic perturbation. Conjugated systems can act as cations or anions, and form energetic salts with their counter ions. For instance, the salt 3,5-Dinitroamine-1,2,4-triazole with hydrazinium was synthesised¹⁰, and Warner *et al.* synthesised azole salts composed of an azotetrazole anion and aminotetrazole cation¹¹. Heterocyclic compounds have a positive formation enthalpy and a high heat value, which enable them to exhibit good energy release even without harmful additives and makes their salts potential candidates for stable 'green' pyrotechnics.

As for salts, 1,2,4-triazole-3-one, TO (Figure 1 (a)) and its alkaline metal salts have been focused on to examine to understand the thermal stability of energetic materials¹². TO has a conjugated heterocyclic system comprising a triazole ring and carbonyl group, and has served as a framework for some valuable energetic materials. One derivative of TO is the nitro-substituted 3-nitro-1,2,4-triazole-5-one (NTO), which is used as a propellant in military ordnance¹³. NTO has a high burning rate, emits large amount of gas, and shows low sensitivity to heat^{14–16}. Another TO derivative is 1,2,4-triazolidine-3,5-dione, urazole, UR (Figure 1 (b)), whose decomposition behaviour was examined¹⁷. This fact raised a question on the mechanism attributed to the characteristic feature of TO framework and led to the study about its salt. Previous studies about its salts revealed that TO formed salts as an anion and the temperature of the endothermic and exothermic peaks of TO salts decreased as the atomic number of the alkali metal ion increased¹².

Based on the previous study, one of the further steps can be in the direction to investigate TO salts for "green" pyrotechnics. One of the benefits for salts as pyrotechnic substances, ion exchange can provide various types of salts once a synthetic route is established for a base substance while the exploring the substituents effect is often accompanied with exploring novel synthetic routes to obtain desired substances, which usually takes time. With regards to triazoles, many salts have been synthesised, including conventional counter ions such as NO_3^- , ClO_4^- , and so forth^{18–20}. Other azole compounds, however, have not been investigated as thoroughly.

In this study, TO and UR ammonium salts were synthesised and their properties were evaluated. Ammonium cation, NH_4^+ , is conducive to the increasing the volume of a gas. By exploiting the acidity of TO and UR, the synthesis was carried out by a direct acid-base reaction with liquid ammonium. The resulting chemical structures and thermal properties were investigated. Sensitivities and combustion rate of the stable substances were measured.

2. Experimental method

2.1 Samples

TO was synthesised from triethyl orthoformate and semicarbazide hydrochloride obtained from Kanto Chemical Co., Inc. as described previously^{12,21}. UR was purchased from Kanto Chemical Co., Inc. Aqueous ammonia (28%, Wako Pure Chemical Industries, Inc.) or ammonia gas (99.9%, Takachiho Chemical Industrial Co., Ltd.) was used for the synthesis.

2.2 Synthesis

In previous studies, ammonium azole salts were synthesised by mixing azole solution with aqueous ammonium. The salt was isolated by evaporation of water²². TO, however, has a boiling point similar to water and would also evaporate after the reaction. Therefore, direct reaction was adopted with liquid ammonia so that it was not necessary to remove water after the reaction.

In a small-scale reaction, a solution of aqueous ammonia released gaseous ammonia by heating. The gaseous ammonia was introduced into a round-bottom flask containing azole, following to dehydration with a drying agent (CaCl_2). After a sufficient amount of ammonia had collected, the flask was sealed and cooled in a dry ice bath to condensate the ammonia. In a larger scale experiment, gaseous ammonia from a cylinder was introduced to a round-flask containing azole, which was cooled in a dry ice bath prior to the introduction. In both experiments, the azole-ammonia mixture was stirred for a few hours and then returned to room temperature to evaporate any unreacted ammonia. Yellow and colourless powders were obtained from TO and UR respectively.

2.3 Instruments

2.3.1 Characterisation

Characterisation was carried out by elemental analysis (EA, Elementar Analysensysteme GmbH, Vario ELIII

Table 1 The summary of synthetic results, IR absorption, and elemental analysis.

