ASSESSING DEGRADATION PATHWAYS OF NTO, DNAN AND NQ BY BIMETAL (FE/CU) REDUCTION

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ABSTRACT

Possible degradation pathways of the reductive removal of energetics (3-nitro-1,2,4-triazol-5-one (NTO), 2,4-dinitroanisole (DNAN) and nitroguanidine (NQ) from wastewater by iron/copper bimetal particles were investigated. Batch experiments were performed and samples taken at different times from the reaction mixtures. Electrospray ionization mass spectrometry (ESI-MS) was used to detect and identify reaction intermediates and products. NTO and DNAN were observed in the negative ionization mode, NTO at m/z 129 ([M-H]⁻) and DNAN at m/z 198 (M⁺). NQ was observed in the positive mode at m/z 105 ([M+H]⁺). All intermediates and products from the three compounds were observed in the positive mode. Collision-induced dissociation (CID) and in-source deuterium exchange experiments (HDX) were used to confirm the identities of the species observed. A nitro to amino degradation pathway is proposed for NTO, DNAN and NQ. A monoamino intermediate was observed for DNAN (aminonitroanisole) and NQ (aminoguanidine); for NTO, the aminotiazolone intermediate is postulated. Urea was identified as an intermediate degradation product of NTO and NQ.

Keywords: NTO, DNAN, NQ, insensitive munitions, reductive decomposition, Fe/Cu bimetals

1. Introduction

Insensitive Munitions eXplosives (IMX), designated as one of the 20 best inventions of 2010 by Time magazine, are designed to only detonate under specific conditions, which reduces the chance of accidents and casualties. IMX components have been known to contaminate soils, sediments, and water bodies. IMX formulations are usually mixtures of 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ) and hexahydro-1,3,5-trinitro-s-triazine (RDX). The goal of this study is to investigate the degradation pathways of NTO, NQ and DNAN in wastewaters subjected to a reductive decomposition treatment process, using mass spectrometry.

There is a need for methods to rapidly detect and identify IMX constituents for research, management and remediation purposes. The U.S. EPA method 8330 [1] uses HPLC separation and detection by UV absorption [2] for the quantification of 17 compounds, only one of which, RDX, is a constituent of IMX [3].. By virtue of its sensitivity, selectivity and speed, mass spectrometry (MS) has become an indispensable tool for structure elucidation and quantification of analytes [4]. Electrospray ionization (ESI) is the most widely used MS technique to study structures, reaction intermediates and reaction mechanisms [5-7]. Collision induced dissociation (CID) is a MS method to obtain structural information from an analyte by selecting an ion and fragmenting it by collisions with an inert gas (Ar). Fragment ions are then analyzed in turn. H/D exchange in the gas phase between analytes and deuterated molecules (CH₃OD, ND₃, D₂O) has been amply demonstrated to provide information about the position and the number of labile hydrogen atoms, e.g. those belonging to amino, carboxyl, or hydroxyl functional groups [7-10]. Attygalle et al demonstrated that such H/D exchanges are
rapidly reversed if the deuterium is depleted, and that the method enables the identification of protonation sites in molecules unambiguously, by the number of H/D exchanges observed in real time [10].

2. Materials and methods
Stock solutions were prepared as follows. For NTO (supplied by Picatinny Arsenal, NJ, USA) and NQ (25% H₂O, from Sigma-Aldrich) pure solids were dissolved in deionized (DI) water. DNAN (98%, from Sigma-Aldrich) was dissolved in 100 mL acetonitrile, then diluted with DI water. The initial concentrations of the laboratory-prepared solutions were 300 mg/L for NQ, 500 mg/L for DNAN and 1000 mg/L for NTO. Bench-scale experiments were performed under acidic conditions in 60 mL tube reactors by adding iron (70 µm, Hepure Technologies H200 Plus™, DE, USA) and copper (45 µm 185E, Acupowder International (NJ, USA)) particles mixture to NTO, DNAN, and NQ solutions. Samples were taken and filtered (Whatman 13mm Puradisc nylon syringe filters; pore size: 0.45µm; non sterile) at selected time intervals (typically, at 0, 2, 5, 10, 20, 30 and 45 min).

A Waters Micromass Quattro Ultima mass spectrometer (Manchester, UK) equipped with a Z-spray source was used in the electrospray ionization mode for the identification of reaction intermediates and decomposition products. The capillary voltage was set at ±3.5kV, the cone voltage 10-15V, and the infusion rate was 10-20 µL/min. Samples taken were directly infused into the mass spectrometer by a syringe pump.

3. Results and discussion
DNAN is observed only in the negative ionization mode as its radical-anion produced by electron capture (M⁻, m/z 198). However, a new peak was observed at m/z 169 in the positive ionization mode from samples taken at intermediate times during the Fe-Cu degradation. Collision-induced dissociation (CID), yielded neutral losses of ·CH₃ (M-15, m/z 154), NO₂ (M-46, m/z 123), and CH₃NO₂ (M-61, m/z 108) (Figure 1).

