4

TECHNICAL REPORT ARAED-TR-88015

THE SYNTHESIS OF TRIAMINOGUANIDINIUM AZIDE (TAZ)

A. J. BRACUTI
C. Y. MANNING

AUGUST 1988

US ARMY
ARMAMENT MUNITIONS
& CHEMICAL COMMAND
ARMAMENT RDE CENTER

U. S. ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER
ARMAMENT ENGINEERING DIRECTORATE
PICATINNY ARSENAL, NEW JERSEY

ERRATA

Technical Report ARAED-TR-88015

THE SYNTHESIS OF TRIAMINOGUANIDINIUM AZIDE (TAZ)

A. J. Bracuti
C. Y. Manning

August 1988

Change text of report as follows:

Arrows in equations 2 and 3 on page 4, and equations 1 and 3 on page 5 should be replaced with ⟷ arrows.

September 1988

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER Technical Report ARAED-TR-88015

5. MONITORING ORGANIZATION REPORT NUMBER

6a. NAME OF PERFORMING ORGANIZATION ARDEC, AED

6b. OFFICE SYMBOL SMCAR-AEE-BR

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS (CITY, STATE, AND ZIP CODE)
Energetics and Warheads Div.
Picatinny Arsenal, NJ 07806-5000

7b. ADDRESS (CITY, STATE, AND ZIP CODE)

8a. NAME OF FUNDING/SPONSORING ORGANIZATION ARDEC, IMD STINFO Br

8b. OFFICE SYMBOL SMCAR-IMI-I

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (CITY, STATE, AND ZIP CODE)
Picatinny Arsenal, NJ 07806-5000

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (INCLUDE SECURITY CLASSIFICATION)
THE SYNTHESIS OF TRIAMINOGUANIDINIUM AZIDE (TAZ)

12. PERSONAL AUTHOR(S) A. J. Bracuti and C. Y. Manning

13a. TYPE OF REPORT

13b. TIME COVERED FROM ________ TO ________

14. DATE OF REPORT (YEAR, MONTH, DAY) August 1988

15. PAGE COUNT 15

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (CONTINUE ON REVERSE IF NECESSARY AND IDENTIFY BY BLOCK NUMBER)
Molecular structure, Synthesis [illegible] Ion exchange
Hydrolysis Triaminoguanidinium azide

19. ABSTRACT (CONTINUE ON REVERSE IF NECESSARY AND IDENTIFY BY BLOCK NUMBER)

Triaminoguanidinium azide (TAZ), a potential propellant ingredient, has been prepared and isolated by a nonaqueous cation exchange technique. Prior to this, others who have attempted to prepare and isolate TAZ with various aqueous and partially nonaqueous approaches had encountered difficulty in characterizing it. These latter methods produced off-white unstable solids which were easily oxidized in air to form a myriad of multicolored products. The nonaqueous method described in this report, however, produces a white compound which is apparently more stable in dry air but reactive in moist air. Comparisons are made among the products formed by both the aqueous and nonaqueous methods.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL I. HAZNEDARI

22b. TELEPHONE (INCLUDE AREA CODE) (201)724-3316

22c. OFFICE SYMBOL SMCAR-IMI-I

DD FORM 1473, 84 MAR

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

CONTENTS

INTRODUCTION

The family of triaminoguanidinium salts (CN_6H_9X or TAGX) was selected by the propellant community in the 1950's as a potential source of propellant ingredients (ref 1). One of the TAG salts of particular interest was the azide (TAZ) whose molecular formula ($CN_6H_9N_3$) suggested that it probably would burn with a relatively low flame temperature and generate large volumes of different low molecular weight gases according to

$$CN_6H_9N_3 + 13/4\ O_2 \longrightarrow CO_2 + 9/2\ H_2O + 9/2\ N_2$$

and produce a relatively high impetus.

Unfortunately, during the intervening years, the synthesis of TAZ while seemingly a straight-forward task has, until recently, been fraught with unexpected and unexplained complications.

In an initial effort to prepare TAZ, the Thiokol Company (ref 2) attempted to react an aqueous solution of triaminoguanidine (TAG) with a hydrous methanolic solution of hydrazoic acid according to the reaction

$$CN_6H_8 + HN_3 \longrightarrow CN_6H_9N_3$$

This reaction product was reported as an initially off-white solid that melted between 181 and 182°C and contained only 83.08% nitrogen. This does not agree with the theoretical nitrogen content of TAZ which is 85.67%. It was also reported that the initial product further discolored quite rapidly in air, going through a gamut of color changes (pink-red-violet). The density of this air sensitive material was 1.432 g/cm^3.