Sample	Yield [%]	Composition	IR absorption [cm ⁻¹]	Anal. Found (Cald.)		
				C	H	N
TO	89	C ₂ H ₃ N ₃ O	1700 (C=O)	28.54 (28.40)	3.56 (3.55)	49.56 (49.40)
TONH ₄	90	C ₂ H ₂ N ₃ O · NH ₄	1685 (C=O)	29.51 (23.52)	6.18 (5.92)	56.42 (54.88)
UR	–	C ₂ H ₃ N ₃ O ₂	1690 (C=O)	(23.77)	(2.99)	(41.57)
URNH ₄	90	C ₂ H ₂ N ₃ O ₂ · NH ₄	1690 (C=O)	20.27 (20.34)	5.28 (5.12)	47.28 (47.44)

CHNOS Elemental analyse). Fourier transform infrared spectroscopy (FT-IR, JASCO FTIR-420) use the KBr method. The thermal properties were investigated with differential scanning calorimetry (SC-DSC, Mettler Toledo HP DSC827e) at a heating rate of 10Kmin⁻¹ over a measurement range 30–500°C. The measurement was conducted in stainless steel cell under air without sealing. Mass spectroscopy coupled with thermal analysis (TD-DTA-MS) was performed with a DTG8120 (Rigaku Corporation) for thermal gravimetry and a GCMS-QP2010 (Shimadzu Corporation) mass spectrometer. About 10 mg of each sample was heated in an aluminum cell from room temperature to 500°C at a heating rate of 10Kmin⁻¹. Helium was used as a carrier gas at flow rate of 200 mlmin⁻¹.

2.3.2 Sensitivity test

The friction sensitivity was measured by the Julius Peter friction tester (BAM). The 1/6 explosion point was determined by rubbing the substances on a moving plate with a fixed pin.

The mechanical impact sensitivity was measured by the Japanese Industrial Standards (JIS) drop hammer test. In the experiments, sample of approximately 0.03 g were placed in a brass cup. The cup was placed in the device and the weight was dropped from a predetermined height. The tests were repeated to determine the 1/6 explosion point.

2.3.3 Combustion behaviour

To obtain some insight into of the combustion behaviour of the compounds, ammonium salts were ignited and their burning rates were measured in a closed strand burner. The linear burning rates were measured under four gauge pressure conditions (1,2,5 and 7MPa).

Samples were mixed with an ammonium nitrate as an oxidizer in stoichiometric proportions and 5 parts CuO was added to 100 parts of stoichiometric mixture. Cylindrical pellets were prepared by compressing approximately 1.5 g of the mixture under 402 MPa for 5 min. The pellets were formed with diametres of about 11 mm. Their side surfaces were coated with silicone adhesive sealant as a restrictor to achieve end-burning.

A chimney-type strand burner (Tohata Denshi K. K.,

TDK-15011) was used as the burning test system. A pelleted sample was placed on the strand holder, and the pellet was ignited by a heated nickelchrome wire (diameter 0.8 mm) in a N₂ atmosphere. The internal pressure of the vessel was monitored using a strain-gauge pressure transducer (Kyowa Electronic Instruments, Co., Ltd., PG-100kV-F). After amplification by a signal conditioner (Kyowa Electronic Instruments Co., Ltd, CDV-700A), the signal was recorded on a data recorder (Keyence Corporation, GR-3000). The time between the onset of the pressure rise and the peak pressure, together with the length of the pellet, were measured to determine the linear burning rate.

3. Result and discussion

3.1 Characterisation

Table 1 summarises the synthetic results, IR absorption, and elemental analysis. As ammonium salts both TO and UR had increased nitrogen content as expected, which is favourable as gas generating agents. FT-IR measurements revealed the characteristic carbonyl absorption at 1700, 1685, 1690, and 1690 cm⁻¹ for TO, TONH₄, UR, and URNH₄ respectively. While many of the ammonium salts previously synthesised were obtained from metal salts via cation exchange, this synthesis gave salts directly by mixing liquid ammonia, whose framework maintained a carbonyl group.

TONH₄ and URNH₄ exhibited N-H absorptions which can be attributed to NH₄⁺. However, the intensity of the absorption in TONH₄ decreased over time and eventually disappeared, resulting in the spectrum becoming identical to that of TO. This change occurred at room temperature, which indicates that gaseous ammonia is easily liberated from TO salts. The pK_a of TO was reported as 8.53 and 5.75 for UR²³, so it is reasonable to assume that UR is a stronger acid and its ammonium salt is more stable than that of TO.

Due to the instability of the TO salt, further investigations were reserved for URNH₄.

