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Advances in the chemical conversion of surplus energetic materials to higher value products

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Abstract

The demilitarization of nuclear and conventional munitions in Russia and the West is producing millions of pounds of surplus energetic materials. Historically, energetic materials (high explosives, propellants, and pyrotechnics) have been disposed by open burning/open detonation (OB/OD). The use of OB/OD is becoming unacceptable due to public concerns and increasingly stringent environmental regulations. Our goal is to develop environmentally sound and cost-effective alternatives to OB/OD. We have investigated the use of recycled high explosives as raw materials for producing a variety of higher value products. In this paper, we review chemical conversion activities with an emphasis on recent work from Lawrence Livermore National Laboratory (LLNL). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Energetic materials; OB/OD; Phloroglucinol

1. Introduction

Our objective has been to develop new and innovative solutions for the disposal of surplus energetic materials. Disposal through open burning/open detonation (OB/OD) is less attractive today due to environmental, cost and safety concerns. We have examined various scenarios using military high explosives as raw materials in the production of higher value products [1–4]. Nitroarene explosives such as Explosive D (ammonium picrate) and TNT (2,4,6-trinitrotoluene) can serve as feedstocks for a variety of higher value products (Fig. 1). After a review of chemical conversion activities by earlier workers, we will discuss the current use of nitroarene explosives to prepare higher value explosives.

2. Early chemical conversion studies

The chemical conversion of surplus energetic materials must yield commercially viable products. While the list of products potentially available from energetic materials is much larger than indicated in Fig. 1, very few of these products will find use in civilian and/or military applications. The conversion of TNT to phloroglucinol (1,3,5-trihydroxybenzene) was developed at the end of World War II as a means of using up the large stockpiles of TNT on hand (Fig. 2) [5]. Phloroglucinol is used in the pharmaceutical, cosmetics, textile-dying and photographic industries and is currently priced at US$ 50/lb (bulk quantities). TNT is first oxidized to 2,4,6-trinitrobenzoic acid (TNBA, 82%) in the presence of sodium dichromate in concentrated sulfuric acid (50–60 °C).

The TNBA is thermally decarboxylated to 1,3,5-trinitrobenzene (TNB) and reduced by iron in hydrochloric

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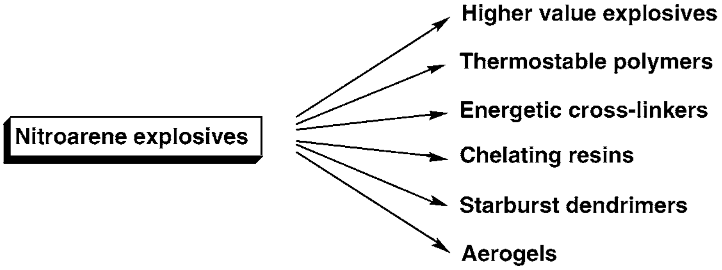


Fig. 1. Use of surplus nitroarene explosives (Explosive D, TNT) as feedstocks for higher value products.

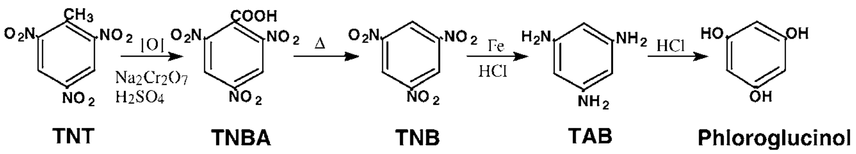


Fig. 2. Commercial production of phloroglucinol from TNT.

acid (90 °C) to 1,3,5-triaminobenzene (TAB, 95%) without isolation of TNB. Hydrolysis of TAB in hydrochloric acid (105 °C) produces phloroglucinol (75%). The conversion of TNT to phloroglucinol proceeds in about 58% overall yield. Unfortunately, this process was discontinued in the USA in the 1970s due to environmental problems associated with the waste disposal of acid liquors, iron, chromium and ammonium salts.

Germany acquired 300,000 tons of old and substandard munitions when the former German Democratic Republic (GDR) was reunited with the Federal Republic of Germany (FRG) in 1989. The disposal program that was undertaken in the early 1990s has been discussed by Wanninger [6,7] and is summarized in Fig. 3.

It was concluded that reformulation of the surplus energetic materials for both civilian or military applications was infeasible. Chemical conversions were explored, but no commercially attractive products were produced. Destruction by OB/OD and biodegradation was ruled out for environmental and economic reasons. Incineration of the surplus munitions in rotary kilns was concluded to be the most efficient mode of destruction that also complied with

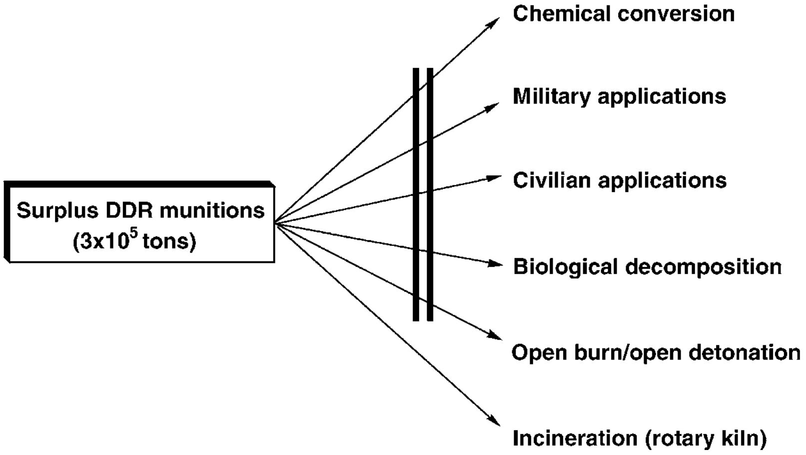


Fig. 3. Disposal of surplus munitions from the former German Democratic Republic.

