



NRC Publications Archive Archives des publications du CNRC

New insights into the photochemical degradation of the insensitive munition formulation IMX-101 in water

Halasz, Annamaria; Hawari, Jalal; Perreault, Nancy N.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1021/acs.est.7b04878>

Environmental Science & Technology, 52, 2, pp. 589-596, 2017-12-15

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=1f65eb06-57a2-4161-b9f7-59f510af6204>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=1f65eb06-57a2-4161-b9f7-59f510af6204>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.



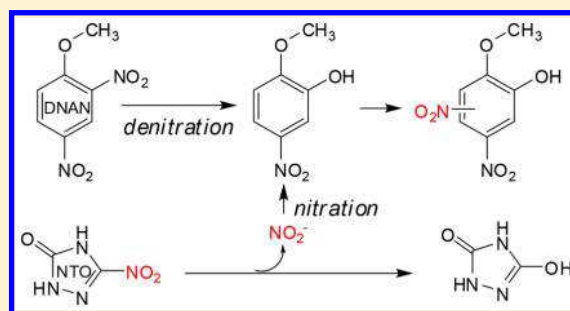
New Insights into the Photochemical Degradation of the Insensitive Munition Formulation IMX-101 in Water

Annamaria Halasz, Jalal Hawari,[†] and Nancy N. Perreault^{*†}

National Research Council Canada, 6100 Royalmount Avenue, Montreal, Quebec H4P 2R2, Canada

Supporting Information

ABSTRACT: This study describes photolysis of the insensitive munition formulation IMX-101 [2,4-dinitroanisole (DNAN), NQ (nitroguanidine), and 3-nitro-1,2,4-triazol-5-one (NTO)] in aqueous solutions using a solar simulating photoreactor. Due to a large variance in the water solubility of the three constituents DNAN (276 mg L⁻¹), NQ (5,000 mg L⁻¹), and NTO (16,642 mg L⁻¹), two solutions of IMX-101 were prepared: one with low concentration (109.3 mg L⁻¹) and another with high concentration (2831 mg L⁻¹). The degradation rate constants of DNAN, NQ, and NTO (0.137, 0.075, and 0.202 d⁻¹, respectively) in the low concentration solution were lower than those of the individually photolyzed components (0.262, 1.181, and 0.349 d⁻¹, respectively). In the high concentration solution, the molar loss of NTO was 4.3 times higher than that of NQ after 7 days of irradiation, although NQ was two times more concentrated and that NQ alone degraded faster than NTO. In addition to the known degradation products, DNAN removal in IMX-101 was accompanied by multiple productions of methoxydinitrophenols, which were not observed during photolysis of DNAN alone. One route for the formation of methoxydinitrophenols was suggested to involve photonitration of the DNAN photoproduct methoxynitrophenol during simultaneous photodenitration of NQ and NTO in IMX-101. Indeed, when DNAN was photolyzed in the presence of ¹⁵NO₂-labeled explosive CL-20, we detected methoxydinitrophenols with an increase of 1 mass unit, indicating that denitration of DNAN and renitration of products simultaneously occurred. As was the case with DNAN, we found that guanidine, a primary degradation product of NQ, also underwent renitration in the presence of NTO and the photocatalyst TiO₂. We concluded that the three constituents of IMX-101 can be photodegraded in surface water and that fate and primary degradation products of IMX-101 can be influenced by the interactions between the formulation ingredients and their degradation products.



INTRODUCTION

The defense industry is currently seeking to replace traditional explosives with insensitive munitions (IM) that are less likely to detonate unintentionally. The U.S. Army already approved the IM formulation IMX-101 as a safer, and yet equally effective, replacement to 2,4,6-trinitrotoluene (TNT).¹ 2,4-Dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO) are key components in emerging IM formulations such as IMX-101, IMX-104, and PAX-48. Additionally, IMX-101 contains nitroguanidine (NQ) (Table 1), and IMX-104 contains hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) commonly used in explosive compositions, e.g., Composition B (RDX, TNT, and wax).² While exhibiting comparable performance and processability, IMX-101 and IMX-104 are significantly less sensitive than TNT and Composition B, making the weapon systems they support safer to manufacture, transport, and handle. Recent studies show that the insensitive nature of the explosive formulation leads to less efficient detonation in some detonation scenarios at the detonation point, which drives the need for better studying their fate in the natural environment.^{3,4} The superior performance of IMX-101 can be explained by a series of complex chemical interactions between the ingredients when the formulation is subjected to a well-controlled thermal

environment.⁵ The thermal stability of DNAN was found to be lower in IMX-101 than when examined alone, and this was attributed to interactions between the ingredients and their degradation products.⁶

In nature, unexploded residues of munitions are bound to undergo some sort of biotic or abiotic degradation caused by soil microorganisms and plants or hydrolysis and photolysis. Biodegradation of IMX-101 in soil, compost and sludge¹⁰ and in surface soils¹¹ was studied, and phytoremediation to treat contaminated soil was reported.¹² Biodegradability of the IMX-101 constituents was also investigated under aerobic and anaerobic conditions.^{13–20} The main biodegradation products were dinitrophenols¹⁵ and the amino and diamino derivatives from DNAN^{13,14} and 3-amino-1,2,4-triazol-5-one¹⁹ from NTO.

Photolysis is one of the major abiotic processes affecting the transformation of energetic compounds in waste streams and surface water bodies²¹ and near the soil surface.²² Photolytic transformation can affect the persistence and toxicity of

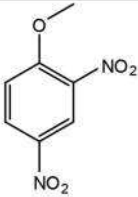
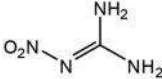
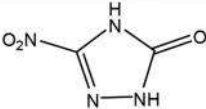
Received: September 20, 2017

Revised: December 6, 2017

Accepted: December 15, 2017

Published: December 15, 2017

Table 1. Structure, Distribution, and Water Solubility of the IMX-101 Constituents

Name	Structure	Distribution % (w/w)	Water solubility* (mg L ⁻¹)
DNAN		40-45	276
NQ		35-40	5,000
NTO		18-23	16,642

*From refs 7 (DNAN), 8 (NQ), and 9 (NTO).

contaminants. Photodegradation of individual munition constituents including NTO, DNAN, NQ, and RDX was previously studied and showed that photodegradation is governed by the initial denitration of the nitro compounds.^{23–28} On the other hand, little information is available on the photodegradation of explosive formulations in water, although explosives generally enter the environment as mixtures. Taylor et al. investigated photodegradation of DNAN as part of the IM formulations IMX-101, IMX-104 and PAX-21 during outdoor dissolution experiments.²⁹ After the rapid dissolution of the most soluble NQ and NTO by precipitation, the remaining DNAN was photodegraded. The main DNAN degradation products identified in the effluent samples were methoxynitrophenols and methoxynitroanilines. An unknown compound, which also appeared during storage of samples in the dark, was suggested to be 2-nitroso-4-nitromethoxybenzene.²⁹ Photodegradation of the other two constituents NQ and NTO was not addressed based on the assumption that both can migrate rapidly through subsurface soil. A study of the aquatic toxicity of IMX-101 and its constituents, irradiated with 350 nm UV light, demonstrated that some photodegradation products were more toxic than the parent compounds, e.g., dinitrophenol (from DNAN), guanidine (from NQ), and 1,2,4-triazol-3,5-dione (from NTO).³⁰

While extensive work has been published on product distribution of DNAN under various conditions including photolysis, microbial degradation, treatment with ZVI, and alkaline hydrolysis, degradation products coming of IMX-101, where DNAN, NTO, and NQ are present, have not been investigated to our knowledge. The aim of this work was to provide data on the photolysis of IMX-101 in water, at low and high concentrations, to address a range of possible environmental scenarios, using artificial sunlight generated from a SolSim solar simulating photoreactor. UV-B irradiation in a Rayonet photoreactor was also used to accelerate photodegradation and to facilitate product identification for determining the effect of interactions among the IMX-101 ingredients and the fate of the formulation in the aqueous environment.