3.2 Thermal behaviour

Figure 2 shows the thermal behaviour obtained by DSC. UR and URNH₄ have endothermic peaks at the same temperatures except some obvious endothermic

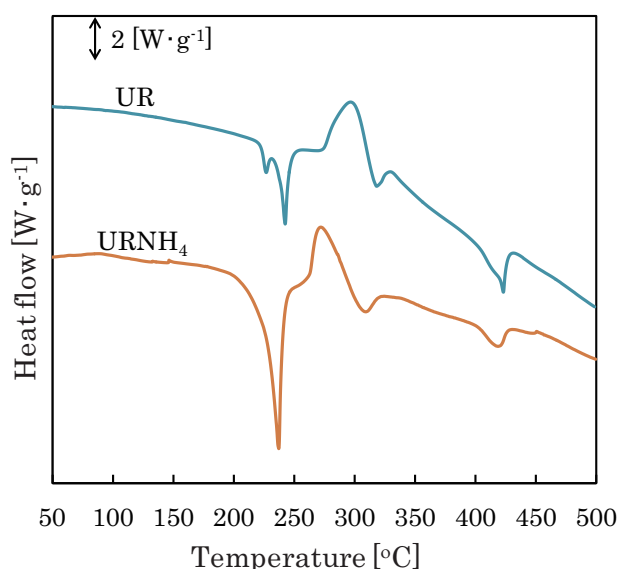


Figure 2 DSC results of UR and URNH₄.

phenomenon ranging from 200–250°C for UR and URNH₄ and slight endothermic behaviour from 100 – 150°C for URNH₄.

The thermal decomposition products of UR and URNH₄ were analysed by TG-DTA-MS as a function of temperature (Figure 3). Both substances had a high gasification rate, 97% for UR and 98% for URNH₄. The DTA curves of UR and URNH₄ are quite similar, and gaseous ammonia was liberated from URNH₄ at 85°C. After the transformation, it decomposed in the same way as its precursor, UR. That implied that URNH₄ conserved the UR framework during the heat stress up to the decomposition temperature of UR. UR molecules in the salt might have changed its structure under coexistence of ammonia, but it should be irreversible because of the behaviour in TG-DTA-MS.

The mass spectrum showed strong M⁺ peaks ($m/z=28$,

43). The peak at $m/z=43$ can be attributed to HNCO, taking into consideration the chemical structure of UR. The peak at $m/z=28$ could correspond to either CO or N₂, both of which are plausible decomposition product. However, it is possible that some bond fission followed by atomic rearrangement might occur without major gas release during the process of experiencing thermal stimuli.

3.3 Sensitivity test

Table 1 reports the results of sensitivity tests. URNH₄ exhibited the least sensitivity in the drop hammer test while it was more friction sensitive than its precursor. Considering that the friction sensitivity of 1H-1,2,4-triazole, was class 5 in the previous report²⁴, URNH₄ does not necessarily require extreme care compared to other conventional energetic materials.

3.4 Combustion behavior

URNH₄/AN and URNH₄/AN/CuO were ignited easily and completed their combustion under each experimental condition. The relation between the pressure and the linear burning rate, given by the Vieille equation, is shown in Figure 4.

The experimental results shown in Figure 4 reveal that UR/AN mixture exhibited a higher burning rate when CuO was added; however, the burning rate was low compared to previously reported activated carbon/AN/CuO²⁵. It was also shown that the pressure index of URNH₄/AN/CuO mixture was higher than URNH₄/AN mixture, which differs from the study by Miyata *et al.* on aminoguanidinium-5,5'-azobis-1H-tetrazolate/AN based mixtures where the pressure index has decreased by adding CuO at 2 MPa (2.8 mm·s⁻¹)²⁶.