German air quality standards. Unfortunately, the disposal options available today were not explored in Germany in the early 1990s. For example, a recent NATO advanced research workshop was convened to discuss the successful and extensive use of surplus explosives in mining and other applications [8]. The chemical conversion of surplus energetic materials, a somewhat more challenging enterprise, will now be discussed.

3. 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)

TATB is a reasonably powerful high explosive whose thermal and shock stability is considerably greater than that of any other known material of comparable energy [9]. It is used in military applications because of its significant insensitivity to thermal and shock environments [10]. In the civilian sector, Schlumberger has designed perforating guns containing TATB for deep oil well explorations where heat-insensitive explosives are required [11]. TATB is also used to produce benzenehexamine, an intermediate in the synthesis of new, advanced materials [12–16]. In addition, the use of TATB to prepare components of liquid crystals for use in display devices is the subject of a German patent [17]. TATB had been priced at US$ 20 to 50/lb before industrial production ceased in the US at the end of the 1980s. TATB is currently available to customers outside of the Department of Energy (DOE) for $\geq$US$ 100/lb.

4. Survey of TATB syntheses

TATB has not been manufactured in the USA for over 10 years. TATB was formerly produced using the synthesis developed by Benziger (Fig. 4) [18,19]. The relatively expensive and domestically unavailable 1,3,5-trichlorobenzene (TCB) is nitrated to give 2,4,6-trichloro-1,3,5-trinitrobenzene (TCTNB), which is then aminated to yield TATB. Elevated temperatures (150 °C) are required for both reactions. The major impurity encountered in this process is ammonium chloride. The inclusion of 2.5% water during the amination step significantly reduces the ammonium chloride content of the TATB. Low levels of chlorinated organic impurities have also been identified. These impurities include TCTNB, 1,3-dinitro-2,4,5,6-tetrachlorobenzene, 1,3-dinitro-2,4,6-trichlorobenzene and their partially aminated products [20]. There is a desire to develop a synthesis of TATB that does not require such harsh reaction conditions (elevated temperature, strong acid). In addition, there is mounting environmental pressure to abandon the use of halocarbons such as TCB in favor of more benign and "greener" feedstocks in industrial processes [21,22].

Atkins et al. described a conversion of TNT to TATB [23,24] with the goal of developing a less costly production of TATB (Fig. 5). Hydrogen sulfide partially reduces TNT to 4-amino-2,6-dinitrotoluene (ADNT), which is then treated with nitric acid in sulfuric acid to provide pentanitroaniline (PNA) via an unexpected oxidative nitration of ADNT. Treatment of PNA with

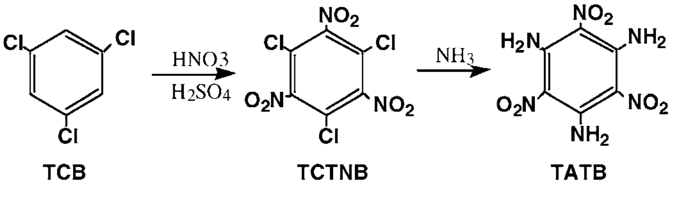


Fig. 4. Benziger synthesis of TATB.

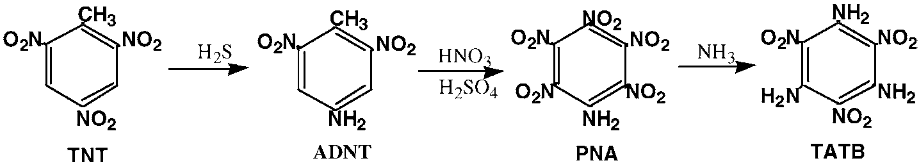


Fig. 5. Atkins synthesis of TATB from TNT.

ammonia provides TATB in addition to polynitrophenol by-products (Atkins, personal communication). The conversion of TNT to TATB proceeds in 44% overall yield. Although all of the reactants are relatively inexpensive, the cost of pollution abatement ultimately prevented the industrial scale-up of this process.

Wolff and Limbach have described the synthesis of ^{15}N-labelled TATB for use in the preparation of ^{15}N-labeled benzenehexamine derivatives [25]. Due to the relatively high cost of ^{15}N-labeled precursors ($^{15}NH_4Cl$, $Na^{15}NO_3$), syntheses that work well with unlabeled materials (Fig. 4) [18,19] can become excessively expensive with labeled compounds. Specifically, benzenehexamine [12–16] is obtained from the reduction (Na/NH_3 or catalytic hydrogenation) of TATB [12–16]. In the Benziger synthesis, TATB is obtained from the ammonolysis of TCTNB by excess ammonia in toluene at elevated temperature (150 °C) and TCTNB is obtained from the nitration of TCB employing *excess nitric acid* at 150 °C (Fig. 4) [18,19]. A more efficient synthesis of TATB that employs ^{15}N-labeled reagents is shown in Fig. 6.