![Figure 1](image-url)  
**Figure 1:** A collision-induced dissociation mass spectrum recorded from the DNAN reaction intermediate at m/z 169

In addition, since the peak at m/z 169 represents the protonated new species, the mass difference between it and DNAN is 30 Da. A reduction of one –NO₂ group on DNAN to an –NH₂ accounts for the difference. That there is an –NH₂ present was confirmed by in-source H/D exchange [10]. D₂O vapor in the MS ion source caused three new peaks to appear in addition to that at m/z 169 – at m/z 170, 171, and 172 – indicating three exchangeable protons (Figure 2). Since protonation in an aromatic amine occurs exclusively on the –NH₂ group [10], three D exchanges conclusively indicate its presence. It should be noted that MS cannot distinguish in this case whether the new
amino group is in the ortho or para position (i.e. where the reduction took place and whether one of the two original nitro groups was reduced preferentially); it is reasonable to assume at this stage that the peak at m/z 169 is generated by both ortho and para-aminonitroanisole, but only the para-amino species can generate the CID fragment at m/z 108.

Figure 2: The effect of deuterium exchange on the DNAN reaction intermediate: (a) Before D$_2$O is introduced to the source; (b) D$_2$O exchange at equilibrium.

NTO, being a fairly strong acid (pK$_a$ 3.5), is observed in the negative ionization mode at m/z 129 for the deprotonated species ([M-H]$^-$). Even in samples withdrawn after 2 minutes of Fe/Cu-mediated degradation, no peak at m/z 129 was observed in the negative mode. Instead, two new MS peaks were observed at m/z 61 and 121, in the positive mode, corresponding to protonated urea and its protonated dimer, respectively. Upon CID, the species at m/z 121 produced a principal fragment at m/z 61 accompanied by a minor one at m/z 103 for a water loss (Figure 3, inset). Samples taken at later stages of the Fe-Cu reduction of NTO did not generate urea peaks. Evidently, even the degradation of urea is effected as the Fe/Cu reduction progresses.

Figure 3: Mass spectrum recorded from an NTO solution at 6 minutes into the degradation. Insert of CID m/z 121.

A peak at m/z 105 is observed in the positive mode for the [M+H]$^+$ for NQ. This peak is seen from samples taken during the first 30 minutes. Other peaks observed as the reaction progressed were at m/z 61, m/z 75, m/z 79 and m/z 121. The peaks at m/z 61 and m/z 121 represent protonated urea and its protonated dimer, respectively, while m/z 79 stands for the protonated water adduct of urea. The m/z 75 represents a 30 Da mass difference from protonated NQ: this is a reduction of the nitro group to an amino group similar to that in the case of DNAN. The fragments (Figure 4, insert) confirmed it to be aminoguandine, with very small amount of fragmentation occurring,
17Da (NH₃) and 32Da (N₂H₄) losses. The major product of the Fe/Cu degradation of NQ is urea, as three of the peaks are related to urea.

No amino intermediate in the NTO degradation was observed, evidently due to the high reaction rate. Such an intermediate can, however, be reasonably postulated: its structure would allow two urea molecules to be generated upon hydrolysis of the original molecule. Figure 5 presents an overall scheme for the proposed degradations.

**Figure 4:** Mass spectrum recorded from a NQ solution at 45 minutes into the degradation. Insert of CID m/z 75

**Figure 5:** Overall scheme for proposed degradation.

a) 3-nitro-1,2,4-triazol-5-one (NTO) (m/z = 129) [M-H]¹
   \[ \text{Fe/Cu reduction} \rightarrow \text{5-amino-3H-1,2,4-triazol-3-one} \] (m/z = 101) [M+H]⁺
   \[ \text{Fe/Cu hydrolysis} \rightarrow 2 \text{Urea} \] (m/z = 61) [M+H]⁺

b) 2,4-dinitroanisole (DNAN) (m/z = 199)
   \[ \text{Fe/Cu reduction} \rightarrow \text{2-methoxy-5-nitroaniline} / \text{4-methoxy-3-nitroaniline} \] (m/z = 169) [M+H]⁺
   \[ \text{4-methoxybenzene-1,3-diamine} \] (m/z = 139) [M+H]⁺
   Not observed
Figure 5: Suggested degradation pathways a) NTO degradation b) DNAN degradation c) NQ degradation

4. Conclusions
Using MS is an effective way to investigate the degradation mechanisms of insensitive munitions. ESI-MS (HePI) and H/D exchange provide a straightforward method to identify intermediates in the reactions. MS information suggests that nitro groups are reduced to amino groups for all three compounds. Urea has been identified as a degradation product of NTO and NQ.

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REFERENCES