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Photo-transformation of Aqueous Nitroguanidine and 3-nitro-1,2,4-triazol-5-one

Emerging Munitions Compounds

Julie B. Becher, Samuel A. Beal, Susan Taylor,
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Samuel A. Beal and Susan Taylor

Cold Regions Research and Engineering Laboratory
U.S. Army Engineer Research and Development Center
72 Lyme Road
Hanover, NH 03775

Julie B. Becher and Dean E. Wilcox

Department of Chemistry
Dartmouth College
Hanover, NH 03775

Katerina Dontsova

Department of Soil, Water, and Environmental Science
University of Arizona
Tucson, AZ 85721

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Preface

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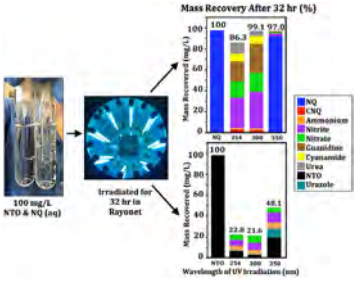
Photo-transformation of aqueous nitroguanidine and 3-nitro-1,2,4-riazol-5-one: Emerging munitions compounds

GRAPHICAL ABSTRACT



ABSTRACT

Two major components of insensitive munition formulations, nitroguanidine (NQ) and 3-nitro-1,2,4-triazol-5-one (NTO), are highly water soluble and therefore likely to photo-transform while in solution in the environment. The ecotoxicities of NQ and NTO solutions are known to increase with UV exposure, but a detailed accounting of aqueous degradation rates, products, and pathways under different exposure wavelengths is currently lacking. Here, we irradiated aqueous solutions of NQ and NTO over a 32-h period at three ultraviolet wavelengths (254 nm, 300 nm, and 350 nm) and analyzed their degradation rates and transformation products. NQ was completely degraded by 30 min at 254 nm and by 4 h at 300 nm, but it was only 10% degraded after 32 h at 350 nm. Mass recoveries of NQ and its transformation products were $\geq$80% for all three wavelengths, and consisted of large amounts of guanidine, nitrate, and nitrite, and smaller amounts of cyanamide, cyanoguanidine, urea, and ammonium. NTO degradation was greatest at 300 nm with 3% remaining after 32 h, followed by 254 nm (7% remaining) and 350 nm (20% remaining). Mass recoveries of NTO and its transformation products were high for the first 8 h but decreased to 22–48% by 32 h, with the major aqueous products identified as ammonium, nitrate, nitrite, and a urazole intermediate. Environmental half-lives of NQ and NTO in pure water were estimated as 4 and 6 days, respectively. We propose photo-degradation pathways for NQ and NTO supported by observed and quantified degradation products and changes in solution pH.

1. Introduction

The U.S. military develops and tests insensitive munitions (IM) that are less sensitive to external stimuli and therefore less likely to

detonate unintentionally. Two IM formulations, IMX 101 and IMX 104, are current IM replacements for the high explosives 2,4,6-trinitrotoluene (TNT) and Composition B (1,3,5-trinitro-1,3,5-triazinane [RDX] and TNT), respectively. IMX 101 has already been approved by the U.S. Army as a safer, yet equally effective, alternative to TNT (Rutkowski et al., 2010). IMX 101 contains nitroguanidine (NQ), 3-nitro-1,2,4-triazol-5-one (NTO), and 2,4-dinitroanisole (DNAN), and IMX 104 contains NTO, DNAN, and RDX (S-Fig. 1). Both formulations are melt-cast, a process in which the crystalline components (i.e., NQ, NTO and RDX) are added to a molten DNAN matrix (Pelletier et al., 2010). Environmental releases of these compounds may occur as manufacturing wastewater or dispersal on soil as particles following detonations (Taylor et al., 2004; Hewitt et al., 2005; Jenkins et al., 2006; Walsh et al., 2013, 2014).

The water solubilities of NQ and NTO are orders of magnitude greater than their conventional counterparts at 4400 and 17000 mg/L, respectively (U.S. Army, 1984; Spear et al., 1989). Correspondingly, these compounds have been found to dissolve rapidly from IM particles upon surface exposure to water (Taylor et al., 2015a, 2015b). Complex biological and photochemical processes result in products that can have vastly different chemical properties than the starting explosives (Taylor et al., 2017a, 2017b; Halasz et al., 2018; Haag et al., 1990; Krzmarzick et al., 2015). Of particular concern is the noted increase in toxicity of NQ and NTO solutions when exposed to visible and ultraviolet light (van der Schalie, 1985; Kennedy et al., 2017; Gust et al., 2017). NTO and NQ absorb strongly at UV wavelengths (S-Fig. 2) making them susceptible to photochemical transformation by sunlight. The identification of photo-transformation rates, products, and pathways improves understanding of the fate, transport, and effects of IM releases.

Aqueous NQ irradiation experiments have found different photo-transformation products, some of which may explain its increased toxicity. Burrows et al. (1988) found guanidine, cyanoguanidine (CNQ), ammonia, nitrite, nitrate, urea and an intermediate (nitrosoguanidine) from 254 nm exposures. Haag et al. (1990a,b) found predominantly hydroxyguanidine and nitrites from sunlight exposures over four to six days. Halasz et al. (2018) found guanidine, nitrosoguanidine, and nitrates from a solar simulator (280−800 nm) and a 300 nm exposure. Although all of these compounds are more toxic than NQ (Burrows et al., 1988), Kennedy et al. (2017) posited that cyanide (CN^-) might result from cyanamide or CNQ transformation. CNQ has been shown to breakdown into hydrogen cyanide under acidic conditions (NIOSH, 1998) and such a transformation would account for the drastic increase in solution toxicity (Kennedy et al., 2017).