Phloroglucinol is converted to phloroglucinol triacetate (PTA) which is then nitrated to trinitrophloroglucinol (TNP, 93%) using a stoichiometric quantity of potassium nitrate in sulfuric acid at room temperature. Excess diazomethane converted TNP to 1,3,5-trimethoxy-2,4,6-trinitrobenzene (TMTB, 100%) which is then ammonolyzed using a 1.6-fold excess of ammonia in ether with warming from −78 to 70 °C to give TATB (97%). This conversion of phloroglucinol to TATB is worth noting for efficient synthetic conversions under relatively mild conditions. There are two major obstacles, however. First, the use of diazomethane, a toxic gas with a history of laboratory scale explosions associated with its use, would seem to be contraindicated for the large-scale production of TATB. The other obstacle is the cost of phloroglucinol at US$ 50/lb (vide supra, Fig. 2) which offers no economic advantage over the Benziger process using TCB as starting material (Fig. 4). Recent developments, however, may remove the first obstacle as Archibald et al. (Aerojet Fine Chemicals) have developed safe procedures for preparing diazomethane in industrial quantities by either a large scale batch process [26] or continuous process [27]. It should be noted that Dubiel and Zaffanti [28] employed excess dimethyl sulfate (>17-fold) to effect the conversion of mono-, di-, and trinitrophloroglucinols to the corresponding trimethyl ethers (no yields were reported). With respect to the cost of phloroglucinol, there are reports on the biosynthesis of pyrogallol (1,2,3-trihydroxybenzene) from glucose [29] and conversion of pyrogallol to phloroglucinol [30].

5. Proposed conversion of nitroarenes to TATB

There is a definite need for a new production of TATB. We (LLNL and Pantex) have been tasked by the Advanced Development and Production Technology (ADAPT) program of DOE to develop a new production of TATB. The new production must be less expensive and more environmentally benign than the

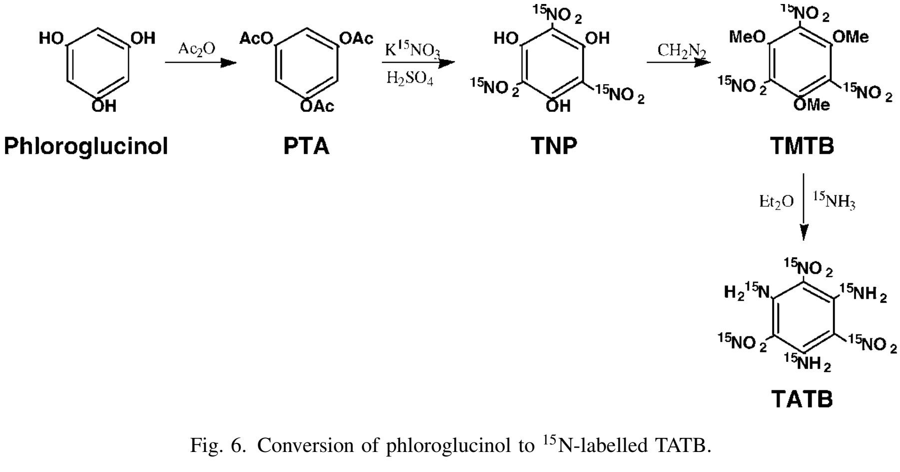


Fig. 6. Conversion of phloroglucinol to ^{15}N-labelled TATB.

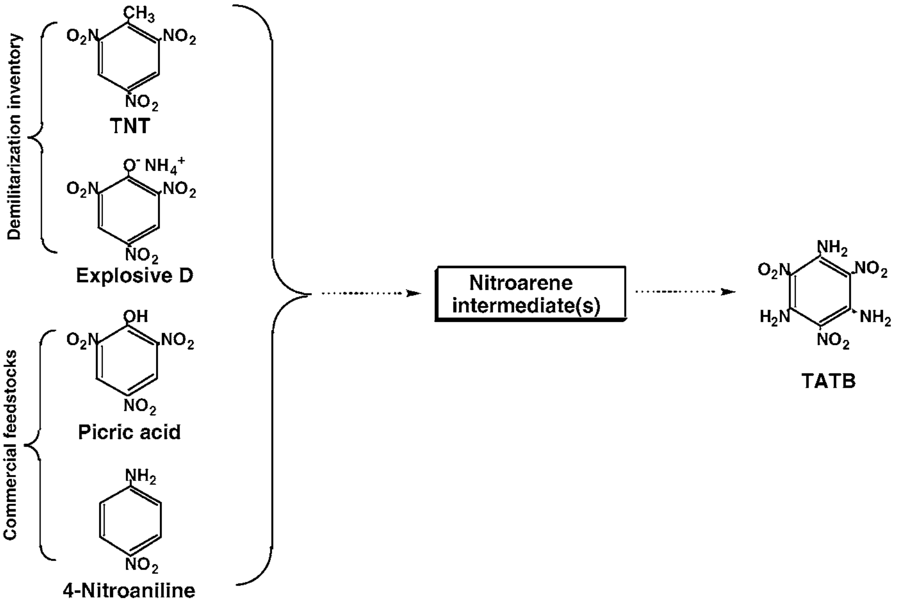


Fig. 7. Proposed production of TATB utilizing either surplus explosives or commodity chemicals.

