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Photo-degradation of 2,4-dinitroanisole (DNAN): An emerging munitions compound

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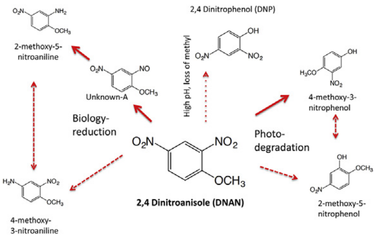
HIGHLIGHTS

- 2,4-dinitroanisole (DNAN) changes color from white to red when exposed to sunlight.
- 2-methoxy-5-nitroaniline and 4-methoxy-3-nitrophenol are the main transformation products.
- Degradation products identified had concentrations <1% of that of DNAN.
- Concentration of 2-methoxy-5-nitroaniline was high when ammonium perchlorate present.
- Unknown A (possibly a nitrosobenzene) was present in most samples.

GRAPHICAL ABSTRACT



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ABSTRACT

The US military is developing insensitive munitions (IM) that are less sensitive to shock and high temperatures to minimize unintentional detonations. DNAN (2,4-dinitroanisole) is one of the main ingredients of these IM formulations. During live-fire training, chunks of IM formulations are scattered by partial detonations and, once on the soil, they weather and dissolve. DNAN changes color when exposed to sunlight suggesting that it photodegrades into other compounds. We investigated the photodegradation of DNAN both as a pure solid and as part of solid IM formulations, IMX101, IMX104 and PAX21. The concentrations of degradation products found were small, <1%, relative to DNAN concentrations. We saw transient peaks in the chromatograms indicating intermediate, unstable products but we consistently found methoxy nitrophenols and methoxy nitroanilines. We also found one unknown in most of the samples and other unknowns less frequently.

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1. Introduction

The US military is developing explosives that are less sensitive to shock and high temperatures to minimize unintentional detonations, the so-called insensitive munitions (IM). DNAN (2,4-dinitroanisole) is a main ingredient in IM formulations currently being tested. The IM formulations studied here are melt-cast, a process where crystalline constituents are added to a molten matrix, in this case DNAN, and then casted and cooled. For IMX101, IMX104 and PAX21 most of the crystals added (3-nitro-1,2,4-

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triazol-5-one (NTO), ammonium perchlorate (AP) and nitroguanidine (NQ)) are more water-soluble and only RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) is less soluble than DNAN (see SM 1).

Explosives are released onto training range soils when UXO casings fail or by incomplete (partial) detonations during training with explosive-filled munitions. The latter process is thought to deposit most of the explosive mass available for dissolution over decade time scales (Taylor et al., 2004). The solid particles of IM explosives, scattered by incomplete detonations, are dissolved by precipitation and can then travel to groundwater. What compounds reach groundwater is determined by their rates of dissolution, photo-transformation (both in solid form and in aqueous solution), and complex interactions of the aqueous explosive solutions with soil constituents during transport through the vadose zone.

Outdoor dissolution tests using chunks of the IM explosives simulated the dissolution of isolated IM pieces scattered onto range soils (Taylor et al., 2015a). These tests showed that the IM pieces change color when exposed to sunlight from cream or white to orange or brick red. DNAN is a nitroaromatic like TNT, which also undergoes a similar color change when exposed to sunlight (e.g. Spanggord et al., 1983). Over time, unknown peaks also appeared in the high performance liquid chromatograms. Particles from indoor (no sunlight) dissolution tests did not change color and had no unknown HPLC peaks (Taylor et al., 2015b). Close examination showed that only DNAN changed color suggesting it was the main component being photo-degraded. DNAN is also one of the least soluble constituents and quickly becomes the main surface constituent of the IM particles when the AP, NTO and NQ dissolve. Surfaces of DNAN are, therefore, the most likely to photo-degrade because the soluble components have either been dissolved or are present below the surface of the particle and shadowed from sunlight. For these reasons we expect less transformation to occur for the highly soluble compounds and focused our attention on DNAN, which persists long enough to photo-degrade.

DNAN transformation pathways and products have been reported for several matrices including cell cultures, soil microcosms, sludge bioassays, treated wastewater (alkaline hydrolysis, zero-valent iron, fluidized-bed bioreactors), toxicity test organisms, irradiated aqueous solutions, and oxic aqueous solutions (SM 2). Most studies focused on biological transformation products (Olivares et al., 2016). The most commonly reported transformation product is 2-methoxy-5-nitroaniline (2-MeO-5-NA). 2-MeO-5-NA forms by reducing the *ortho* nitro group of DNAN, reported to be favored over reduction of the *para* nitro group. Under anaerobic conditions, reduction of both nitro groups forms 2,4-diaminoanisole (Olivares et al., 2016).