Identified UV photo-transformation products of aqueous NTO include 3-hydroxy-1H-1,2,4-triazol- 5(4H)-one, the tautomer of urazole, urazole, nitrates, triazolone, and carbon dioxide gas (Halasz et al., 2018; Singh et al., 2001; Le Campion et al., 1997). The reduced transformation product 3-amino-1,2,4-triazol-5-one (ATO) has been found from biotransformation under strictly anaerobic conditions but not photo-transformation of NTO (Le Campion et al., 1999a; Krzmarzick et al., 2015). In the presence of TiO_4 or ferric salts, which catalyze Fenton chemistry, Le Campion et al. (1999b) demonstrated that NTO is entirely mineralized to carbon dioxide, ammonia and nitrate.

Transformation rates for NQ and NTO varied widely based on the irradiation wavelength and power used in the experiments (Halasz et al., 2018; Burrows et al., 1988; Haag et al., 1990; Kennedy et al., 2017). We aimed to understand the transformation pathways occurring in nature by establishing the NQ and NTO transformation rates at three different wavelengths and connecting these to sunlight exposure. To this end, we irradiated aqueous solutions of NQ and NTO in a reactor chamber at UV-C, −B, and -A wavelengths to identify the photo-transformation products and rates at each UV wavelength. Although UV-C radiation is extremely low at the Earth's surface, the end products at this germicidal wavelength represent a sterile breakdown pathway. The identity of the photochemical transformation products of NQ and NTO and their rates of production are needed to determine their environmental impact.

2. Materials and methods

2.1. Experimental setup

NQ and NTO standards were obtained from BAE (97% pure). One liter bottles of 100 mg/L aqueous solutions of NQ and NTO were prepared using Milli-Q water. Eight mL of this stock solution were placed in quartz tubes and sealed with corks and parafilm. The samples were then placed in a rotating carousel in a Rayonet (RPR-100) reaction chamber (S-Fig. 3). Triplicate aqueous samples were irradiated for 0, 15 min, 30 min, 1 h, 2 h, 4 h, 8 h, 24 h, or 32 h at three different UV wavelengths. Eight bulbs at each wavelength had peak output at 254 nm, 300 nm, or 350 nm. The irradiation took place in a 4 °C cold room to counteract the heat produced by the bulbs. The inside of the irradiator had an average temperature of 18.5 ± 1.6 °C minimizing thermal degradation of the samples. The pH of the samples was measured using a Mettler-Toledo pH meter and a micro pH probe, calibrated using pH 4, 7 and 10 standards.

2.2. Transformation product standards

Cyanoguanidine (99%), cyanamide (99%), urazole (97%), and guanidine hydrochloride (≥99%) standards were purchased from Sigma Aldrich. Urea (99%) was purchased from Bio-Rad. A standard of ATO was obtained from Ed Hunt (U. Arizona). Ammonium, nitrate, and nitrite ion chromatography (IC) standards were purchased in solution from Inorganic Ventures. All reagents for cyanide analysis were purchased from Sigma Aldrich. We were not able to obtain nitrosoguanidine and hydroxyguanidine standards.

2.3. Chromatography analyses

Aqueous samples were measured for NQ, cyanoguanidine, NTO, and urazole using a Hypercarb porous graphitic column (50 × 2.1 mm, 3 μm) on an Agilent 1200 HPLC with a diode array detector (modified from Le Campion et al., 1999a,b). For NQ, the mobile phase was 0.5% trifluoroacetic acid (TFA) in water from 0 to 10 min, 15/85 (v/v) acetonitrile/water with 0.1% TFA from 10 to 15 min, and 0.5% TFA in water from 15 to 19 min. For NTO, the mobile phase was 0.5% TFA from 0 to 5 min, 15/85 (v/v) acetonitrile/water with 0.1% TFA from 5 to 12 min, and 0.5% TFA in water from 12 to 17 min. The sample injection volume was 10 μL, the flow rate was 0.4 mL/min, and the column temperature was 28 °C. Detection wavelengths and retention times were: 263 nm at 8.6 min for NQ; 216 nm at 2.8 min for CNQ; 315 nm at 9.6 min for NTO; and 216 nm at 3.0 min for urazole. The estimated detection limit for each analyte was 0.02 mg/L.

Aqueous NQ samples were analyzed for cyanamide and urea using a ProntoSIL 200-5-C30 column (250 × 4.6 mm, 5 μm) on an Agilent 1200 Series HPLC with a diode array detector (Turowski and Deshmukh, 2004). The mobile phase was 100% water at 0.8 mL/min and 28 °C. The total run time was 10 min and the injection volume was 20 μL. The retention time was 3.9 min for cyanamide and 3.8 min for urea. This method also detected cyanoguanidine at 5.3 min and NQ at 6.6 min. The UV detector was set at 200 nm for all analytes. The estimated detection limit for each analyte was

0.02 mg/L.

Aliquots of each sample were diluted 1:10 and analyzed by ion chromatography with conductivity detection (Thermo Integrion). Ammonium and the guanidinium ion (reported as guanidine) were separated on an IonPac CS19 column (250 × 4 mm, 4 μm) with 7 mM methane sulfonic acid (Burrows et al., 1984). The flow rate was 1 mL/min, injection volume 25 μL, and column temperature 30 °C. Nitrate and nitrite were separated on an IonPac AS18 column (150 × 4 mm, 4 μm) with 25 mM KOH isocratic eluent. The estimated detection limit for each analyte was 0.2 mg/L.

2.4. Cyanide analysis

We analyzed for HCN gas from the irradiated solutions using modified EPA methods 9010 for the scrubber solution and 9014 for the colorimetric analysis. A tiny test tube was suspended inside the quartz irradiation vials and filled with 0.5 mL of NaOH scrubber solution (5 g of NaOH in 100 mL of water). The scrubber solution should have absorbed any HCN gas evolved from the aqueous solutions of NQ and NTO. For the colorimetric analysis, a 1 M sodium phosphate solution, a 0.44% Chloramine-T solution, a pyridine-barbituric acid solution, and KI starch paper were used according to EPA method 9014 guidelines to measure HCN gas absorbed by the NaOH scrubber solution based on the solution absorbance at 578 nm (U.S. EPA, 2014).