■ MATERIALS AND METHODS

Chemicals. IMX-101, a yellow formulation composed of DNAN (40–45% w/w), NQ (35–40% w/w), and NTO (18–23% w/w), was provided by Defence Research Development Canada (DRDC)-Valcartier. NTO (white powder) and DNAN (98.4%, yellow powder) were also provided by DRDC-Valcartier. NQ was purchased from Aldrich Chemical Co. (Milwaukee, WI) and contained 25% water as a stabilizer. NQ was air dried for 72 h under a fume hood prior to use. A stock solution of uniformly nitro-group-labeled [¹⁵NO₂]CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitan, 99.4% purity), purchased from ATK Thiokol Propulsion (Brigham City, UT), was prepared in acetonitrile to be used as a source of ¹⁵NO₂ during photolysis. This explosive degrades at 300 nm via N-NO₂ cleavage to produce 4 mol of NO₂ and NO₃⁻ for each mole of disappearing CL-20.³¹ Titanium(IV) oxide (rutile nanopowder; <100 nm particle size; 99.5% trace metals basis) and guanidine hydrochloride (98%) were purchased from Sigma-Aldrich (Oakville, ON, Canada). All other chemicals used in this work were of analytical grade.

Due to the extremely different water solubility of the IMX-101 constituents (Table 1), two formulation solutions, a low concentration solution designated as *L*-IMX-101 and a high concentration solution designated as *H*-IMX-101, were prepared. For the *L*-IMX-101 solution, we dissolved 109.3 mg of the solid formulation in 1 L of deionized water and found 0.229 mmol L⁻¹ of DNAN, 0.382 mmol L⁻¹ of NQ, and 0.186 mmol L⁻¹ of NTO. For the preparation of the *H*-IMX-101 solution, we conducted a batch dissolution experiment by adding a piece (~1 g) of IMX-101 formulation to 200 mL of deionized water in a glass bottle that was then shaken (150 rpm) in a thermostated incubator (20 °C) protected from light for 66 days. The actual concentrations of DNAN, NQ, and NTO in the aqueous phase of *H*-IMX-101 were 218.1, 1572.7, and 1040.1 mg L⁻¹ (1.1, 15.1, and 8.0 mmol L⁻¹), respectively. The drastic variation in the distribution of IMX-101 in this later dissolution experiment is obviously governed by the solubility of these constituents (Table 1). For comparison, solutions of DNAN (0.256 mmol L⁻¹), NQ (0.270 mmol L⁻¹), and NTO (0.223 mmol L⁻¹) were prepared in water at concentrations almost similar to those measured in the *L*-IMX-101 solution.

Irradiation Experiments. Irradiation experiments were conducted using artificial sunlight generated from a SolSim solar simulating photoreactor (Luzchem Research, Inc., Canada). The total power of the solar simulator output spectrum was calibrated to the best approximation of ASTM Air Mass 1.5 Global Tilt Standard in the 280–800 nm regions: total irradiance of 590 W m^{-2} . Experiments were conducted at $25 \text{ }^\circ\text{C}$ in 20 mL quartz tubes containing 5 mL of aqueous solutions of *L*-IMX-101 or *H*-IMX-10. In some photolysis experiments with *L*-IMX-101, TiO_2 nanopowder ($0.5 \pm 0.1 \text{ g L}^{-1}$) as a photocatalyst was added to enhance photodegradation in SolSim photoreactor. Controls of each experiment containing the same ingredients with same concentration but protected from light by wrapping in aluminum foil were prepared in the same way. To help identify new degradation products related to DNAN, DNAN alone, diluted *H*-IMX-101 fortified with DNAN, and a mixture of DNAN and $^{15}\text{NO}_2\text{-CL-20}$ (Table 2) were also irradiated in a Rayonet photoreactor

Table 2. Composition of the DNAN Solutions Subjected to Photolysis at 300 nm

ID ^a	composition of <i>H</i> -IMX-101 diluted 100 times				$^{15}\text{NO}_2\text{-CL-20}$ (mmol L ⁻¹)
	DNAN (mmol L ⁻¹)	DNAN (mmol L ⁻¹)	NQ (mmol L ⁻¹)	NTO (mmol L ⁻¹)	
A	0.243	0.011	0.151	0.080	
B	0.243				
C	0.243				0.022

^aKey: A (mixed with diluted *H*-IMX-101); B (DNAN alone); and C (mixed with $^{15}\text{NO}_2\text{-CL-20}$).

(Branford, CT) equipped with 16 ultraviolet lamps (300 nm). The experiments were carried out in duplicate or triplicate with results showing standard deviations of less than 5%.

Analytical Methods. DNAN, NQ, and NTO were analyzed by a Waters HPLC system (Milford, MA) equipped with a Model 2996 photodiode array detector, a Model 600 pump, a Model 717 plus injector, and a temperature control module. DNAN analysis was performed on a Discovery C18 column ($250 \times 4.6 \text{ mm}$, $5 \mu\text{m}$) (Supelco, Oakville, Canada) at $35 \text{ }^\circ\text{C}$. An injection volume of $50 \mu\text{L}$ was used. The mobile phase (50% methanol/50% water) was run isocratically at 1 mL min^{-1} . The detector was set to scan from 192 to 450 nm. The detection limit was estimated to be 0.01 mg L^{-1} at 298 nm. NTO and NQ were analyzed on a Hypercab column ($150 \times 4.6 \text{ mm}$, $5 \mu\text{m}$) (Cole-Parmer, Montreal, Canada) at $35 \text{ }^\circ\text{C}$. An injection volume of $50 \mu\text{L}$ was used. A gradient composed of water acidified with 0.5% trifluoroacetic acid (A) and acetonitrile (B) was run at 1 mL min^{-1} . The starting mobile phase was 90% A, 10% B; these conditions were held for 3 min, a linear gradient was run over 1 min to proportion of 40% A, 60% B and held for 6 min, returned to initial conditions over 1 min, and held an extra 7 min. The detector was set to scan from 192 to 450 nm. The detection limit was estimated to be 0.005 mg L^{-1} at 265 nm for NQ and 0.01 mg L^{-1} at 315 nm for NTO.