There are a few studies of photo-transformation products in DNAN aqueous solutions. Both Hawari et al. (2015) and Rao et al. (2013) found 2-methoxy-5-nitrophenol (2-MeO-5-NP) and dinitrophenol (DNP), considered intermediates not end products, and nitrate/nitrite. The final products of a DNAN aqueous solution photolyzed over 21 days were, nitrate anion (0.7 mol), ammonium (1 mol), and formaldehyde/formic acid (0.9 mol), per mole of DNAN degraded (Hawari et al., 2015). Using FTIR, Rao et al. (2013) found $-COOH$ or $-C{=}O$ in aqueous DNAN samples after 5 days of irradiation.

As IM chunks are scattered onto range soils during partial detonations (Walsh et al., 2015) it is likely that their surfaces will photo-transform and, if the products are soluble, that these compounds could travel with the precipitation into the soil and possibly to surface or groundwater. DNAN in solution, however, was found to be strongly absorbed by a variety of soils and the amount absorbed was positively correlated with the organic carbon and cation exchange capacity of the soil (Arthur et al. in review). Arthur et al. also found that during transport through the soil the DNAN transformed into its amino products 2-methoxy-5-nitroaniline (2-MeO-5-NA) and 4-methoxy-3-nitroaniline (4-MeO-3-NA). However, no studies have reported on the photo-transformation products that form on the surface of IM formulations or their subsequent fate in the environment.

In this paper, we investigated the photo-degradation of DNAN as a pure solid and in IM formulations, IMX101, IMX104 and PAX21. DNAN is known to be toxic to humans and the environment (Dodard et al., 2013; Dumitras-Hutanu et al., 2009) yet the identities of photo-degradation products formed on its surface are unknown and might also be toxic. We selected and analyzed samples that would allow us to compare products formed on IM surfaces, in the effluent from those surfaces and in sunlight exposed DNAN crystals. Identifying degradation compounds will help environmental managers detect and quantify them in surface and groundwater and avoid regulatory actions and base closures.

2. Methods

2.1. Samples

We analyzed samples from a multi-year, outdoor dissolution study of IM formulations (Taylor et al., 2015b). The aqueous effluent, resulting from precipitation interacting with these IM pieces, was analyzed for both the dissolved IM constituents and the photo-degradation products formed on their surfaces. We also extracted and analyzed some of the red-stained support frits holding these IM chunks.

To increase the concentration of the degradation compound(s) we also exposed thin films, made by evaporating 5 mL of DNAN acetonitrile standard solutions or 5 mL of aqueous DNAN solutions to sunlight and to UV light (312 nm) in petri dishes in the laboratory (Fig. 1). After irradiation these samples were dissolved in 5 mL of acetonitrile and analyzed. Our goal for these samples was to produce photo-degradation products of DNAN in the absence of other IM constituents for comparison. Fig. 1 shows examples of samples we analyzed.

Some of DNAN's transformation products are known because DNAN was used in dyes and as reagents for chemical synthesis (SM 3). We were able to purchase standards for some of these including: 2,4-dinitrophenol (DNP), 2-methoxy-5-nitrophenol (2-MeO-5-NP), 4-methoxy-3-nitrophenol (4-MeO-3-NP), 1,2,4-benzenetriol, 2-methoxy-5-nitroaniline (2-MeO-5-NA), and 4-methoxy-3- nitroaniline (4-MeO-3-NA). These standards were analyzed along with our samples using the analytical techniques described below.

2.2. Preparation of standard solutions of DNAN and transformation products

Standard solutions of 2,4-DNAN and potential transformation products were prepared from solid material obtained from the sources listed in SM 4. With the exception of 4-MeO-3-NP, slightly more than 100 mg of each compound was air-dried in a desiccator in the dark. Then 100.0 mg of each compound were transferred to individual 100-mL volumetric flasks containing a volume (<80 mL) of acetonitrile. Each flask was wrapped in foil to protect the contents from light and then the solutions were agitated on a platform shaker overnight. Then each flask was brought to volume with acetonitrile and inverted at least 20 times to ensure thorough mixing. The stock solution for 4-MeO-3-NP was prepared in a similar manner but with 10 times less mass and volume due to the limited amount available. These solutions served as 1000 mg/L stock solutions. Working standards were prepared by dilution of the stock solutions.