previously used processes described above. Our ultimate goal is to develop a versatile production of TATB that goes beyond the completion of demilitarization programs. The proposed production will use feedstocks from either demilitarization inventories or suppliers of commodity chemicals. A process that can utilize Explosive D and TNT (surplus nitroarene explosives) as well as picric acid and 4-nitroaniline (commodity chemicals) as starting materials is outlined in Fig. 7. At the outset of this study, we found the chemistry available for the conversion of starting materials to the appropriate nitroarene intermediates marginally acceptable at best with respect to cost, safety and environmental impact. The greatest technical challenge, however, was to develop a conversion of nitroarene intermediates to TATB that precluded the use of haloarene compounds.

6. Vicarious nucleophilic substitution (VNS) of hydrogen

VNS of hydrogen is a well-established procedure for the introduction of carbon nucleophiles into electrophilic aromatic rings [31,32]. The reaction involves the addition of a carbanion bearing a leaving group (X) to an electrophilic aromatic ring and subsequent rearomatization by loss of the leaving group through elimination as HX (Fig. 8, $Z = CH_2$). This reaction has been applied to a wide variety of nitroarenes and nitro-substituted heterocycles [32]. By analogy, VNS reactions can also take place with amine nucleophiles. Such reagents are of the common form $X–NH_2$, where X is an auxiliary group capable of stabilizing a negative charge, thus driving rearomatization of the sigma-intermediate adduct (Fig. 8, $Z = NH$). An early example of amination by VNS of hydrogen was provided by Meisenheimer and Patzig who reacted 1,3-dinitrobenzene (DNB) with hydroxylamine in the presence of strong base and methanol to yield 1,3-diamino-2,4-dinitrobenzene (DADNB, Fig. 9) [33]. This reaction was reinvestigated by Norris and Chafin in 1985, who employed "*hydroxylamine in water*" to convert 4,6-dinitrobenzofuroxan (DNBF) to 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14) (Fig. 10) [34]. This finding is intriguing as virtually all VNS reactions are run in anhydrous organic solvents with the exclusion of moisture [31].

The use of water, the ultimate "green" solvent, in a chemical reaction greatly reduces the cost of the reaction and also provides a more environmentally benign chemistry. Unfortunately, the conditions used

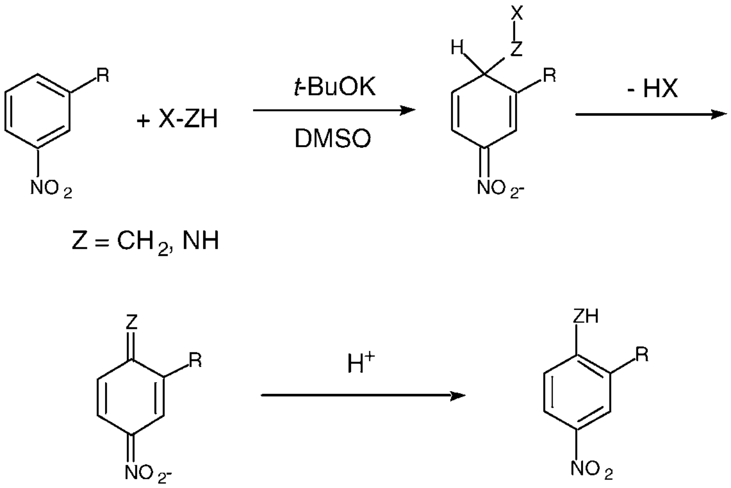


Fig. 8. Vicarious nucleophilic substitution of hydrogen.

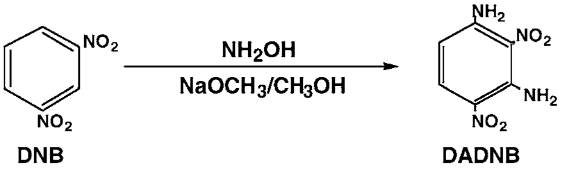


Fig. 9. VNS amination of DNB to DANB.

to produce CL-14 (Fig. 10) did not work for the conversion of picramide or TNB to TATB (Fig. 11). 1,3-Diamino-2,4,6-trinitrobenzene (DATB) was obtained in a low yield (16%) after removal of unreacted picramide. The replacement of aqueous base with sodium methoxide in anhydrous methanol or DMSO raised the yield of DATB from 16 to over 50%. The use of alkoxy derivatives (CH_3ONH_2, $C_6H_5CH_2ONH_2$) gave exclusively DATB in 87–91% crude yields. The reaction of picramide with hydroxylamine or its *O*-alkyl derivatives in NaOMe/DMSO never yielded more than trace quantities of TATB at room temperature. Recently, a number of more active aminating reagents such as 4-amino-1,2,4-triazole (ATA) [35] and substituted sulfenamides [36] have been developed. These reagents were designed to be

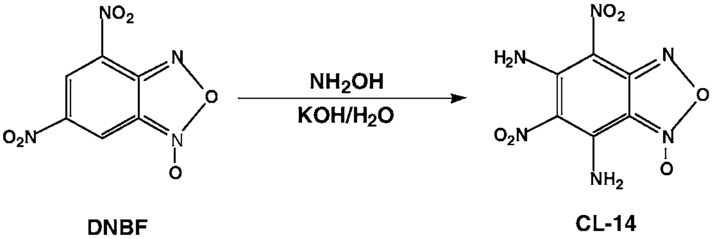


Fig. 10. VNS amination of DNBF to CL-14.