2.5. Irradiance measurements and rate calculations

Ultraviolet irradiance was measured in the reactor using an optometer (Gigahertz Optik P-9710). Three detector heads were used for the optometer corresponding to UV-A (Gigahertz Optik UV-3701; 315–400 nm), UV-B (UV-3702; 280–315 nm), and UV-C (UV-3703; 250–280 nm). Irradiance measurements were made inside the reactor at the location of the samples both in front of and between each bulb and averaged since the samples were rotating in the chamber. Assuming 100% transmission through the quartz tubes, we calculated fluence (J/m^2) as the product of irradiance of a given detector head and irradiation time. We calculated first-order photolysis transformation rates (k_{obs}) by the linear fit of the natural logarithm of normalized compound concentration and fluence (intercept forced through 0). Using the same detector heads, we measured irradiance at noon in Hanover, New Hampshire, United States (43.7 °N), on a clear day (7 May 2017) and a cloudy day (4 May 2017). We estimated environmental half-lives at each tested wavelength using k_{obs} and an estimate of daily fluence as half the clear day noon-measured irradiance over 8 h per day.

3. Results and discussion

3.1. NQ transformation rates and products

All 101.5 mg/L of starting NQ was degraded by 30 min at 254 nm and by 4 h at 300 nm (Fig. 1). Approximately 92% of the original NQ remained after 32 h at 350 nm. The total mass recoveries of all measured compounds at the end of each 32-hr experiment were 86 ± 1%, 99.1 ± 0.9%, and 97.0 ± 0.1% for the 254 nm, 300 nm, and 350 nm bulb irradiations, respectively.

The rapid transformation of NQ from irradiation at 254 nm yielded relatively constant concentrations of guanidine, urea, cyanamide and CNQ (Fig. 1b). HCN gas was not detected in any of the irradiated solutions at 254 or 300 nm after 32 h exposure. Of the terminal aqueous nitrogen products, ammonium concentrations remained minimal throughout the experiment, while nitrate dominated from 15 min until after 8 h when a reversal occurred with nitrite becoming the predominant product. Solution pH tracked the shift in NO_3^-/NO_2^- with an initial decrease followed by a return to neutral pH by 24 h.

At 300 nm, the slower transformation of NQ yielded fairly constant relative abundances of nitrite, guanidine, nitrate, cyanamide, urea, and CNQ (Fig. 1c). The 300 nm irradiation produced greater guanidine concentrations and lesser urea concentrations, compared with the 254 nm irradiation. Nitrite concentrations were greater than nitrate throughout the irradiation, but longer irradiation times increased nitrate at the expense of nitrite, which was reflected in the solution pH that decreased throughout the experiment. Interestingly, after 30 min more oxygen was recovered than was in the initial NQ (S-Fig. 4), likely due to the oxidation of ammonia to nitrate, which has been observed under UV irradiation of pH ≥ 7 solutions when hydroxyl radicals are present (Huang et al., 2008). Photoreactions of nitrate and nitrite can create the hydroxyl radicals necessary for ammonia oxidation (Mack and Bolton, 1999), and the pH of the 300 nm solutions was high enough to enable this process. This positive oxygen mass balance was not observed for irradiation at 254 nm, likely because its relatively acidic pH inhibited ammonia oxidation, which in turn may partially explain the negative nitrogen mass balance in those samples as loss of ammonia gas. The additional oxygen in the 300 nm samples artificially increased the total percent mass recoveries by ~6%.

After 32 h of 350 nm irradiation, NQ concentrations were 93.6 ± 0.1 mg/L with ~1–3 mg/L each of nitrate, nitrite, ammonium, and guanidine, and no detectable CNQ or urea. The pH of these solutions was constant during irradiation, indicating that a change in pH is related to NQ breakdown. Slow transformation at 350 nm likely reflects NQ's relatively low photon absorption at this wavelength (λ_{max} 264 nm, S-Fig. 2).

An unknown peak was observed in the HPLC analyses of the 254 and 300 nm samples. On the Hypercarb column the unknown compound had a retention time of 2.44–2.56 min and an absorbance peak at 240 nm (Fig. 2). On the ProntoSIL column the unknown peak was observed at 4.48 min with an absorbance maximum at 258 nm. We attribute the 18 nm shift in the maximum to differences in the mobile phase solution, and suggest these peaks correspond to the same unknown.

The unknown was transient, increasing in concentration as NQ concentrations decreased, and then steadily decreasing in concentration until it disappeared around 8 h for the 254 nm samples. The timing of the unknown's appearance and disappearance is consistent with nitrosoguanidine found by Burrows et al. (1988). For the first 4 h of irradiation, not all of the nitro groups from NQ decomposition were recovered as nitrate and nitrite. By 8 h, however, all of the nitro group mass was detected as these two ions. The concentration of guanidine also did not peak until 2 h in the 254 nm irradiated samples, yet NQ was fully degraded after 30 min. This suggests that a portion of the nitro groups and guanidine initially existed in an intermediate compound but was transformed into guanidine and nitrates with longer UV exposure. The nitrosoguanidine intermediate observed by Burrows et al. (1988) follows this same behavior. Furthermore, Burrows et al. (1988) observed nitrosoguanidine to absorb radiation strongly at 235 nm, which is close to the absorbance peak of the unknown intermediate (240–258 nm).