The degradation products were analyzed by liquid chromatography–mass spectrometry (LC–MS) using a MicroTOF-Q mass analyzer (Bruker) attached to an HPLC system (Agilent 1200 Series) equipped with a DAD detector. Aliquots ($10 \mu\text{L}$) were injected into a $3 \mu\text{m}$ pore size Gemini

C18 column ($3 \mu\text{m i.d.} \times 150 \text{ mm}$; Phenomenex, USA) at $25 \text{ }^\circ\text{C}$. The solvent system was composed of a MeOH/ H_2O mixture at a flow rate of 0.15 mL min^{-1} . For mass analysis, negative electrospray ionization mode (ESI⁻) was used with the exception of guanidine, which was detected in positive electrospray ionization (ESI⁺) mode. Mass range was scanned from m/z 40 to 1000. Nitrite and nitrate anions were monitored using an HPLC ICS-3000 from Dionex equipped with an ionic conductivity detector (Sunnyvale, CA). The separation was carried out on a DIONEX IonPac AS15 column ($2 \times 250 \text{ mm}$) at $35 \text{ }^\circ\text{C}$. The anions were separated using an isocratic method with KOH mobile phase (33 mM KOH) at a flow rate of 0.3 mL min^{-1} . The detection limits were 0.05 mg L^{-1} and 0.1 mg L^{-1} for nitrite and nitrate anions, respectively.

RESULTS AND DISCUSSION

Photodegradation of *L*-IMX-101 by Artificial Solar Light. Figure 1 summarizes the photodegradation of DNAN,

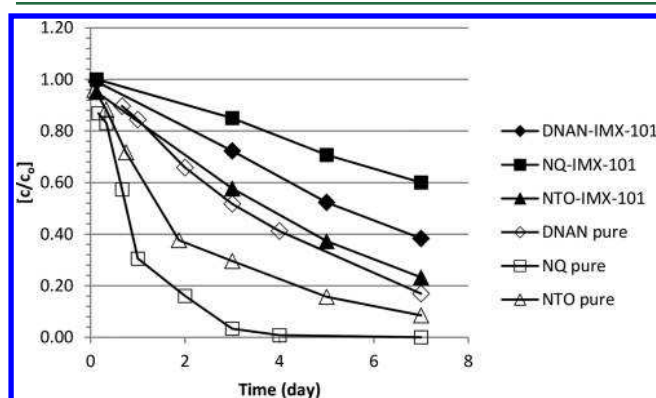


Figure 1. Normalized time course of the photodegradation of DNAN, NQ, and NTO in pure form and as part of IMX-101 (109 mg L^{-1}) in water in a sunlight simulator SolSim. The standard deviation of data from duplicates or triplicates experiments was $<5\%$.

NQ and NTO irradiated individually and in the *L*-IMX-101 solution for 7 days in a SolSim solar simulating photoreactor. The plots of C/C_0 vs time gave straight lines with $r^2 = 0.99$ for each constituent in the mixture, indicating that the photolysis of IMX-101 proceeded with zero order rate kinetics. However, the plots of $\ln\{C/C_0\}$ vs time ($r^2 = 0.99$) of the individually photolyzed components proceeded with a first-order rate kinetics (Figure S1). We therefore calculated first order rate constants (k) for comparison. The initial degradation rate constants (k) of the individually irradiated DNAN and NTO were 0.262 and 0.349 d^{-1} , respectively; however, their rate constants decreased to 0.137 and 0.202 d^{-1} , respectively, in the IMX-101 mixture. Surprisingly, although the individually irradiated NQ degraded rapidly (1.181 d^{-1}), its degradation rate reduced sharply (0.075 d^{-1}) in the mixture: 60% of NQ still remained at the end of the 7-day experiment (Figure 1). Increased photostability of the IMX-101 constituents in aqueous solution relative to individually irradiated compounds is opposite to results obtained by Oxley et al. during thermal stability studies of solid IMX-101.⁶ They reported a half-life of ~ 5 days for DNAN at $200 \text{ }^\circ\text{C}$, which was drastically reduced to 15 min in the IMX-101 mixture.

Titanium dioxide (TiO_2) was previously shown to enhance the photodegradation rates of nitroaromatic explosives^{25,32–34} and NTO.²⁴ The capacity of TiO_2 to improve photo-

degradation of IMX-101 was assessed. Although the anatase form of TiO_2 appears to be the most photoactive, we chose a rutile-type TiO_2 because it can also absorb some visible rays and be applied in heterogeneous photocatalysis using artificial sunlight.³⁵ Figure 2 shows photocatalytic degradation of the L-

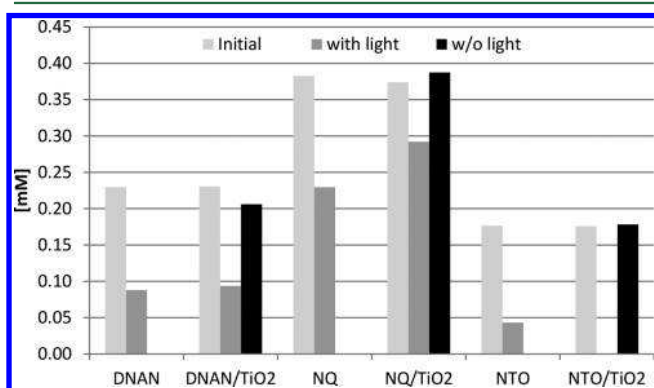


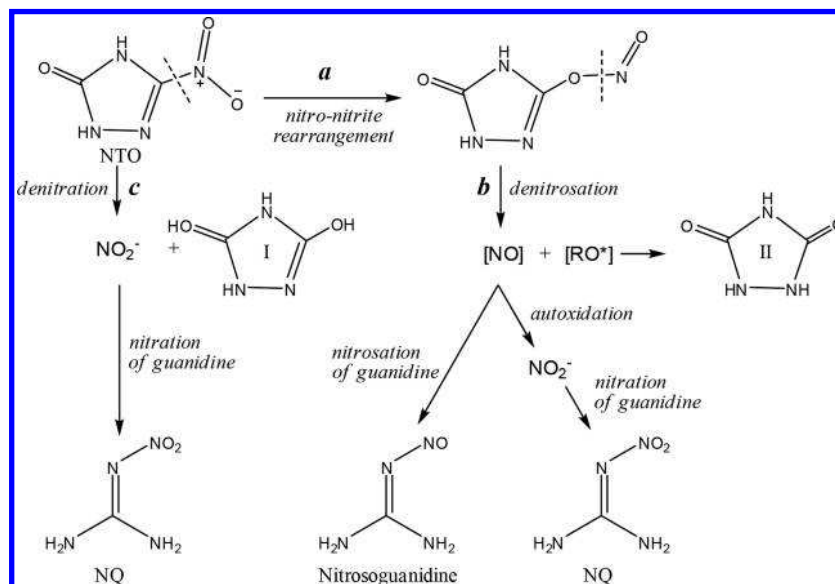
Figure 2. Degradation of DNAN, NQ, and NTO as part of *L*-IMX-101 in water, with and without TiO_2 ($0.5 \pm 0.1 \text{ g L}^{-1}$), irradiated in a SolSim photoreactor for 7 days.