In an alternate attempt by the Dow Company (ref 3) to synthesize TAZ, methanol was added to an aqueous solution of sodium azide and triaminoguanidinium sulfate to precipitate Na_2SO_4. TAZ was recovered from the filtered solution by evaporation.

$$2NaN_3 + (TAG)_2SO_4 \longrightarrow 2CN_6H_6N_3 + Na_2SO_4$$

This technique resulted in 70% yields of product which always contained a trace contamination of Na_2SO_4.

Finally, Dow (ref 4) modified the Thiokol process in an effort to obtain a pure product. In this technique, freshly generated aqueous hydrazoic acid (NH_3) was reacted in water with freshly prepared triaminoguanidine (TAG) according to the reaction

$$CN_6H_8 + HN_3 \longrightarrow CN_6H_9N_3$$

The reactants, in this case, were freshly generated by the following aqueous ion exchange reactions

$$CN_6H_9C + R\text{-}OH \longrightarrow CN_6H_8 + R\text{-}C + H_2O$$

$$NaN_3 + R\text{-}H \longrightarrow HN_3 + R\text{-}Na$$

The compound obtained in this manner, initially a white solid, contained 85.4 to 85.7% nitrogen (which agrees with the theoretical value); had a density of 1.682 g/cm^3; a melting point range of 150 to 151°C; and, a decomposition temperature range of 177 to 183°C. This compound also discolored quite rapidly in air with an accompanying loss of nitrogen to 83.08% and a decrease in density to 1.432 g/cm^3 (both of which agree with the values observed for the Thiokol product). This method suffers from two disadvantages: (1) TAG is a starting material that is very difficult to prepare and maintain in a relatively pure state, (2) water is present in all the reactions.

It was later reported (ref 4) that the Thiokol product also melted between 151 to 157°C and that the 183°C melting point originally reported by Thiokol was actually the decomposition temperature. A mixture of the Thiokol and Dow products, however, resulted in both a lower melting point and lower decomposition temperature. This suggests that the two products are chemically similar but not identical.

Previous x-ray crystallographic studies of an assumed TAZ sample (ref 5), thought to be prepared by the Dow method, revealed that the sample was actually an equimolar substitutional solid solution of triaminoguanidinium azide (TAZ) and triaminoguanidinium nitrate (TAGN). This probably occurred because this material was prepared by eluting an aqueous stream of hydrazoic acid (from a cation exchange resin in the H+ form eluted with aqueous sodium azide) into a solution containing triaminoguanidinium nitrate, sodium hydroxide, water, and dimethylformamide.

$$NaN_3 + H\text{-}R \longrightarrow HN_3 + Na\text{-}R$$

$$HN_3 + CN_6H_9NO_3 + NaOH \longrightarrow CN_6H_9NO_3N_3 + 1/2\ NaNO_3 + 1/2\ NaOH + H_2O$$

In an effort by this laboratory to synthesize TAZ by the metathetical reaction route, triaminoguanidinium sulfate was added to an aqueous solution of sodium azide, followed by the addition of methanol. This yielded a pink-white powder containing 61% nitrogen (table 1) which further discolored upon exposure to air.

An investigation was initiated by this laboratory to devise alternate more reliable procedures for TAZ synthesis because all previous attempts by this laboratory and others to synthesize TAZ by either the Dow or Thiokol method resulted in unexpected and unwanted products. Since the presence of water seemed to be the apparent root cause of the problems associated with TAZ synthesis, a completely nonaqueous method which did not depend on the formation of TAG as an intermediate was sought to produce pure TAZ. The nonaqueous cation exchange technique developed previously by this laboratory (ref 6) to synthesize the air sensitive TAG seemed to be ideally suited to satisfy this goal.