3.2. NQ photo-transformation pathways

The weakest bond in NQ is the N–NO_2 bond with a dissociation energy of 199.1 kJ/mol (Xue et al., 2017). When the N–NO_2 bond is photolytically cleaved, NQ separates into the guanidine radical and nitro radical. The guanidine radical can form guanidine by abstraction of a hydrogen atom from the solution, form

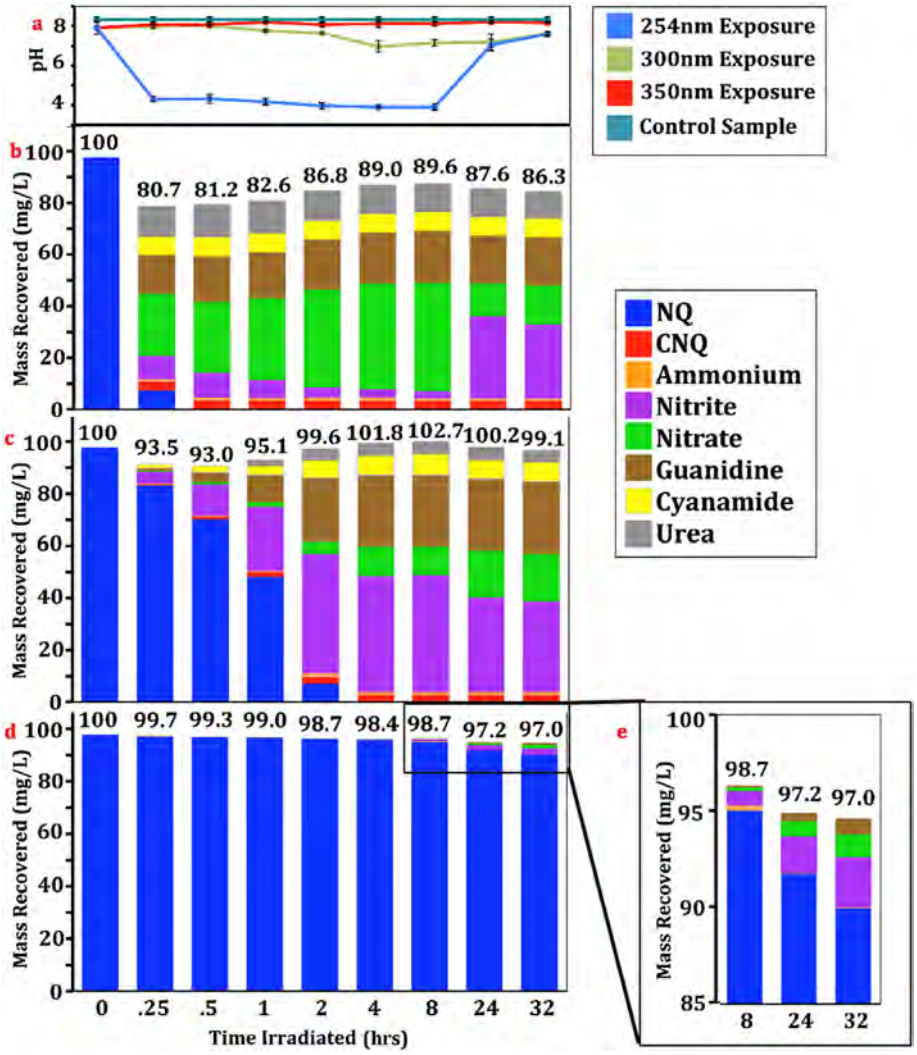


Fig. 1. NQ sample pH (a.) and chemical concentrations at 254 nm irradiation (b.), 300 nm irradiation (c.), and 350 nm irradiation (d. and e.). pH error bars are ±1 standard deviation. Bars reflect the mean concentration of each compound from triplicate samples. The mass percentages recovered for each time step are shown above each bar.

hydroxyguanidine by reacting with water, or breakdown into ammonia and cyanamide (intramolecular collapse). The latter can then dimerize into CNQ or be hydrolyzed to urea (Fig. 3). The nitro radical either gains one electron and becomes nitrite or is oxidized further to become nitrate. Although we had no standard for hydroxyguanidine, our high mass recoveries make its existence in large quantities unlikely. Burrows et al. (1988) proposed an alternative pathway to produce the nitrosoguanidine intermediate—the disproportionation of NQ into nitrosoguanidine and an oxidized intermediate. Our data suggest that this pathway is minor compared to the homolytic cleavage of the N—N bond, since very little of the nitro and guanidine mass came from this intermediate.

Under 254 nm irradiation, over half of the carbon from the guanidine portion of the molecule was recovered as cyanamide, urea, and CNQ, indicating that intramolecular collapse of the guanidine radical is a major pathway at this wavelength. Cyanamide persisted in solution in significant amounts (~8 mg/L), with preferential hydrolysis into urea, rather than dimerization into CNQ. Cyanamide formed when the samples were acidic (~pH 4), which favors the reaction toward urea, while the reaction toward CNQ is favored at a pH > 5 (Urbanyi and Walter, 1971).

More guanidine was formed with 300 nm irradiation, compared to 254 nm irradiation, and there was less cyanamide, suggesting that higher energy is needed to collapse the guanidine radical. Correspondingly lower concentrations of urea and CNQ were observed at 300 nm. Although more of the guanidine carbon was recovered as guanidine than as intramolecular collapse products (cyanamide, urea, CNQ), more of the carbon recovered from intramolecular collapse remained as cyanamide than was converted to either CNQ or urea. This finding differs from the predictions of Burrows et al. (1988) who suggested that cyanamide was an unstable intermediate in the breakdown pathway, rather than an end-stage transformation product, as we found. Under 350 nm irradiation, no CNQ, cyanamide or urea were detected, but some guanidine was found, suggesting that homolytic cleavage of the N—NO_2 bond is not favored and intramolecular guanidine radical collapse is not a viable pathway at this wavelength.