IMX-101 constituents in the aqueous phase after 7 days of irradiation in a SolSim photoreactor using TiO_2 nanopowder. Despite the fact that the experiments were conducted in static mode, rapid degradation of NTO (94.0%) was observed after 3 days of irradiation in the presence of TiO_2 , which is in agreement with the data reported by Le Campion et al.²⁴ However, the presence of TiO_2 nanoparticles had no impact on the photodegradation kinetic of DNAN in *L*-IMX-101, although alone, it was rapidly degraded in a TiO_2 -anatase suspension (0.1% and 1%) using UV-B light.²⁵ A loss of 10.6% of DNAN measured in the light-protected controls was attributed to sorption of DNAN onto TiO_2 particles. There was no loss of NTO and NQ in the light-protected controls (Figure 2).

Unexpectedly, only 21.9% of NQ in *L*-IMX-101 was degraded in the presence of TiO_2 versus 40.0% without TiO_2

after 7 days of irradiation (Figure 2). Among the possible explanations, it could be that the advanced degradation of NTO created an imbalance in the NQ denitration process or that NQ was produced in situ from intermediates formed during photolysis of IMX-101. When NTO alone was photolyzed, a molar yield of 0.47 mol of nitrite and nitrate for each mole of NTO degraded was measured, and 3-hydroxy-1*H*-1,2,4-triazol-5(4*H*)-one (I) or its keto tautomer 1,2,4-triazolidine-3,5-dione (II) ($\text{C}_2\text{H}_3\text{N}_3\text{O}_2$, MW 101) were identified (Scheme 1). We suspect that the incomplete N-mass balance is due to the release of nitric oxide (NO) following the nitro-nitrite rearrangement shown in Scheme 1 (path a). Thermal nitro-nitrite rearrangement of NTO leading to the loss of NO was reported before.³⁶ Being highly reactive, NO should recombine with the adjacent nitrogen of the nitrite rearrangement product of NTO to form 1-nitroso-1,2,4-triazolidine-3,5-dione³⁶ or, as hypothesized in the present work, NO would react with guanidine, a photodegradation product of NQ, to form nitrosoguanidine (Scheme 1, path b). When NQ alone was photolyzed, a molar yield of 0.94 mol of guanidine and 0.82 mol of nitrite and nitrate for each mole of NQ degraded was measured. Nitrosation of guanidine by nitrous acid (HNO_2) has been reported.³⁷ Nitric oxide may also transform to nitrite by autoxidation,³⁸ which in turn could renitrate guanidine (Scheme 1, path b). Nitroguanidine could also be formed by nitrite ion, coming from NTO denitration, reacting with guanidine (Scheme 1, path c). Indeed, when we photolyzed a mixture of NTO (0.4 mmol L^{-1}) and guanidine (0.04 mmol L^{-1}) in the SolSim reactor in the presence of TiO_2 , 98.9% of NTO was degraded after 4 days, and 4.0% of guanidine was converted to NQ after 7 days. In addition, a compound with m/z 87.04 Da and m/z 89.04 Da, using ESI- and ESI+ ionization modes, respectively, was detected by LC-MS and tentatively identified as nitrosoguanidine (chemical formula: $\text{CH}_4\text{N}_4\text{O}$, exact mass: 88.04). In experiments without TiO_2 , only 49.1% of NTO was degraded after 4 days of irradiation and traces of the suspected nitrosoguanidine were identified. Traces of NQ were detected only after 6 days of irradiation, while nitrosoguanidine disappeared, suggesting that the production of

Scheme 1. Proposed Nitration and Nitrosation Routes of Guanidine in Water during Photodegradation of NTO in SolSim Reactor



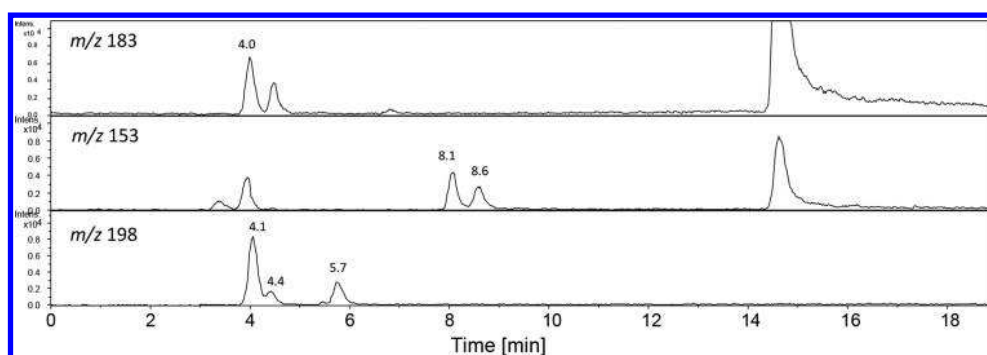


Figure 3. Extracted ion chromatograms at m/z 183 (top), m/z 153 (middle), and m/z 198 (bottom) of *H*-IMX-101-D photolyzed in a Rayonet at 300 nm for 6 h.

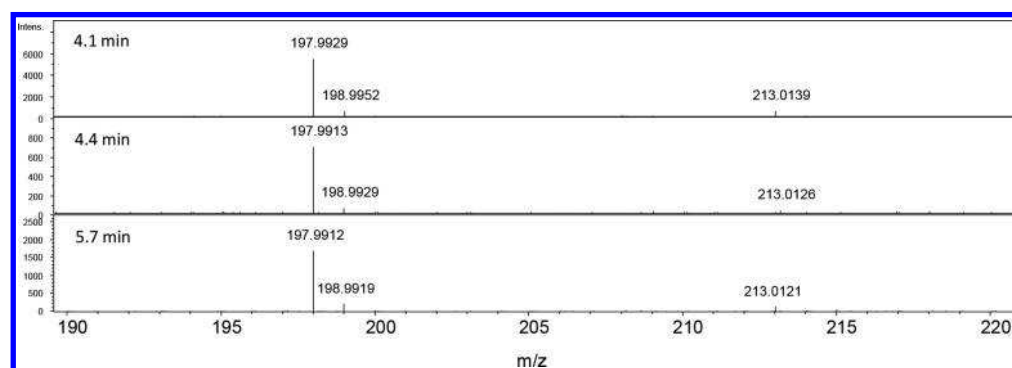


Figure 4. Mass spectra of the peaks at m/z 197.99 Da at retention times of 4.1, 4.4, and 5.7 min shown in Figure 3.

these compounds was transient and dependent on NTO denitration/denitrosation rates. The presence of TiO_2 might have also enhanced photonitration of guanidine.