EXPERIMENTAL

A lightly cross linked,, strong acid cation resin was loaded with TAG ion by passing an excess aqueous solution of TAGN slowly through the column

$$\text{R-H} + \text{TAGN} \longrightarrow \text{R-TAG} + HNO_3$$

After the TAGN feed solution was depleted, the column was rinsed with deionized water until the effluent had a ph of 7 (neutral). Water and dissolved oxygen were removed by displacement of the water by an excess of anhydrous methanol that previously had been deaerated by nitrogen ebullition. Triaminoguanidinium azide was then eluted from the column with an oxygen-free anhydrous methanolic solution of sodium azide

$$\text{R-TAG} + NaN_3 \longrightarrow \text{TAZ} + NaNO_3$$

The effluent was protected from aerial oxidation by collection under a layer of iso-octane (or any inert nonpolar liquid). Overnight refrigeration of the protected effluent resulted in the precipitation of white TAZ crystals which were filtered and dried in vacuums.

Elemental analyses (C, H, N, O, and Na) were performed on a sample of the metathetical product and on two different batches of TAZ produced by the nonaqueous method.

DISCUSSION AND RESULTS

The product initially obtained by this method is white and quite hygroscopic. The product does not rapidly discolor when exposed to dry air, but will rapidly change color in humid air. This suggests that pure TAZ is relatively stable to dry air, but is highly reactive when moisture is present.

There is evidence that the free base produced during hydrolysis is probably the primary cause for the discoloration observed with some TAG salts (ref 7). This increased reactivity of the TAG molecule has been attributed to its localized C=N bond which is far more reactive than the resonating double-bond system found in the TAG cation (ref 8). Hence, hygroscopicity and hydrolysis may be the keys to instability of TAZ in air. Apparently, in dry air TAZ may be as insensitive to oxidation as TAGN, but in moist air TAZ is readily oxidized and TAGN is not.

A better understanding of these effects can be obtained by comparing the hydrolysis of the "sensitive" TAZ with that of TAGN. In this report, TAZ and $TAGN_3$ are defined as synonymous terms which will be used interchangeably, and TAG′ refers to the free base obtained from $TAGN_3$ during hydrolysis. The following mechanism is proposed:

Initially in a humid environment, TAZ extracts water from the air to form a TAZ solution

$$\text{TAZ} + \text{H}_2\text{O(g)} \longrightarrow \text{TAZ(sol) or TAGN}_3\text{(sol)}$$

The TAZ solution then hydrolyzes to form TAG and hydrazoic acid

$$\text{TAGN}_3 + \text{H}_2\text{O(1)} \longleftarrow \text{TAG}' + \text{HN}_3$$

The equilibrium reaction for the dissociation of the TAG free-base is

$$\text{TAG} + \text{H}_2\text{O} \longleftarrow \text{TAG}^+ + \text{OH}^-$$

whose equilibrium constant may be written

$$Kb = [\text{TAG}^+]\,[\text{OH}^-] / [\text{TAG}]$$

For hydrazoic acid, the dissociation reaction equation is

$$HN_3 \longleftarrow H^+ + N_3^-$$

As previously observed, TAG is very easily oxidized by the oxygen in the air

$$TAG + O_2 \longrightarrow \text{oxidation products}$$

Since TAGN is not hygroscopic, it first must be dissolved in liquid water for hydrolysis to occur. This would explain why TAGN is more stable in air than is TAZ. This does not, however, explain why aqueous solutions of TAGN are relatively more stable than TAZ solutions. To answer this question, one must compare the hydrolysis reactions of the two salts.

With TAGN, the hydrolysis products are the weak base TAG and the strong acid HNO_3

$$TAGN + H_2O \longleftarrow TAG + H^+ + NO_3^-$$

which yields the resulting hydrolysis equilibrium constant (Kh)

$$Kh = [TAG]\,[H^+] / [TAG^+]$$

Multiplying the denominator and numerator by $[OH^-]$ results in

$$Kh = [TAG]\,[H^+]\,[OH^-] / [TAG^+]\,[OH^-]$$

which upon substituting the ionization constant of water (Kw) for $[H^+]\,[OH^-]$ reduces to

$$Kh = [TAG]\,Kw/[TAG^+]\,[OH^-]$$

Since $[TAG^+]\,[OH^-] / [TAG]$ is the ionization constant (Kb) of TAG, the hydolysis constant can be written

$$Kh = Kw/Kb$$

In contrast, TAZ hydrolyzes to form the weak hydrazoic acid HN_3 as well as the weak free-base TAG

$$TAGN_3 + H_2O \longrightarrow HN_3 + TAG'$$

which obeys the following hydrolysis equilibrium equation

$$Kh' = [TAG'] [HN_3] / [TAG'^+] [N_3^-]$$

Multiplying the numerator and denominator by $[H^+] [OH^-]$ yields

$$Kh' = [TAG'] [HN_3] [H^+] [OH^-] / [TAG'^+] [OH^-] [N_3^-] [H^+]$$

which reduces to $Kh' = [(Kw/KaKb)]$

in which Ka is the ionization constant for HN_3 (2.5×10^{-5}) and Kb is again the ionization constant for the free base (TAG).