Rapid breakdown of NQ from homolytic cleavage of the N—NO_2 bond likely forms many nitro radicals, which dimerize into N_2O_4, an intermediate in the photoreaction pathway that transforms nitrite into nitrate (S-Fig. 5; Mack and Bolton, 1999). Protons are liberated by this transformation in water, which accounts for the initial pH drop observed for the 254 nm solutions. Low pH inhibits the photoreactions that convert nitrate to nitrite (Mack and Bolton, 1999), leading to high nitrate concentrations during the early stages of the exposure period. Once NQ was fully degraded and nitro radicals

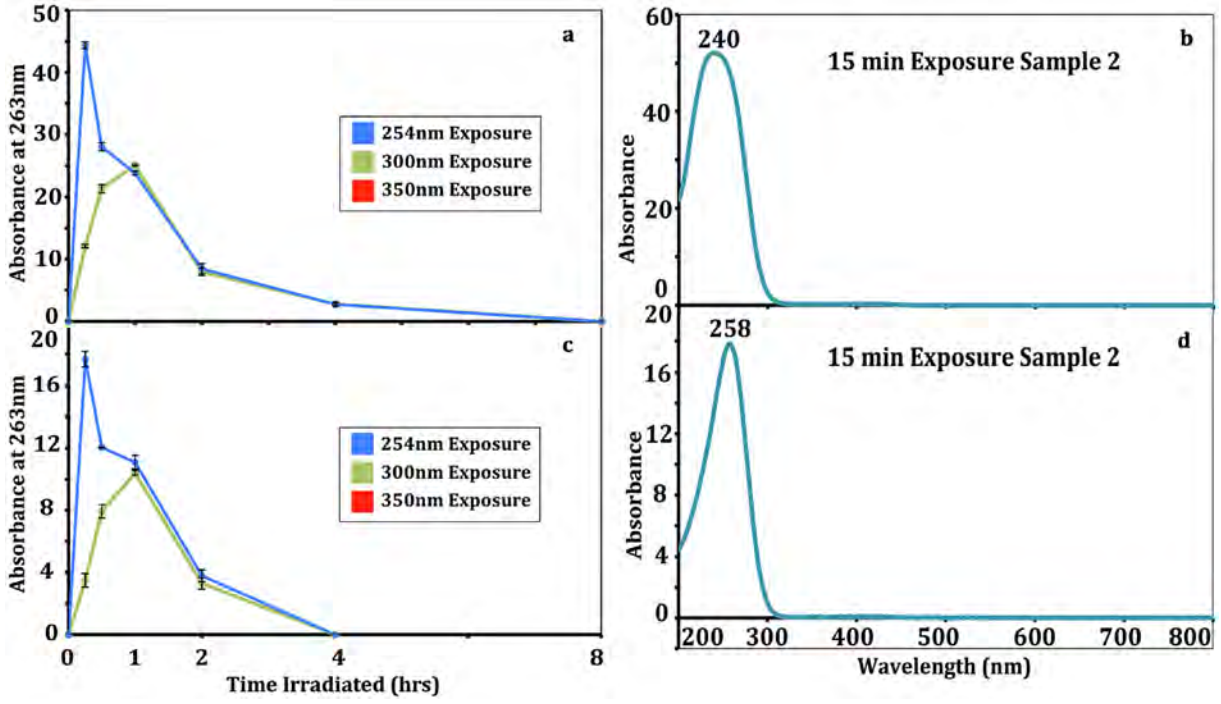


Fig. 2. HPLC absorbance and DAD spectra of the NQ irradiation unknown, suspected to be nitrosoguanidine, using a Hypercarb column (a–b) and ProntoSIL column (c–d).

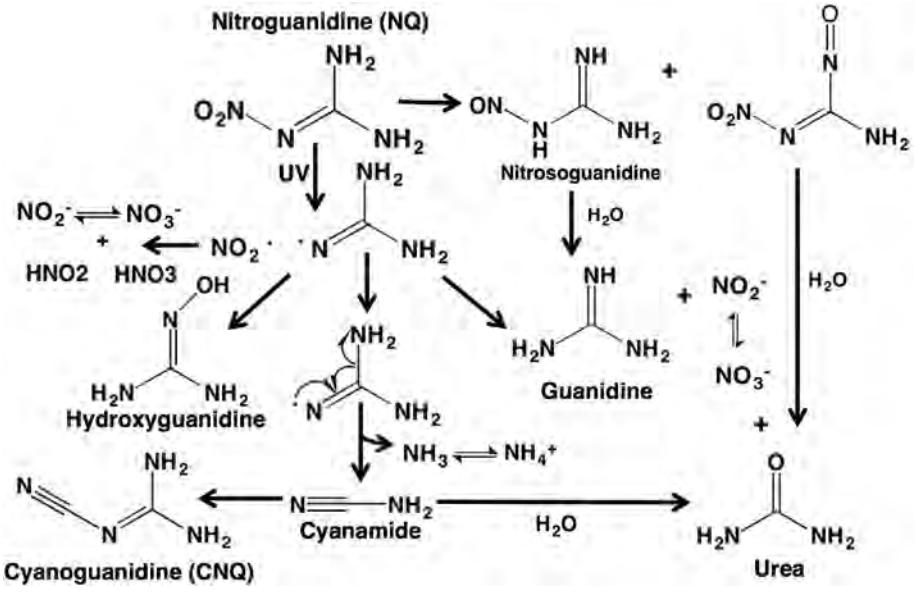


Fig. 3. Breakdown pathways of nitroguanidine (NQ) under UV irradiation. Major predicted transformation products are labeled. Adapted from Burrows et al., (1988) and Haag et al., (1990).

were no longer generated, photoreactions transforming nitrate into nitrite lead to intermediates ($^{\bullet}OH$, $O_2^{\bullet-}$) that scavenged protons from solution, thereby increasing the solution pH. This same process likely occurred in all of the irradiated solutions but the kinetics varied based on the wavelength of irradiation and rate of NQ transformation.