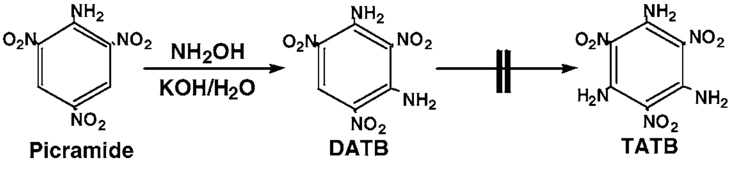


Fig. 11. Reaction of picramide with hydroxylamine in aqueous base.

good nucleophiles that easily add to electrophilic aromatic rings and also possess good leaving groups (Fig. 8, X).

7. Use of 1,1,1-trimethylhydrazinium iodide (TMHI) as a VNS reagent

We were intrigued by the announcement in 1995 that Russia was intending to dispose of 30,000 metric tons of liquid rocket propellant (1,1-dimethylhydrazine, unsymmetrical dimethylhydrazine, UDMH) originally prepared for use in intercontinental ballistic missiles [37]. We alkylated UDMH with methyl iodide to provide TMHI [38] which we evaluated as a VNS aminating reagent. Although quaternary hydrazinium compounds have been known for over 100 years [39,40], they have not been employed as VNS reagents. We reasoned that TMHI would be sufficiently nucleophilic to substitute into nitro-substituted aromatic rings but would be superior to the examples described above because the leaving group would be the neutral trimethylamine (TMA) instead of a stabilized anionic species. In addition, there is a possibility that the hydrazinium halide would react with base to form the neutral ylide species, $[(CH_3)_3N^+{-}NH^-]$, which may be the reactive species in the amination process. Indeed, when TMHI was reacted with various nitro-substituted aromatics the amino functionality was introduced in good to excellent yields. We found that the number of amino-groups which may be added to the electrophilic aromatic ring is equal to the number of nitro-groups present on the ring.

A study of product yields and distribution of various 3-substituted nitrobenzene derivatives was performed using TMHI (Fig. 12) (Table 1) [41]. The results of our study were compared with the findings reported for ATA [35]. ATA was found to be regioselective, giving substitution exclusively *para*- to the nitro-group. TMHI gave all possible product isomers thereby showing no selectivity, but presumably greater reactivity. There was a general tendency for TMHI to yield products in which the amine substitution occurs *ortho*- to the nitro-group as the major components although some exceptions were noted. Picramide reacts with TMHI in dimethylsulfoxide in the presence of strong base (NaOMe or KO*t*-Bu) at room temperature (3 h) to yield, depending on the quantity of TMHI used, either DATB or TATB and TMA (Fig. 13) [42]. Picramide also reacts with ATA in dimethylsulfoxide in the presence of strong base (NaOMe or KO*t*-Bu) at a slower rate (24 h) to yield either DATB or TATB, depending on the quantity of ATA used [43].

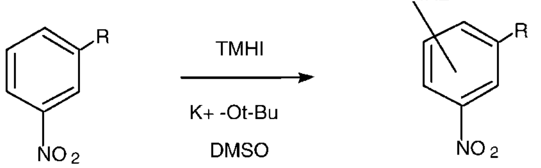


Fig. 12. Amination of 3-substituted nitroaromatics.

Table 1
Amination of 3-substituted nitrobenzenes

R	Total yield (%)	Position of NH_2[a]	Isomer (%)
H	85	2	61
		4	39
CH_3	84	2	38
		4	35
		6	27
Cl	82	2	32
		4	49
		6	19
COOH	95	4	71
		6	29
OCH_3	66	2	90
		4	10
F	84	2	45
		4	47
		6	8
I	76	2	45
		4	38
		6	17
CN	41	2	20
		4	44
		6	36

[a] Relative to NO_2.

In theory, the TMA released from the reaction of picramide with TMHI (Fig. 13) can be used to regenerate VNS aminating reagent through the reaction of TMA with chloramine to yield 1,1,1-trimethylhydrazinium chloride (TMHCl) (Fig. 14) [40]. TMHCl and TMHI, as expected, serve equally well as reagents for the nucleophilic aminations of nitroarenes.