Dividing the equation for TAZ hydrolysis by that for TAG hydrolysis yields

$$\begin{aligned} Kh' &= Kh / Ka \\ &= 4 \times 10^4\ Kh \end{aligned}$$

which clearly demonstrates that the hydrolysis of TAZ is several orders of magnitude greater than that of TAGN. This means that for any given amount of dissolved salt, TAZ will produce significantly more free-base than will TAGN. Hence, problems associated with the presence of the free base will be more severe with TAZ than with TAGN.

As a specific example, one can compare a saturated TAGN soltuion (0.3 m) at room temperature with a TAZ solution of similar concentration. To do this, the last equation can be modified by substitution with the Kh expressions to produce

$$[TAG'] [HN_3] / [TAG'^+] [N_3^-] = 4 \times 10^4 [TAG] [H^+] / [TAG^+]$$

By substitution of the following approximations:

$$\begin{aligned} [TAG'^+] = [N_3^-] = [TAG^+] &= [0.3] \\ [TAG] &= [H^+] \\ [HN_3] &= [TAG'] \end{aligned}$$

this equation reduces to

$$[TAG'] = 2 \times 10^2 [TAG] [TAG^+]1/2 = 100 [TAG]$$

which clearly predicts that a 0.3- m solution of TAZ will generate 100 times more free base than will a 0.3- m solution of TAGN.

The data in table 1 reveal close agreement between the theoretical composition of TAZ and the elemental analysis of the product prepared by the nonaqueous cation exchange method. Batch 1 contains a small amount of oxygen which indicates some oxidation occurred either during the synthesis or storage of the sample. The absence of oxygen in batch 2 indicates that oxidation can be eliminated in this method if careful techniques are used.

On the other hand, the metathetical product contains unacceptable levels of sodium and oxygen. This corroborates the contention that Na_2SO_4 is an unavoidable impurity in this method.

Some physico-chemico properties of this compound are presented in table 2. The positive heat of formation (99 Kcal/mole), derived from the experimental heat of combustion value (500 Kcal/mole), was used in the Blake Thermodynamic Code (ref 9) to calculate the relatively low isochoric flame temperature (2300 K) and high impetus value (1094 J/g).

The density value obtained form x-ray diffraction lattice parameters measurements (1.45 g/cm^3) agrees with the density reported by Thiokol (1.432 g/cm^3, ref 2) but is significantly smaller than that reported for the Dow product (1.682 g/cm^3, ref 3). This is an apparent contradiction. Since the Dow product (rather than the Thiokol product) has the correct nitrogen content, it's density would also agree with the density of the ARDEC product which also has the correct nitrogen content.

CONCLUSIONS AND RECOMMENDATIONS

Nonaqueous cation exchange has been demonstrated as a convient method to prepare or synthesize salts whichare sensitive to either air or water.

A single-crystal x-ray diffraction study of TAZ will be initiated in order to determine its crystal and molecular structure. This determination should reveal if there is some structural peculiarity responsible for the increased reactivity of the TAG ion in TAZ.

A DSC investigation will also be initiated in order to determine unequivocally the melting point and the decomposition temperature of TAZ.

Table 1. Elemental analyses of triaminoguanidinium azide made by the nonaqueous and the metathetical methods

Element, %	Theory	Batch 1	Batch 2	Metathetical
C	8.16	8.21	8.22	2.52
H	6.12	6.12	6.15	2.05
N	85.7	85.46	85.52	61.11
O		0.01		4.96
Na				23.15

Table 2. Physico-chemico properties for TAZ at 0.2 loading density (Blake code calculations)

Property	Value
Flame temperature (Tf, K)	2300
Impetus (I, J/g)	1094
Molecular weight (Mw)	147
Hc (Kcal/mol)	500
Hf (Kcal/mol)	99
Density (g/cm^3)*	1.45

---

*Calculated from x-ray diffraction data.