Photodegradation of *H*-IMX-101 by Artificial Solar Light and by UV at 300 nm. Irradiation of *H*-IMX-101 (1.1 mmol L^{-1} of DNAN, 15.1 mmol L^{-1} of NQ and 8.0 mmol L^{-1} of NTO) for 7 days in the SolSim system led to the loss of 0.087 mmol L^{-1} DNAN, 0.286 mmol L^{-1} NQ and 1.234 mmol L^{-1} NTO. The molar loss of NTO was 4.3 times higher than that of NQ, although NQ was 2 times more concentrated than NTO in the solution. This is different from what was observed in *L*-IMX-101, where the loss of NQ (0.153 mmol L^{-1}) was close to that of NTO (0.143 mmol L^{-1}), although the molar ratio of NQ to NTO is 2:1 in both cases. Obviously, the simultaneous degradation of the constituents is influenced by their concentrations in solution and by the interactions with the degradation products.

To further enhance photodegradation and gain more information on degradation products, irradiation of the *H*-IMX-101 solution diluted 10 times (*H*-IMX-101-D) was performed in a Rayonet photochemical chamber at 300 nm. About 50% of DNAN and NTO and all NQ were degraded after 6 h of irradiation. Interestingly, when Kennedy et al. photolyzed an IMX-101 aqueous solution (349 $\text{mg}\cdot\text{L}^{-1}$) containing 107 $\text{mg}\cdot\text{L}^{-1}$ of DNAN, 139 $\text{mg}\cdot\text{L}^{-1}$ of NQ and 103 $\text{mg}\cdot\text{L}^{-1}$ of NTO at 350 nm for 4 h, only 76.5% of NQ and 14.3% of NTO was degraded, and no DNAN degradation was observed.³⁰ This highlights that photodegradation of explosive formulations is greatly complex and that multiple mechanisms may occur, influenced by the interactions of IMX-101 constituents DNAN, NQ, and NTO and their initial degradation products, to say the least.

Since previous work^{7,24–26,29} already described photoproducts, here we focused only on the identification of new products. Samples were thus analyzed by LC–MS using electrospray negative ionization mode, ESI[−] (Figure S2). The major products detected in *H*-IMX-101-D were 2,4-dinitrophenol (2,4-DNP, deprotonated molecular mass ion $[\text{M} - \text{H}]^{-}$ at m/z 183.00 Da, chemical formula $\text{C}_6\text{H}_3\text{N}_2\text{O}_5$ and retention time of 4.0 min (Figure 3, top) and 2-methoxy-5-nitrophenol ($[\text{M} - \text{H} - \text{CH}_3]^{-}$ at m/z 153.00 Da, chemical formula $\text{C}_7\text{H}_6\text{NO}_4$ and retention time of 8.1 min (Figure 3, middle). Both photoproducts were previously reported during photolysis of DNAN in a solar simulator.^{7,25} The compound detected at a retention time of 8.6 min with $[\text{M} - \text{H} - \text{CH}_3]^{-}$ at m/z 153.00 Da (Figure 3, middle) showed a mass spectrum similar to 2-methoxy-5-nitrophenol and was tentatively identified as its isomer 4-methoxy-3-nitrophenol. The two methoxynitrophenols (2-methoxy-5-nitrophenol and 4-methoxy-3-nitrophenol) were also found during sunlight photolysis of DNAN and IMX-101 particles.²⁹

We also detected peaks at retention times of 4.1, 4.4, and 5.8 min (Figure 3, bottom) with a major mass ion at m/z 197.99 Da and minor at m/z 213.01 Da (Figure 4). A loss of 15.02 mass units from the presumed $[\text{M} - \text{H}]^{-}$ at m/z 213.01 Da suggested that m/z 197.99 Da is a fragment like $[\text{M} - \text{H} - \text{CH}_3]^{-}$. Similar ionization behavior $[\text{M} - \text{H} - \text{CH}_2]^{-}$ and $[\text{M} - \text{H} - \text{CH}_3]^{-}$ was observed during LC–MS analysis of methoxy-2,4-dinitrobenzene (DNAN) and its methoxynitrophenol derivatives, respectively, suspecting that fragments of m/z 197.99 Da are related to compounds with a methoxy group. The peaks were tentatively identified as methoxydinitrophenols (MW 214) with a proposed chemical formula of $\text{C}_7\text{H}_6\text{N}_2\text{O}_6$. A similar chemical formula ($\text{C}_7\text{H}_6\text{N}_2\text{O}_6$) was proposed for a compound with a mass spectrum of 214 detected by GC–MS

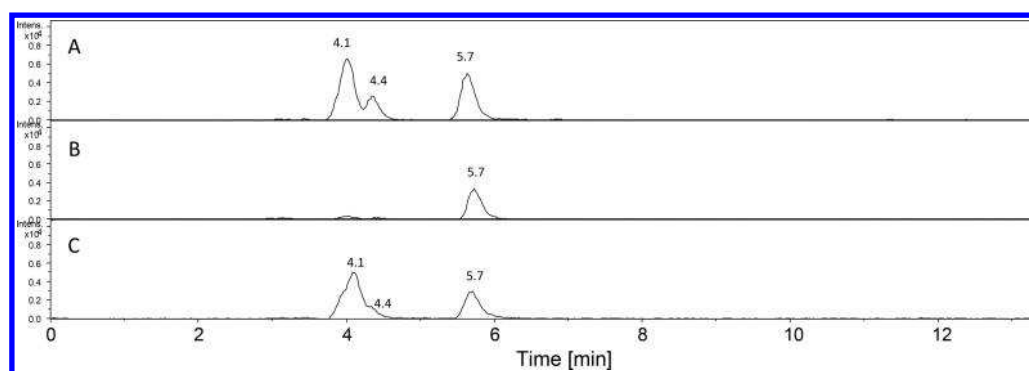


Figure 5. Extracted-ion chromatograms at m/z 198 of solutions A (DNAN + 1/100 *H*-IMX-101), B (DNAN alone), and C (DNAN + $^{15}\text{NO}_2$ -CL-20) photolyzed at 300 nm for 6 h.