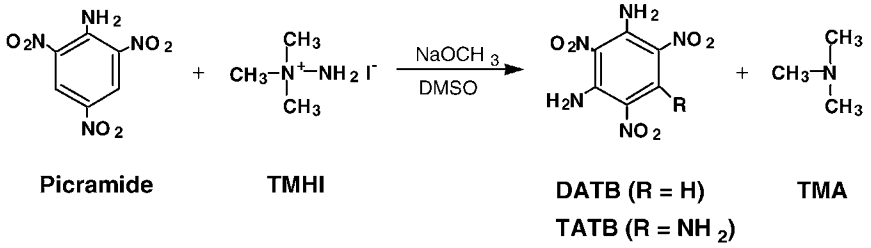


Fig. 13. Reaction of picramide with TMHI.

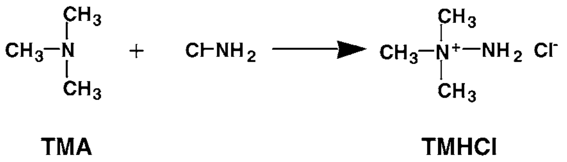


Fig. 14. Conversion of TMA to TMHCl.

8. Conversion of Explosive D to picramide

We have described efficient conversions of picramide (2,4,6-trinitroaniline) and TNB to TATB using VNS chemistry [42–44]. Our large-scale synthesis of TATB has been designed so that either surplus energetic materials (Explosive D, TNT) or inexpensive, commercially available chemicals (picric acid, 4-nitroaniline) can be used to make the necessary starting materials (picramide, TNB). Several million pounds of Explosive D (ammonium picrate) are available for disposal in the USA. Ammonium picrate can be converted to picramide by the pathways shown in Fig. 15. There is one report describing the direct conversion of picric acid to picramide [45]. Molten picric acid and urea were heated at 173 °C for 36 h to produce a mixture of picramide, urea and cyanuric acid. Removal of the urea and cyanuric acid by extractions with the appropriate solvents (water, acetone) afforded picramide in 88% yield. This procedure has major drawbacks, as molten picric acid, especially at such an elevated temperature (173 °C), creates a serious explosive hazard. Furthermore, the picramide is produced as a solid glass product that cannot be safely and efficiently removed from an industrial scale reactor. What about the direct conversion of Explosive D to picramide (Fig. 15, dotted arrow)? We have not found any reports in the chemical literature describing such a conversion. There are suggestions, however, that the reaction of Explosive D with urea at elevated temperature has been attempted and little or no picramide was produced [46]. The reaction of picric acid and urea was reinvestigated and conditions were discovered that promoted the reaction of either Explosive D or picric acid with urea to provide picramide. Good yields (>90%) were obtained irrespective of the starting material. In each case, however, cyanuric acid was present as an unwanted by-product formed from excess urea in the reaction mixture. We have recently developed proprietary conditions under which both Explosive D and picric acid are directly converted to picramide (>90%) without the formation of cyanuric acid [47].

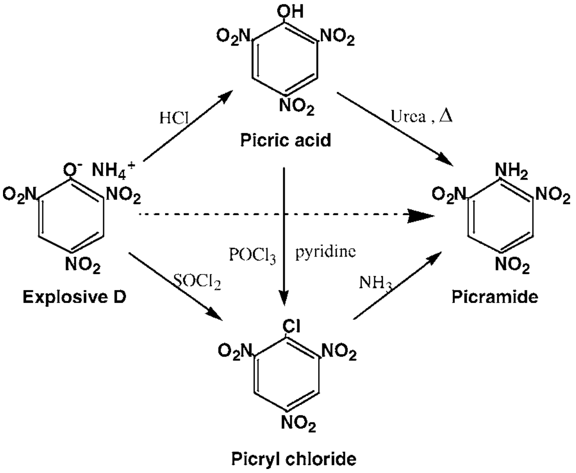


Fig. 15. Pathways to picramide from Explosive D.

9. Conversion of TNT to TNB and TATB

TNT will replace Explosive D as a chemical feedstock as the existing inventory of Explosive D (5

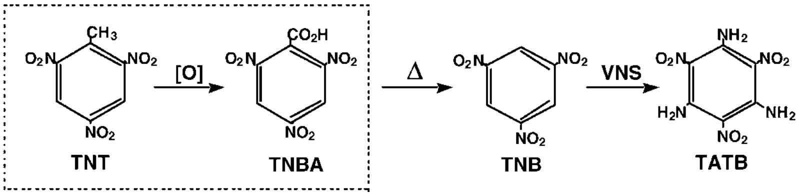


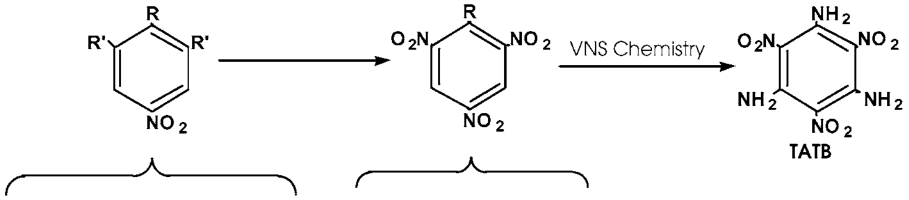
Fig. 16. Conversion of TNT to TNB and VNS production of TATB.

million pounds) will soon be consumed by demilitarization through either resource recovery and reuse R^3 or destruction activities. In addition, there are no future military requirements for the production or use of Explosive D. On the other hand, TNT remains an important military explosive. There may be future requirements for a less polluting production of TNT as well as viable R^3 programs when demilitarization is required.