Our results show that cyanamide, urea and CNQ (in small amounts) are the final transformation products, and not intermediates, of NQ photo-transformation. The amounts of nitrate and nitrite produced vary depending on the time of exposure and the UV wavelength used, but are produced in large amounts that could have harmful environmental effects. Nitrates are quite toxic to aquatic life (Camargo et al., 2005) and nitrite is a potential carcinogen, due to the formation of N-nitrosamine compounds in the stomach, when consumed by humans (Mirvish, 1975). While cyanide would explain the extreme toxicity of irradiated NQ solutions, we did not detect HCN vapor above the irradiated solutions. Possibly a more sensitive cyanide detection method is required. In the presence of the weak acid NTO, as would occur from IMX-101 dissolution in the environment, CNQ could be transformed into

extremely toxic HCN.

3.3. NTO rates and products

After 32 h of irradiation at 254 nm, 300 nm, and 350 nm, only 7%, 3%, and 20% of the initial NTO remained, respectively (Fig. 3). The mass recovery of these samples was initially high (74–101%) but decreased dramatically after 8 h and was quite low by 32 h of irradiation (22.8 ± 2.8%, 21.6 ± 0.5%, and 48.1 ± 0.7% for 254 nm, 300 nm, and 350 nm, respectively; Fig. 4). The final transformation products from NTO irradiation at all three wavelengths were ammonium, nitrate, and nitrite, with urazole appearing transiently. Formation of bubbles in irradiated NTO solutions (S-Fig. 6) suggests gaseous transformation products that were not quantified and may explain the poor mass recoveries. Interestingly, the highest amounts of ammonium, nitrate, nitrite, unknown anion, and urazole per mg of degraded NTO were observed in the 350 nm samples, even though NTO breakdown was slowest at this wavelength.

Nitrite increased before reaching stable concentrations by 8 h in the 254 and 300 nm samples and by 24 h in the 350 nm samples. Nitrate and ammonium concentrations increased at all three wavelengths throughout the experiment. Nitrite and nitrate concentrations in the NTO samples were significantly lower, and ammonium significantly higher, than those produced by irradiation of NQ. Urazole concentrations increased linearly until a maximum of ~12 mg/L was detected at 8 h in the 254 nm and 300 nm samples, and at 24 h in the 350 nm samples, before linearly decreasing until 32 h. An unknown anion that formed transiently, similarly to urazole, was identified by ion chromatography in 254 nm and 300 nm samples but persisted throughout the experiment at 350 nm (Fig. 5, S-Fig. 7). Cyanate was rejected as the identity of the unknown

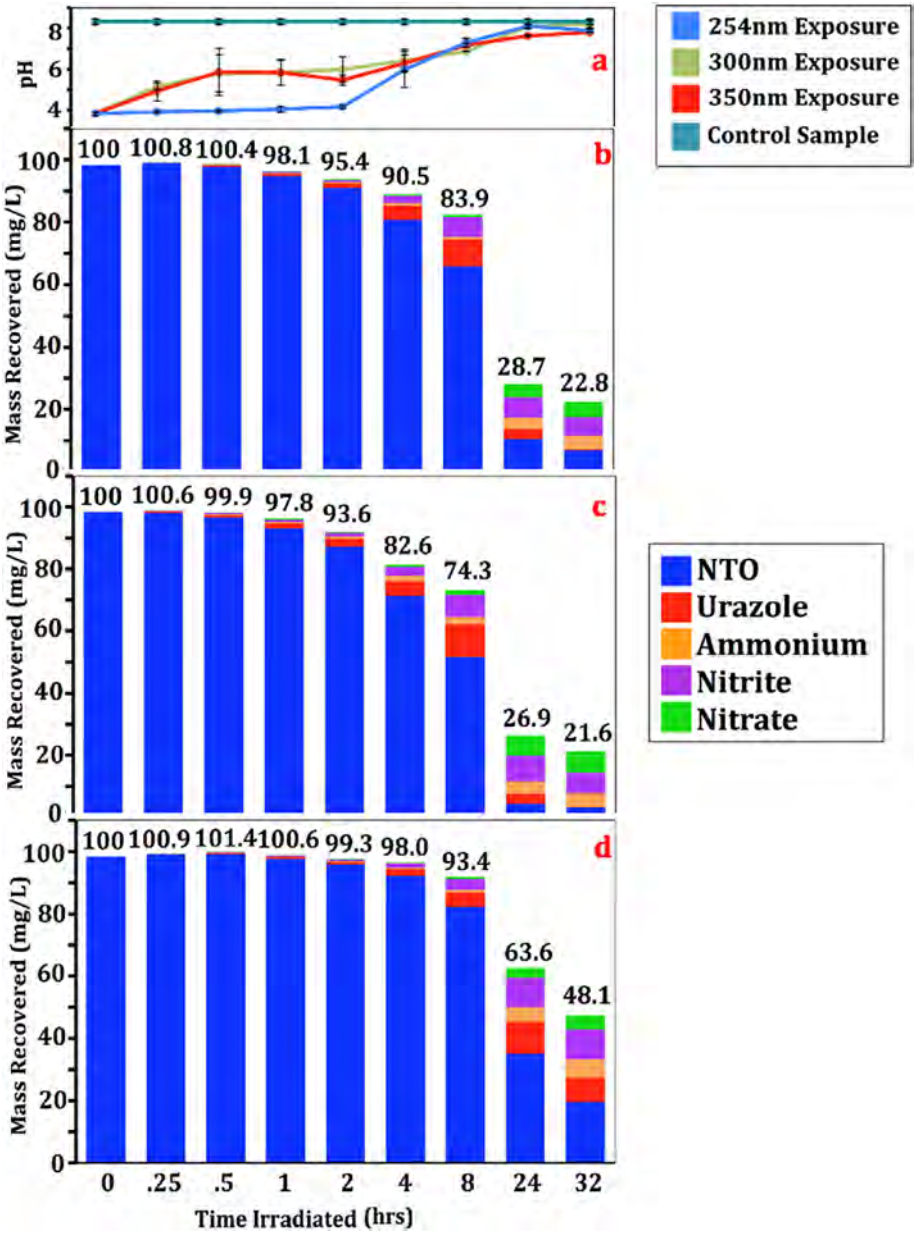


Fig. 4. NTO sample pH (a.) and chemical concentrations at 254 nm irradiation (b.), 300 nm irradiation (c.), and 350 nm irradiation (d.). pH error bars are ±1 σ. Bars reflect the mean concentration of each compound from triplicate samples. The mass percentages recovered for each time step are shown above each bar.