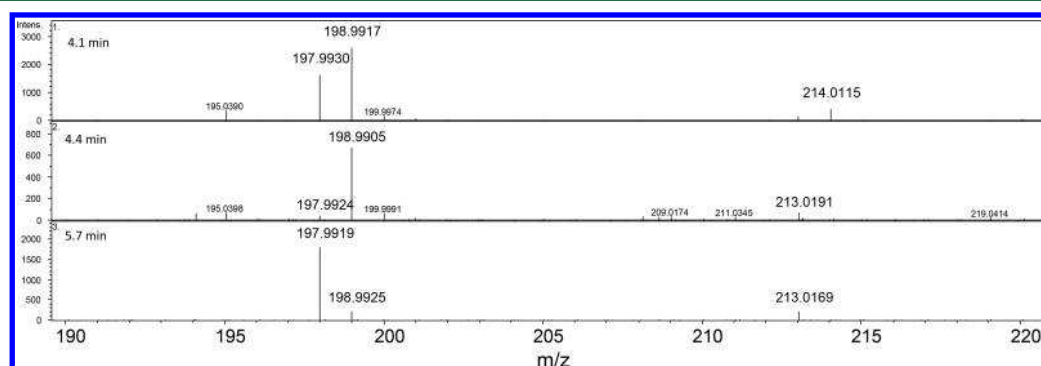


Figure 6. Mass spectra of the peaks at 4.1, 4.4, and 5.7 min from Figure 5, sample C.

in a IMX-101 sample from an outdoor experiment; the identity of the compound was unknown.²⁹

The presumed methoxydinitrophenols can be produced by oxidation of DNAN or nitration of methoxy nitrophenol, a major degradation product of DNAN. To elucidate the origin of the mass peaks (m/z 197.99 Da) with retention times of 4.1, 4.4, and 5.7 min, three additional irradiation experiments were conducted with DNAN: one containing a mixture of DNAN and *H*-IMX-101 diluted 100 times (solution A), a second containing a solution of DNAN alone (solution B), and a third containing DNAN mixed with $^{15}\text{NO}_2$ -CL-20 (solution C) (Table 2). As mentioned previously, the $^{15}\text{NO}_2$ -labeled polycyclic nitramine explosive CL-20 is an excellent source of ^{15}N -nitrite and ^{15}N -nitrate upon photolysis.³¹ Although NaNO_2 and NaNO_3 can be used for photochemically induced nitration and hydroxylation of 4-methoxyphenol,³⁹ the use of ^{15}N -labeled CL-20 may provide a more relevant insight into the role of nitrite and/or nitrate anions produced during photodegradation of the explosives mixtures. Figure 5 shows the extracted ion chromatogram at m/z 198 Da of solutions A, B, and C photolyzed at 300 nm for 6 h. The three peaks were found in the samples A and C, but in solution B containing only DNAN a single peak appearing at 5.7 min was detected. The presence of $^{15}\text{NO}_2$ -CL-20 during DNAN photolysis (solution C) led to the formation of compounds detected at 4.1 and 4.4 min with a $[\text{M} - \text{H} - \text{CH}_3]^-$ at m/z 198.99 Da (Figure 6, top and middle), indicating the inclusion of ^{15}N , considered to be coming from nitrite (or nitrate) cleaved off ^{15}N -labeled CL-20, in the DNAN products. However, the m/z value (197.99 Da) of the peak at a retention time of 5.7 min did not change (Figure 6, bottom) suggesting that this DNAN photoproduct was produced by a different pathway. The presence of ^{15}N in

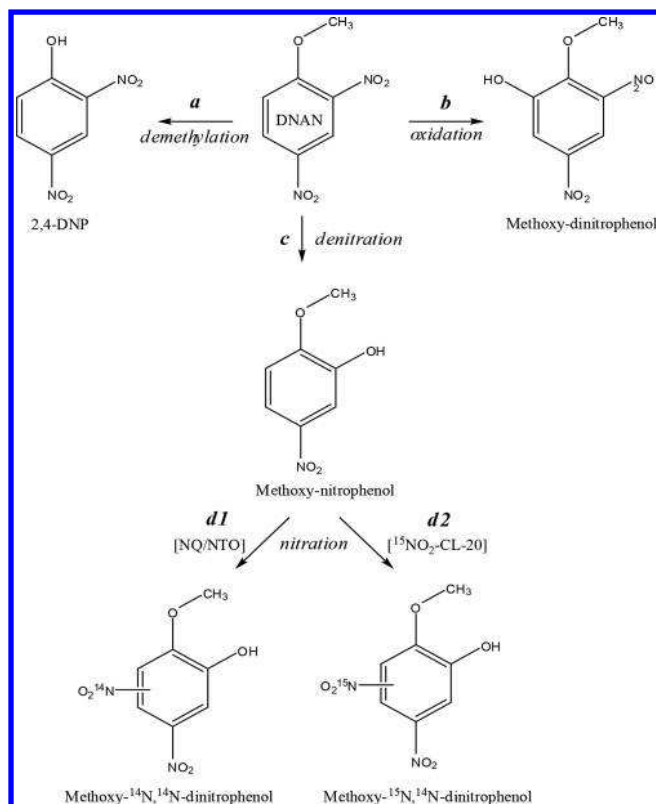
the peaks at 4.1 and 4.4 min suggested that a recombination of the monodenitrated DNAN derivatives (methoxynitrophenols) and $^{14}\text{NO}_2$ and/or $^{15}\text{NO}_2$ have occurred to form dinitro compounds. With respect to DNAN alone (Figure S3 B), only a small amount of the monodenitrated DNAN derivatives (methoxynitrophenols), detected at 8.1 and 8.6 min with $[\text{M} - \text{H} - \text{CH}_3]^-$ at m/z 153 Da, was produced in the presence of CL-20 (Figure S3C), supporting our hypothesis that the methoxynitrophenol derivatives were photonitrated by the excess of nitrite (or nitrate) from CL-20. Phototransformation routes of DNAN at 300 nm involving (a) demethylation to produce 2,4-dinitrophenol, (b) oxidation to methoxydinitrophenol and (c) denitration followed by the nitration of methoxynitrophenol (d) when mixed with *H*-IMX-101 and $^{15}\text{NO}_2$ -CL-20 are proposed in Scheme 2.

Photonitration of nitrophenols and substituted phenols such as methoxyphenol in aqueous solution has been reported.^{39–41} Complete degradation of NQ and of half of NTO after 6 h of photolysis of solution *H*-IMX-101-D at 300 nm likely created an excess of nitrite (or nitrate), which can explain the nitration of the DNAN derivative methoxynitrophenol via nitrogen dioxide, $\bullet\text{NO}_2$, a powerful nitrating agent produced from nitrite and nitrate by light^{39,42} (Scheme 2, paths d1 and d2).

In addition, photonitration of guanidine was again observed when an IMX-101 solution of 10.9 mg L^{-1} (0.023, 0.039, and $0.018 \text{ mmol L}^{-1}$ of DNAN, NQ, and NTO, respectively) with $^{15}\text{NO}_2$ -CL-20 ($0.011 \text{ mmol L}^{-1}$) was photolyzed in a SolSim reactor. About 1.8% NQ with the inclusion of one ^{15}N was found in the remaining NQ (50%) after 3 days of irradiation.

Photodegradation of IMX-101 dissolved in water was determined to help in understanding the fate of this new insensitive munition formulation in surface water bodies.