REFERENCES

1. Bracuti, A. J. and Picard, J. P., "TAG Nitrate Gun Propellant," Proceedings of the Third International Gun Propellant Symposium, ARDEC, Picatinny Arsenal, New Jersey 07806-5000, October 1987.

2. Cohen, M. S., "High Performance Solid Rocket Propellants," Technical Report No. RMD 210-Q8, p 41, Reaction Motors Div, Thiokol Chemical, Denville, New Jersey, May 1960.

3. Karpuik, R. S., "Advanced Research on Solid Rocket Propellants," Report No. AF-2Q-60, p 29, Dow Chemical Co., Midland, Michigan, May 1960.

4. Karpuik, R. S., "Advanced Research on Solid Rocket Propellants," Report No. AF-1Q-61, pp 38-39, Dow Chemical Co., Midland, Michigan, May 1961.

5. Bracuti, A. J., "Triaminoguanidinium Azide Nitrate (TAZN)," Technical Report ARAED-TR-87017, ARDEC, Picatinny Arsenal, New Jersey 07806-5000, June 1987.

6. Bracuti, A. J. and Manning, C. Y., "The Isolation of the Free Base of the Triaminoguanidinium Ion," Technical Report ARAED-TR-87019, ARDEC, Picatinny Arsenal, NJ 07806-5000, June 1987.

7. Fong, C. W., "The Formation of Colored Impurities in Triaminoguanidine Nitrate and Related Incompatibility Problems in Gun Propellants," Technical Report AFATL-TR-81-101, Air Force Armament Laboratory, Eglin Air Force Base, Florida, 1981.

8. Bracuti, A. J. and Manning, C. Y., "The Chemical and Molecular Characterization of Triaminoguanidine (TAG)," Proceedings of the 22d Combustion Meeting, CPIA Publication 432, vol. I, pp 249-256, California Institute of Technology, Passadena, California, October 1985.

9. Freedman, E., "Blake--A Thermodynamic Code Based on Tiger: Users' Guide and Manual," Technical Report ARBRL-TR-02411, Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland, July 1982.

DISTRIBUTION LIST

Commander
Armament Research, Development and
Engineering Center
U.S. Army Armament, Munitions and
Chemical Command
ATTN: SMCAR-IMI-I (5)
SMCAR-AEE (4)
SMCAR-AEE-BR, A. Bracuti (10)
C. Y. Manning
Picatinny Arsenal, NJ 07806-5000

Commander
U. S. Army Armament, Munitions and
Chemical Command
ATTN: AMSMC-GCL
Picatinny Arsenal, NJ 07806-5000

Administrator
Defense Technical Information Center
ATTN: Accessions Division (12)
Cameron Station
Alexandria, VA 22304-6145

Director
U.S. Army Materiel Systems Analysis Activity
ATTN: AMXSY-MP
Aberdeen Proving Ground, MD 21005-5066

Commander
Chemical Research, Development and
Engineering Center
U.S. Army Armament, Munitions and
Chemical Command
ATTN: SMCCR-MSI
Aberdeen Proving Ground, MD 21010-5423

Commander
Chemical Research, Development and
Engineering Center
U.S. Army Armament, Munitions and
Chemical Command
ATTN: SMCCR-RSP-A
Aberdeen Proving Ground, MD 21010-5423

Director
Ballistic Research Laboratory
ATTN: AMXBR-OD-ST, J. Frasier
J. Rocchio
I. May
Aberdeen Proving Ground, MD 21005-5066

Chief
Benet Weapons Laboratory, CCAC
Armament Research, Development and
Engineering Center
U.S. Army Armament, Munitions and
Chemical Command
ATTN: SMCAR-CCB-TL
Watervliet, NY 12189-5000

Commander
U.S. Army Armament, Munitions and
Chemical Command
ATTN: SMCAR-ESP-L
Rock Island, IL 61299-6000

Director
U.S. Army TRADOC Systems Analysis Activity
ATTN: ATAA-SL
White Sands Missile Range, NM 88002

Director of Army Research and Technology
ATTN: DAMA-AR, L. M. Cameron
Pentagon Room 3E474
Washington, DC 20310

Director
LABCOM
Harry Diamond Laboratory
2800 Powder Mill Road
Adelphia, MD 20783-1145