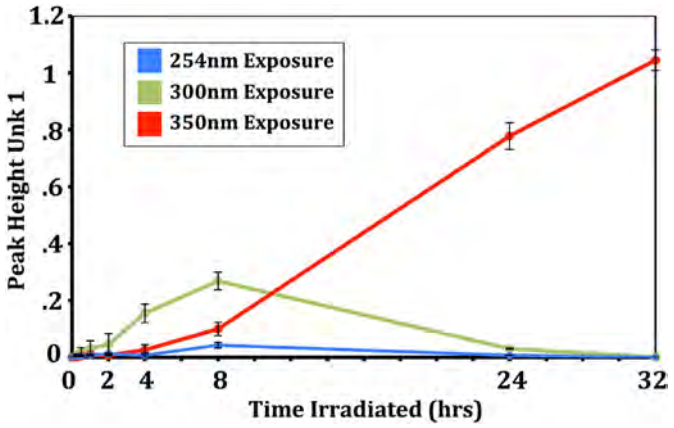


Fig. 5. Peak height of an unknown in the anion IC chromatograms for NTO. Error bars are ±1σ of triplicate samples at each wavelength.

intermediate, based on analysis of a known standard. The pH of these samples was initially acidic because of NTO's pK_a of 3.76 (Smith and Cliff, 1999) but increased over the course of the experiment and reached neutral values.

3.4. Transformation pathways for NTO

The NTO solutions were initially yellow, but became clear when irradiated, indicating ring cleavage or a loss of aromaticity. For NTO, the C–NO_2 bond is weakest with a dissociation energy of 281 kJ/mol (Hadisaputra and Prasetyo, 2016). Breaking this bond results in a nitro radical and a triazolone radical, which reacts with water to form urazole, the major intermediate product of NTO (Singh et al., 2001; Halasz et al., 2018).

We propose that ring hydrolysis of either urazole or NTO directly forms an intermediate that can break down into isocyanic acid or other derivatives (Fig. 6). These derivatives are further hydrolyzed into the volatile products ammonia and carbon dioxide (Borduas et al., 2016). This pathway is analogous to that proposed for ATO, which forms cyanamide in soil before being mineralized further (FAO, 1999). The proposed pathway explains both the presence of ammonium and the gas bubbles we observed (S-Fig. 6). We found urazole but the other potential intermediates (hydrazine, (hydrazinocarbonyl)-carbamic acid) would need to be detected and identified to confirm the proposed pathway. The unknown anion found in the NTO samples may be an intermediate in this breakdown pathway.

Since the NTO transformation products were found in approximately equal ratios and amounts at all three wavelengths, the NTO transformation pathway does not depend on the wavelength of irradiation. The wavelength does, however, determine the rate at which the NTO degrades. NTO should photo-transform most quickly at 350 nm, the wavelength closest to its absorbance peak. Interestingly, NTO photo-transformed most quickly at 300 nm (Fig. 3), suggesting that other species affected its transformation rate rather than direct photolysis. These species could include ozone, possibly singlet oxygen species, or other reactive oxygen species created as nitrite and nitrate build up in solution.

The low mass recovery for the irradiated NTO solutions was likely due to both unidentified transformation products and the mass loss from gaseous products, as indicated by gas bubbles in the irradiated NTO solutions (S-Fig. 6). Based on the mass of transformed NTO, if we assume full mineralization of the missing C mass as CO_2, and the missing ring N as NH_3, as observed by Le Campion et al. (1999b), ~63 mg of CO_2 and 39 mg of NH_3 could have been produced per liter of our 99.8 mg/L NTO solution during the 32-h experiment at 254 nm, 65 mg CO_2 and 51 mg NH_3 at 300 nm, and 54 mg CO_2 and 42 mg NH_3 at 350 nm.

3.5. Environmental transformation rates

The amount of UV and visible light that reaches the Earth's surface varies as a function of many parameters, including latitude, time of year, and atmospheric and weather conditions (Brennan and Fedor, 1994). Although neither direct nor indirect photolysis guidelines (i.e., U.S. EPA OPPTS 835.5270 and 835.2210) were followed in this study due to our focus on mechanisms at individual UV wavelengths, we estimated environmental half-lives of NTO and NQ in pure water. We applied the fluence-based first-order transformation rates from the reactor experiments to measurements of

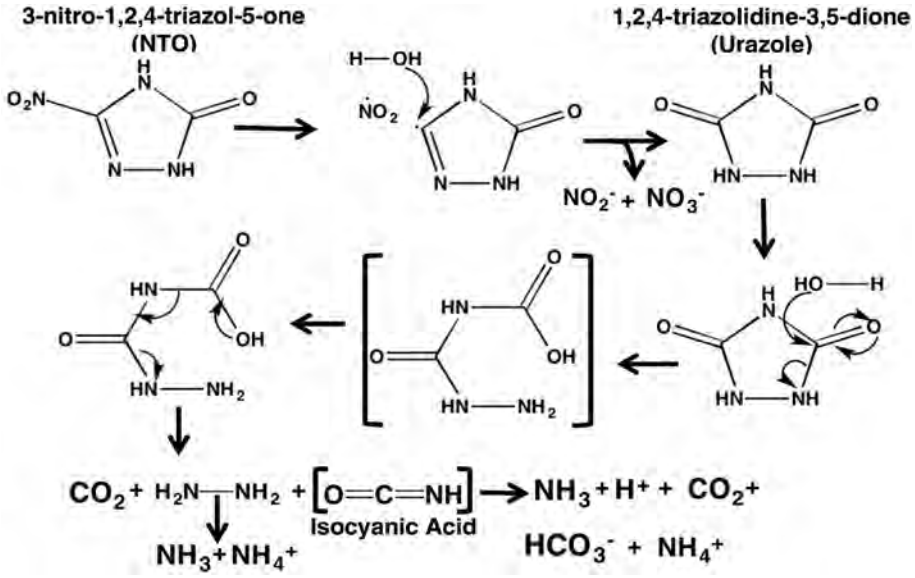


Fig. 6. Breakdown pathways of NTO under UV irradiation. Major predicted transformation products are labeled. Adapted from Halasz et al., (2018), FAO and and WHO, 1999, Singh et al., (2001), and Borduas et al., (2016).