4. Conclusion

Thermally stable “green pyrotechnics” can be prepared

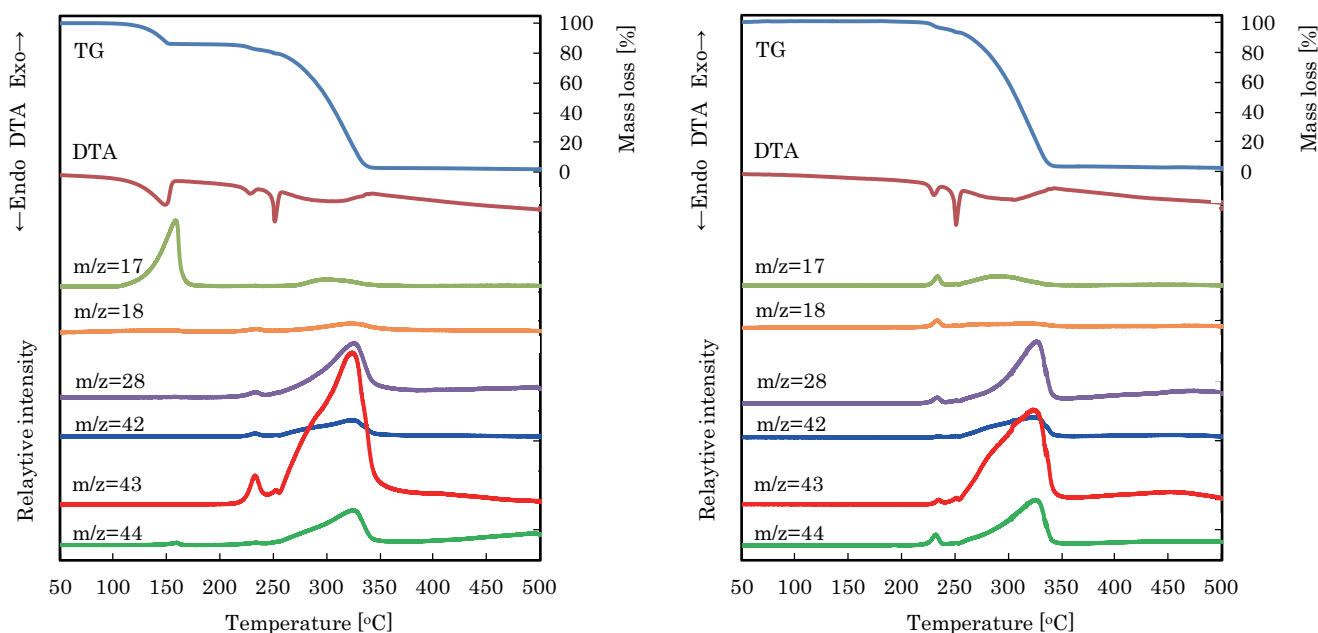
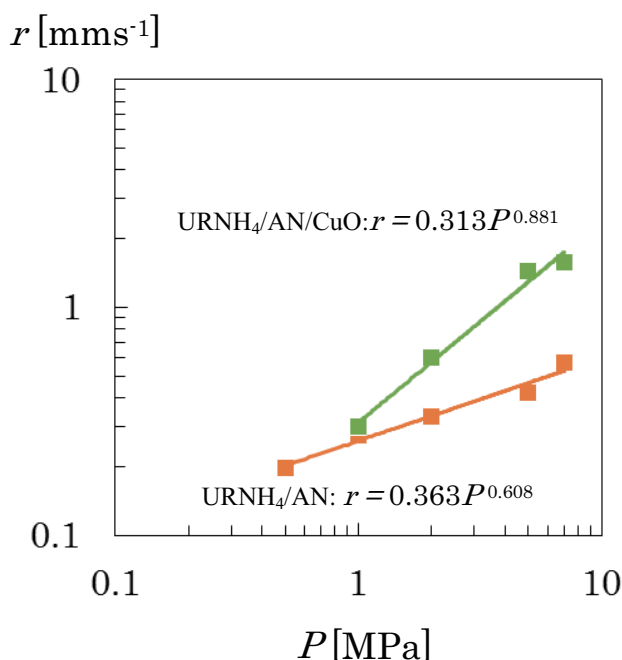


Figure 3 The result of TG-DTA-MS URNH₄ (left), UR (right).

Table 2 The summary of sensitivity test.

	Drop Hammer Test	Friction Test
UR	Class7	Class6
URNH ₄	Class8	Class5

**Figure 4** Relation between linear burning rate of URNH₄/AN (indicated as URNH₄) and URNH₄ AN/CuO/mixture in the function of gauge pressure.

from salts of nitrogen-rich conjugated systems. In this study, ammonium salts of TO and UR were synthesised and their properties were evaluated. Due to the low boiling point of TO, direct reaction with liquid ammonia was adopted.

The elemental analysis of the ammonium salts indicated high nitrogen content, while the FT-IR spectra confirmed that the conjugated frameworks were preserved through the reaction. However, the TO salts were unstable and released gaseous ammonia at room temperature, whereas UR salts maintained their composition.

Thermal decomposition gave a high gasification rate, i.e. 97% for UR and 98% for URNH₄, respectively. URNH₄ liberated gaseous ammonia at 85°C in this experiment condition and transformed back into UR. The sensitivity of the UR salt was considered stable enough by comparison with conventional energetic materials. UR salts and AN mixture exhibited a higher burning rate by adding CuO; however, the burning rate was still low compared to previously reported activated carbon/AN/CuO; and there was also an increase in the pressure index when CuO was added.

This study examined the potential for azole-ammonium salts to be used as pyrotechnic materials. By manipulating the azole framework, stable nitrogen-rich salts were prepared which leave fewer residues than conventional pyrotechnics. These results suggest that azole salts will be conducive to the further step to design favourable “green

pyrotechnics” and add a novel and useful dimension to researches.

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