Scheme 2. Proposed Phototransformation Routes of DNAN at 300 nm: (a) Demethylation To Produce 2,4-Dinitrophenol, (b) Oxidation to Methoxydinitrophenol and (c) Denitration Followed by the Nitration of Methoxynitrophenol (d) when Mixed with H -IMX-101 and $^{15}\text{NO}_2$ -CL-20



Interactions between DNAN, NQ, and NTO, and with their degradation products, greatly changed the dynamics of photodegradation compared to the photolytic behavior of the individual explosive. This has environmental implications since, in nature, explosives are rarely found as pure compounds but rather as mixtures. IM explosives spread more residues upon detonation than conventional explosives (S. Thiboutot, personal communication). Explosives can enter the environment through manufacturing, transport, and training in the field. Wastewater stream from manufacture, load, assemble, and pack (LAP) operations, and from the deactivation of old munitions contain dissolved explosives. Dissolution of the explosive charge from heavily corroded unexploded ordnance (UXO) is significant. Two solutions of IMX-101 with different concentrations (low and high) and constituent distributions were tested in this study to address the range of possible environmental scenarios that can be met once the IMX formulation reaches the environment. Indeed, dissolution rates of chunks of IMX-101 and concentrations of dissolved explosives in nature will vary greatly depending on the source of contamination, and will also change with time. Based on our study, photodegradation of the formulation constituents (DNAN, NQ and NTO) dissolved in water bodies is expected to be significantly slower than it would have been predicted by studying photolysis on the compounds individually. We hypothesize that the abundance of nitrogen dioxide produced during NTO photolysis slowed the degradation of DNAN and NQ. Our results nevertheless suggest that photolysis by

sunlight will contribute significantly to the natural attenuation of IMX-101 dissolved in surface water. The transformation products should also be different: new DNAN transformation products, methoxy-dinitrophenols, were found, which were shown to be produced by reinitiation of the known DNAN photoproducts methoxy-nitrophenols. This may change the degree of ecotoxicity of IMX-101; the toxicity of methoxydinitrophenols is not yet known.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b04878.

Three supporting figures (S1–S3) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nancy.perreault@cnrc-nrc.gc.ca. Tel: (514) 496-6279. Fax: (514) 496-6265.

ORCID

Nancy N. Perreault: 0000-0003-4503-9374

Present Address

[†](J.H.) Department of Civil, Geological and Mining Engineering, Ecole Polytechnique de Montréal, Montreal, Quebec H3C 3A7, Canada.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Defence Research Development Canada, Department of National Defence. We thank Sonia Thiboutot for her valuable review of the manuscript. We also thank the U.S. Strategic Environmental Research and Development Program (SERDP) for their continued interest and support of JH.

■ REFERENCES

- Lee, K. E.; Balas-Hummers, W. A.; Di Stasio, A. R.; Pate, C. H.; Samuels, P. J.; Roos, B. D.; Fung, V. Qualification testing of the insensitive TNT replacement explosive IMX-101. *Insensitive Munitions Energetic Materials Technology Symposium*; Munich, Germany, 2010; pp 11–13.
- Akhavan, J. *The Chemistry of Explosives*; The Royal Society of Chemistry: Cambridge, U.K., 1998; pp 10–11.
- Walsh, M. R.; Walsh, M. E.; Ramsey, C. A.; Thiboutot, S.; Ampleman, G.; Diaz, E.; Zufelt, J. E. Energetic residues from the detonation of IMX-104 insensitive munitions. *Propellants, Explos., Pyrotech.* **2014**, *39*, 243–250.
- Walsh, M. R.; Walsh, M. E.; Taylor, S.; Ramsey, C. A.; Ringelberg, D. B.; Zufelt, J. E.; Thiboutot, S.; Ampleman, G.; Diaz, E. Characterization of PAX-21 insensitive munition detonation residues. *Propellants, Explos., Pyrotech.* **2013**, *38*, 399–409.
- Maharrey, S. P.; Wiese-Smith, D.; Highkey, A.; Behrens, R.; Kay, J. J. Interactions between ingredients in IMX-101: Reactive chemical processes control insensitive munitions properties. *Report SAND2014–2012*; Sandia National Laboratories, 2014.
- Oxley, J. C.; Smith, J. L.; Donnelly, M. A.; Colizza, K.; Rayome, S. Thermal stability studies comparing IMX-101 (dinitroanisole/nitroguanidine/NTO) to analogous formulations containing dinitrotoluene. *Propellants, Explos., Pyrotech.* **2016**, *41*, 98–113.
- Hawari, J.; Montel-Rivera, F.; Perreault, N. N.; Halasz, A.; Paquet, L.; Radovic-Hrapovic, Z.; Deschamps, S.; Thiboutot, S.; Ampleman, G. Environmental fate of 2,4-dinitroanisole (DNAN) and its reduced products. *Chemosphere* **2015**, *119*, 16–23.