Table 1
First-order photo-transformation rates and estimated environmental half-lives based on measured sunlight irradiance (S-Table 2).

Irradiation Wavelength	NQ k_{obs} ($m^2/J \pm 1SE$)	NTO k_{obs} ($m^2/J \pm 1SE$)	NQ est. $t_{1/2,\ env}$ (days)	NTO est. $t_{1/2,\ env}$ (days)
254 nm	$-3.75 \pm 0.02 \times 10^{-5}$	$-2.9 \pm 0.1 \times 10^{-7}$	68	8700
300 nm	$-7.2 \pm 0.9 \times 10^{-6}$	$-7.2 \pm 0.3 \times 10^{-7}$	4	41
350 nm	$-7.8 \pm 0.6 \times 10^{-9}$	$-1.70 \pm 0.09 \times 10^{-7}$	130	6

outdoor surface UV irradiance (S-Table 2) at each UV band in order to estimate the environmental half-lives (Table 1, S-Fig. 8). In sunlight, NQ is estimated to degrade most rapidly by 300 nm (UV–B) light with a half-life of ~4 days. NTO is estimated to degrade most rapidly by 350 nm (UV-A) light with a half-life of ~6 days. The estimated NQ half-life has a similar order-of-magnitude to that determined in aqueous solutions by outdoor photolysis (0.68–0.70 days; Haag et al., 1990a,b) and by solar simulator (0.59 days; Halasz et al., 2018). The estimated NTO half-life also has a similar order-of-magnitude to that determined in aqueous solution by solar simulator (2.0 days; Halasz et al., 2018). These environmental half-lives by sunlight are comparable to those for RDX (0.8–2.5 days), nitroglycerin (26–123 days), and DNAN (2.6 days) dissolved in pure water (Bordeleau et al., 2013; Halasz et al., 2018). In natural waters, however, quenching or indirect photolysis of NQ and NTO by dissolved species (e.g., dissolved organic matter, other energetic compounds) may affect photo-transformation rates and products (Haag et al., 1990; Dontsova et al., 1984; Halasz et al., 2018).

4. Conclusions and environmental implications

NQ and NTO are likely to undergo photo-transformation in wastewater or in surface water impacted by post-detonation particles with half-lives on the order of days. Increased toxicity of photo-transformed NQ may result from the formation of the terminal products cyanamide, CNQ, guanidine, and/or high levels of nitrate and nitrite, or from the transient formation of nitrosoguanidine. Further studies on these transformation compounds, particularly guanidine and nitrosoguanidine, could reveal the mechanism of irradiated NQ's toxicity. Additionally, although HCN gas was not observed during the irradiations, concentrations may have been below the method detection limit yet still significantly toxic, requiring a more sensitive detection method in future work. Irradiation of NTO solutions has been shown to slightly increase its eco-toxicity, but this study's irradiations produced predominantly mineralized gases, moderate nitrate and nitrite concentrations, and minimal amounts of the transient compound urazole, the latter of which has unknown toxicity. Since both NTO and NQ are present in the IMX 101 formulation, these compounds are probably found in the same surface water and may interact to promote or inhibit certain transformation pathways. For instance, the weak acid NTO could favor the transformation of photo-produced CNQ into extremely toxic HCN. Irradiation experiments of complete formulations (IMX 101 and 104) in natural waters are needed to confirm these results and enable environmental efforts to focus on transformation products that are both toxic and persistent in the environment.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.04.131.

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14. ABSTRACT

Two major components of insensitive munition formulations, nitroguanidine (NQ) and 3-nitro-1,2,4-triazol-5-one (NTO), are highly water soluble and therefore likely to photo-transform while in solution in the environment. The ecotoxicities of NQ and NTO solutions are known to increase with UV exposure, but a detailed accounting of aqueous degradation rates, products, and pathways under different exposure wavelengths is currently lacking. We irradiated aqueous solutions of NQ and NTO over a 32-h period at three ultraviolet wavelengths and analyzed their degradation rates and transformation products. NQ was completely degraded by 30 min at 254 nm and by 4 h at 300 nm, but it was only 10% degraded after 32 h at 350 nm. Mass recoveries of NQ and its transformation products were ≥80% for all three wavelengths. NTO degradation was greatest at 300 nm with 3% remaining after 32 h, followed by 254 nm (7% remaining) and 350 nm (20% remaining). Mass recoveries of NTO and its transformation products were high for the first 8 h but decreased to 22–48% by 32 h. Environmental half-lives of NQ and NTO in pure water were estimated as 4 and 6 days, respectively. We propose photo-degradation pathways for NQ and NTO supported by observed and quantified degradation products and changes in solution pH.

15. SUBJECT TERMS

UV irradiation, Nitroguanidine (NQ), 3-nitro-1,2,4-triazol-5-one (NTO), Transformation products, Transformation pathways

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Environmental Laboratory
U.S. Army Engineer Research and Development Center
3992 Halls Ferry Road
Vicksburg, MS 39180

Department of Chemistry
Dartmouth College
Hanover, NH 03755

Department of Soil, Water, and Environmental Science
University of Arizona
Tucson, AZ 85721