TNB is a key intermediate in the conversion of TNT to TATB that employs VNS chemistry (Fig. 16). TNB is readily obtained in high yield from the thermal decarboxylation of TNBA (Fig. 2) [5]. The technical challenge is to effect the oxidation of TNT to TNBA (Fig. 16, dotted box) in an environmentally acceptable manner. The industrial conversion of TNT to TNBA, a key step in the production of phloroglucinol [5], was discontinued in the USA in the 1970s due to problems associated with the waste disposal of acid liquors and chromium salts. We are evaluating the report of Astratev et al. who have effected the conversion of TNT to TNBA using a narrow range of conditions (80% nitric acid, 194 °C, 20 min) [48]. We are also exploring other reagents and conditions that may promote efficient and environmentally acceptable oxidations of TNT to TNBA [49].

10. Towards a versatile production of TATB

The information provided in the previous sections and published reports [41–44] indicates that we are closing in on our goal of a versatile production of TATB utilizing either surplus explosives or commodity chemicals (Fig. 17). Feedstocks from both demilitarization inventories (Explosive D, TNT) and/or commercial sources (4-nitroaniline, picric acid) are employed. The four feedstocks are converted to two intermediates (picramide, TNB) which are then transformed to TATB using VNS chemistry. To date, the most extensively used feedstock in our TATB studies has been 4-nitroaniline. 4-Nitroaniline is readily nitrated [50] to furnish the picramide used in our VNS syntheses of TATB. The conversions in Fig. 17 are readily executed on a laboratory scale (5–10 g). Needless to say, considerable process development is required to take a new bench-top process to production levels. Some of our process development studies will now be discussed.



Feedstock	R	R'	Intermediate	R
Explosive D	$O^-NH_4^+$	NO_2	Picramide	NH_2
TNT	CH_3	NO_2	Trinitrobenzene	H
Picric acid	OH	NO_2	Picramide	NH_2
4-Nitroaniline	NH_2	H	Picramide	NH_2

Fig. 17. Conversion of nitroarene feedstocks to TATB.

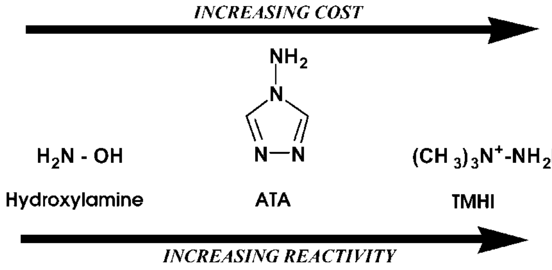


Fig. 18. VNS amination reagents.

11. Process development studies for TATB production

11.1. VNS amination reagents

We have reported the use of three reagents for the amination of picramide and TNB to TATB by VNS of hydrogen [41–44]. The reagents in order of increasing reactivity, as well as increasing cost, are hydroxylamine, ATA and TMHI (Fig. 18). Hydroxylamine is an inexpensive chemical obtained in bulk quantities as the hydrochloride or sulfate salt [51]. ATA is obtained from formylhydrazide, which is prepared from relatively inexpensive hydrazine and ethyl formate (or formic acid) [52]. TMHI is prepared from reaction of the more expensive 1,1-dimethylhydrazine and methyl iodide [41]. We have produced TMHI in situ by allowing 1,1-dimethyl-hydrazine and methyl iodide to react in DMSO. Subsequent addition of picramide and base produces TATB in yields comparable to VNS syntheses of TATB employing isolated TMHI [44]. We realized at the outset of our work with TMHI that methyl iodide, a relatively expensive halocarbon, would ultimately have to be replaced with a less expensive alkylating agent that was also halogen-free. We have demonstrated that dimethyl sulfate reacts with 1,1-dimethylhydrazine to produce 1,1,1-trimethyl-hydrazinium methosulfate (TMHM) in situ which reacts with picramide in the presence of base to produce TATB [44]. While the in situ production and use of TMHM in place of TMHI represents a significant cost reduction, the use of 1,1,1-trimethylhydrazinium salts in VNS reactions cannot compete economically with hydroxylamine or ATA until there is a significant decrease in the cost of 1,1-dimethylhydrazine.

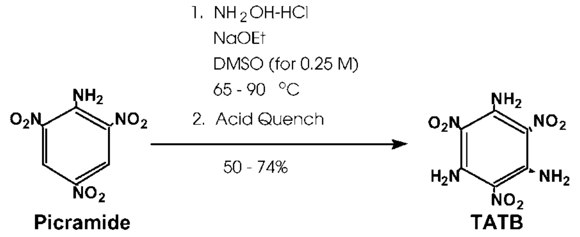


Fig. 19. VNS synthesis of TATB using hydroxylamine hydrochloride.

11.2. Reaction condition studies

Initially, the conversion of picramide to TATB was studied using inexpensive hydroxylamine and aqueous base as reported for the preparation of CL-14 [34]. Only DATB was obtained (16%) after isolation from unreacted picramide. The conditions of the reaction were modified and the yield of DATB increased (90%), but still no TATB was produced (Fig. 11). This reaction warrants additional study in light of the significant cost and environmental payoffs that accrue if VNS reactions producing TATB can be run in water, the ultimate inexpensive, "green" solvent. The combination of strong base, aprotic dipolar solvent (DMSO) and elevated temperature (65–90 °C) forces the reaction of hydroxylamine with picramide to yield TATB in 50–74% yield with about 97% purity (Fig. 19) [44].