- (8) Morris, J. B. Extraction of nitroguanidine (NQ) from triple-base gun propellant. *ARL-TR-2669*; Army Research Laboratory; Aberdeen Proving Ground, MD, 2002.
- (9) Dontsova, K.; Brusseau, M.; Arthur, J.; Mark, N.; Taylor, S.; Lever, J.; Walsh, M.; Pesce-Rodriguez, R.; Simunek, J. Dissolution of NTO, DNAN and Insensitive Munitions Formulation and their fates in soils. *Final Report ERDC/CRREL TR-14-23*; US Army Corps of Engineers, 2014.
- (10) Richard, T.; Weidhaas, J. Biodegradation of IMX-101 explosive formulation constituents: 2,4-Dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and nitroguanidine. *J. Hazard. Mater.* **2014**, *280*, 372–379.
- (11) Indest, K. J.; Hancock, D. E.; Crocker, F. H.; Eberly, J. O.; Jung, C. M.; Blakeney, G. A.; Brame, J.; Chappell, M. A. Biodegradation of insensitive munitions IMX101 and IMX104 in surface soils. *J. Ind. Microbiol. Biotechnol.* **2017**, *44*, 987–995.
- (12) Richard, T.; Weidhaas, J. Dissolution, sorption, and phytoremediation of IMX-101 explosive formulation constituents: 2,4-Dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and nitroguanidine. *J. Hazard. Mater.* **2014**, *280*, 561–569.
- (13) Olivares, C.; Liang, J.; Abrell, L.; Sierra-Alvarez, R.; Field, J. A. Pathways of reductive 2,4-dinitroanisole (DNAN) biotransformation in sludge. *Biotechnol. Bioeng.* **2013**, *110*, 1595–1604.
- (14) Olivares, C. I.; Madeira, C. L.; Sierra-Alvarez, R.; Kadoya, W.; Abrell, L.; Chorover, J.; Field, J. A. Environmental fate of ¹⁴C radiolabeled 2, 4-dinitroanisole (DNAN) in soil microcosms. *Environ. Sci. Technol.* **2017**, *51*, 13327–13334.
- (15) Fida, T. T.; Palamuru, S.; Pandey, G.; Spain, J. C. Aerobic biodegradation of 2,4-dinitroanisole by *Nocardioideis* sp. strain JS1661. *Appl. Environ. Microbiol.* **2014**, *80*, 7725–7731.
- (16) Williams, R. T.; Sisk, W. E.; MacGillivray, A. R. Degradation of nitroguanidine wastewater components in soil. *Environ. Toxicol. Chem.* **1989**, *8*, 469–475.
- (17) Perreault, N.; Halasz, A.; Manno, D.; Thiboutot, S.; Ampleman, G.; Hawari, J. Aerobic mineralization of nitroguanidine by *Variovorax* strain VC1 isolated from soil. *Environ. Sci. Technol.* **2012**, *46*, 6035–6040.
- (18) Le Champion, L.; Vandais, A.; Ouazzani, J. Microbial remediation of NTO in aqueous industrial wastes. *FEMS Microbiol. Lett.* **1999**, *176*, 197–203.
- (19) Krzmarzick, M. J.; Khatiwada, R.; Olivares, C. I.; Abrell, L.; Sierra-Alvarez, R.; Chorover, J.; Field, J. A. Biotransformation and degradation of the insensitive munitions compound, 3-nitro-1,2,4-triazol-5-one, by soil bacterial communities. *Environ. Sci. Technol.* **2015**, *49*, 5681–5688.
- (20) Schroer, H. W.; Langenfeld, K. L.; Li, X.; Lehmler, H.-J.; Just, C. L. Biotransformation of 2,4-dinitroanisole by a fungal *Penicillium* sp. *Biodegradation* **2017**, *28*, 95–109.
- (21) McGrath, C. J. Review of formulations for processes affecting the subsurface transport of explosives. *Tech. Rep. IRRP-95-2*; US Army Corps of Engineers, 1995.
- (22) Juhasz, A. L.; Naidu, R. Explosives: fate, dynamics, and ecological impact in terrestrial and marine environments. *Rev. Environ. Contam. Toxicol.* **2007**, *191*, 163–215.
- (23) Menapace, J. A.; Marlin, J. E.; Bruss, D. R.; Dascher, R. V. Photochemical and thermochemical decomposition of 3-nitro-1,2,4-triazol-5-one and perdeuterio-3-nitro-1,2,4-triazol-5-one in neat and mixed systems. *J. Phys. Chem.* **1991**, *95*, 5509–5517.
- (24) Le Champion, L.; Giannotti, C.; Ouazzani, J. Photocatalytic degradation of 5-nitro-1,2,4-triazol-3-one NTO in aqueous suspension of TiO₂, comparison with Fenton oxidation. *Chemosphere* **1999**, *38*, 1561–1570.
- (25) Rao, B.; Wang, W.; Cai, Q.; Anderson, T.; Gu, B. Photochemical transformation of the insensitive munitions compound 2,4-dinitroanisole. *Sci. Total Environ.* **2013**, *443*, 692–699.
- (26) Burrows, W. D.; Schmidt, M. O.; Chyrek, R. H.; Noss, C. I. Photochemistry of aqueous nitroguanidine. *Technical Report 8808*; U. S. Army BRDL: Fort Detrick, Frederick, MD, 1988.
- (27) Capellos, C.; Papagiannakopoulos, P.; Liang, Y.-L. The 248 nm photodecomposition of hexahydro-1,3,5-trinitro-1,3,5-triazine. *Chem. Phys. Lett.* **1989**, *164*, 533–538.
- (28) Hawari, J.; Halasz, A.; Groom, C.; Deschamps, S.; Paquet, L.; Beaulieu, C.; Corriveau, A. Photodegradation of RDX in aqueous solution: A mechanistic probe for biodegradation with *Rhodococcus* sp. *Environ. Sci. Technol.* **2002**, *36*, 5117–5123.
- (29) Taylor, S.; Walsh, M. E.; Becher, J. B.; Ringelberg, D. B.; Mannes, P. Z.; Gribble, G. W. Photo-degradation of 2,4-dinitroanisole (DNAN): An emerging munitions compound. *Chemosphere* **2017**, *167*, 193–203.
- (30) Kennedy, A. L.; Poda, A. R.; Melby, N. L.; Moores, L. C.; Jordan, S. M.; Gust, K. A.; Bednar, A. J. Aquatic toxicity of photo-degraded insensitive munition 101 (IMX-101) constituents. *Environ. Toxicol. Chem.* **2017**, *36*, 2050–2057.
- (31) Hawari, J.; Deschamps, S.; Beaulieu, C.; Paquet, L.; Halasz, A. Photodegradation of CL-20: insights into the mechanisms of initial reactions and environmental fate. *Water Res.* **2004**, *38*, 4055–4064.
- (32) Dillert, R.; Brandt, M.; Fornefett, I.; Siebers, U.; Bahnemann, D. Photocatalytic degradation of trinitrotoluene and other nitroaromatic compounds. *Chemosphere* **1995**, *30*, 2333–2341.
- (33) Son, H.-S.; Lee, S.-J.; Cho, I.-H.; Zoh, K.-D. Kinetics and mechanism of TNT degradation in TiO₂ photocatalysis. *Chemosphere* **2004**, *57*, 309–317.
- (34) Perchet, G.; Merlina, G.; Revel, J.-C.; Hafidi, M.; Richard, C.; Pinelli, E. Evaluation of a TiO₂ photocatalysis treatment on nitrophenols and nitramines contaminated plant wastewaters by solid-phase extraction coupled with ESI HPLC-MS. *J. Hazard. Mater.* **2009**, *166*, 284–290.
- (35) Kwon, S.; Fan, M.; Cooper, A. T.; Yang, H. Photocatalytic applications of micro- and nano-TiO₂ in environmental engineering. *Crit. Rev. Environ. Sci. Technol.* **2008**, *38*, 197–226.
- (36) McMillen, D. F.; Erlich, D. C.; He, C.; Becker, C. H.; Shockey, D. A. Fracture-induced and thermal decomposition of NTO using laser ionization mass spectrometry. *Combust. Flame* **1997**, *111*, 133–160.
- (37) Fernandez, I.; Herves, P.; Parajo, M. Kinetic study of nitrosation of guanidines. *J. Phys. Org. Chem.* **2008**, *21*, 713–717.
- (38) Goldstein, S.; Czapski, G. Kinetics of nitric oxide autoxidation in aqueous solution in the absence and presence of various reductants. The nature of the oxidizing intermediates. *J. Am. Chem. Soc.* **1995**, *117*, 12078–12084.
- (39) Matykiewiczova, N.; Kurková, R.; Klanova, J.; Klan, P. Photochemically induced nitration and hydroxylation of organic aromatic compounds in the presence of nitrite and nitrate in ice. *J. Photochem. Photobiol., A* **2007**, *187*, 24–32.
- (40) Vione, D.; Maurino, V.; Minero, C.; Pelizzetti, E. Aqueous atmospheric chemistry: Formation of 2,4-dinitrophenol upon nitration of 2-nitrophenol and 4-nitrophenol in solution. *Environ. Sci. Technol.* **2005**, *39*, 7921–7931.
- (41) Barzaghi, P.; Herrmann, H. Kinetics and mechanisms of reactions of nitrate radical (NO₃) with substituted phenols in aqueous solution. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5379–5388.
- (42) Machado, F.; Boule, P. Photonitration and photonitrosation of phenolic derivatives induced in aqueous solution by excitation of nitrite and nitrate ions. *J. Photochem. Photobiol., A* **1995**, *86*, 73–80.