We have shown that TMHI is the most efficient aminating reagent available for the VNS synthesis of TATB [41–44]. Picramide, TMHI and base (sodium alkoxide or hydroxide) react in DMSO to provide TATB in 80–90% yield (Fig. 20). The reaction is conducted at room temperature and is complete in <3 h. Under these reaction conditions, no DATB ($\leq 0.5\%$) is detected by FTIR spectroscopy or direct insertion solids probe mass spectroscopy (DIP-MS).

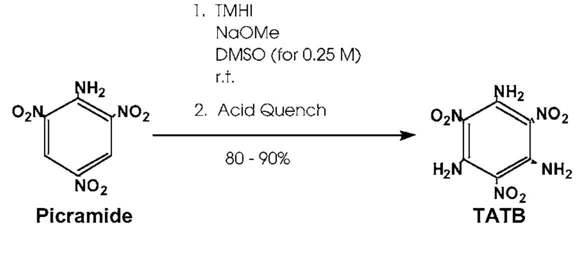


Fig. 20. VNS synthesis of TATB using TMHI.

The largest scale attempted thus far has been at the 50 g level. While TMHI is very reactive and efficiently produces TATB, there are significant disadvantages to its use. The reagents used to generate TMHI (UDMH and methyl iodide) are toxic and relatively expensive. In addition, the by-product of amination using TMHI is TMA, a volatile and noxious gas which must be scrubbed from the reaction exhaust system. In contrast, hydroxylamine is much cheaper, less toxic and does not release gaseous products.

The first VNS synthesis of TATB was accomplished at LLNL in 1994 using ATA as the VNS amination reagent [43]. ATA is less reactive than TMHI and more reactive than hydroxylamine (Fig. 18). The use of elevated temperature (60–70 °C), however, does make ATA equivalent to TMHI in VNS aminations with respect to yield of TATB. Our use of ATA was discontinued after the more reactive TMHI was discovered and evaluated in VNS aminations [41,42]. We have now reevaluated the use of ATA in light of the quality of TATB produced with TMHI and hydroxylamine (see Section 11.3).

11.3. Product analysis

TATB prepared from the VNS process will have to satisfy purity and testing profiles (DSC, CRT, DH_{50}, spark and friction tests, etc.) established for conventionally prepared TATB [10]. FTIR and DIP-MS show TATB using TMHI and ATA is chemically >99% pure while the use of hydroxylamine gives TATB that is typically >97% pure. Differential scanning calorimetry (DSC) values are 10–20 °C low for TATB prepared with hydroxylamine or TMHI. In addition, hydroxylamine or TMHI furnish TATB preparations that are tan to dark brown in color while pure TATB is typically yellow. In contrast, TATB prepared with ATA has good color and higher DSC values.

At this time, ATA represents the best compromise of VNS reagents with respect to the yield, quality and cost of TATB produced. ATA has been used in syntheses of TATB (>90% yield) on a 100 g scale in Livermore (HEAF facility). The synthesis was taken to the Site 300 facility of LLNL and run on a 600-g scale to provide TATB in 76% yield with a 24-μm median particle size. Our collaborators at Pantex (Amarillo, TX) have obtained comparable results using ATA in syntheses of TATB.

11.4. Use of alternative solvents in VNS reactions

Most VNS reactions, with some notable exceptions (vide supra) [33,34], employ dipolar aprotic solvents (DMSO, DMF, NMP) that are more expensive than most organic solvents used in industrial processes. While we have not been able to use water in the VNS production of TATB (Fig. 11), we have been able to replace DMSO with less expensive solvents under certain conditions. The preliminary results are very encouraging and indicate a potentially significant cost reduction in the VNS production of TATB.

11.5. Purification of TATB

It is significant to note that TATB, unlike other high explosives (RDX, HMX, TNT, and HNS), cannot be purified using conventional techniques [10]. The extremely low solubility [53] and involatility [54] of TATB precludes the use of recrystallization, chromatography and sublimation for large-scale operations. In the past, production batches of TATB that exceeded the allowable limits for ammonium chloride and/or other impurities had to be discarded. This is clearly economically and environmentally undesirable. We are developing a proprietary process for the purification of TATB. Our initial results have been encouraging as we have been able to remove DATB (resulting from incomplete amination of picramide) and a variety of low-level, deeply colored impurities. The process produces purified TATB with a particle size ≥ 20 μm and is amenable to scale-up. Our goal is to reclaim rejected or substandard TATB, irrespective of source (synthesis, demilitarization activities).

12. Summary and conclusions

We have described in some detail our progress in converting surplus energetic materials (Explosive D, TNT) to TATB, a higher value explosive with civilian and military applications. Improved conversions of selected nitroarenes (picramide, TNB) to TATB using VNS chemistry bring us closer to a less expensive and more environmentally acceptable production of TATB. The scale-up of TATB production based on ongoing process development studies is in progress.

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