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Photochemical transformation of the insensitive munitions compound 2,4-dinitroanisole

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HIGHLIGHTS

- ► DNAN photo-transformation kinetics was dependent on light source and temperature.
- ► Photolysis produced harmful by-products that included dinitrophenol and nitrate.
- ► Photo-oxidation was determined to be the likely pathway of DNAN photolysis.

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ABSTRACT

The insensitive munitions compound 2,4-dinitroanisole (DNAN) is increasingly being used as a replacement for traditional, sensitive munitions compounds (e.g., trinitrotoluene [TNT]), but the environmental fate and photo-transformation of DNAN in natural water systems are currently unknown. In this study, we investigated the photo-transformation rates of DNAN with both ultraviolet (UV) and sunlight irradiation under different environmentally relevant conditions. Sunlight photo-transformation of DNAN in water was found to follow predominantly pseudo-first-order decay kinetics with an average half-life ($t_{1/2}$) of approximately 0.70 d and activation energy (E_a) of 53 kJ mol^{-1}. Photo-transformation rates of DNAN were dependent on the wavelength of the light source: irradiation with UV-B light (280–315 nm) resulted in a greater quantum yield of transformation ($\phi_{UV\text{-}B}=3.7\times10^{-4}$) than rates obtained with UV-A light ($\phi_{UV\text{-}A}=2.9\times10^{-4}$ at 316–400 nm) and sunlight ($\phi_{sun}=1.1\times10^{-4}$). Photo-oxidation was the dominant mechanism for DNAN photo-transformation, based on the formation of nitrite (NO_2^-) and nitrate (NO_3^-) as major N species and 2,4-dinitrophenol as the minor species. Environmental factors (e.g., temperature, pH, and the presence or absence of naturally dissolved organic matter) displayed modest to little effects on the rate of DNAN photo-transformation. These observations indicate that sunlight-induced photo-transformation of DNAN may represent a significant abiotic degradation pathway in surface water, which may have important implications in evaluating the potential impacts and risks of DNAN in the environment.

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1. Introduction

Defense agencies in the United States and other countries are phasing out the use of certain conventional munitions compounds (e.g., 2,4,6-trinitrotoluene [TNT]) and replacing them with “insensitive” munitions compounds (e.g., 2,4-dinitroanisole [DNAN]) due to safer handling and transporting advantages (Phil and Arthur, 2006; Gray, 2008; Perreault et al., 2012; Xu et al., 2011). An example of an insensitive munitions currently in production is PAX-21 (Picatinny Arsenal eXplosive 21, Picatinny Arsenal, NJ), which is a mixture of DNAN, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), n-methyl-p-nitroaniline (MNA) and ammonium perchlorate (Picatinny Arsenal, 2011; Arnett et al., 2009). Historically, DNAN has also been used to manufacture insecticides and azo-dyes (Schechter and Haller, 1944; Fierz-David and Blangey, 1949). As militaries transition from conventional munitions to insensitive munitions, the production, storage and use of DNAN could result in increased occurrences in the environment (e.g., natural water bodies and wastewater systems). Currently, limited information is available on the chronic toxicity of DNAN; although, studies on rats indicated that the acute toxicity of DNAN ($LD_{50}=199$ mg/kg) could be even higher than that of TNT ($LD_{50}=794$–1320 mg/kg) (Phil et al., 2006). The environmental fate and behavior of DNAN are poorly characterized, and only a few studies have examined the biological transformation of DNAN under aerobic and anaerobic conditions (Perreault et al., 2012; Platten et al., 2010).

Nitroaromatic (e.g., TNT) and nitramine (e.g., RDX) compounds are subject to photo-transformation through sunlight irradiation, affecting the environmental fate, transformation and toxicity of these

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compounds in surface water bodies (Spanggord et al., 1981, 1983; Mabey et al., 1983). These energetic compounds can undergo photo-transformation through oxidation or reduction of the methyl or nitro groups and polymerization resulting in the formation of nitrobenzenes, nitrophenols, benzaldehydes and azoxydicarboxylic acids (Spanggord et al., 1981, 1983; Mabey et al., 1983). Therefore, understanding the photo-transformation rates, mechanisms and products of DNAN in natural surface water is important to determine its fate in the environment, to evaluate its potential toxicity, and to develop photo-catalyzed remedial technologies (Carp et al., 2004).

In this study, we evaluated the photo-transformation characteristics of DNAN in water, with a particular emphasis on environmental implications. We determined the reaction rates and quantum yields of DNAN photo-transformation with both UV and sunlight sources. Further, the sunlight degradation of DNAN in water was evaluated under different conditions (i.e., temperature, pH, and light intensity). Insights on the reaction mechanisms and products from the photo-transformation of DNAN were obtained with multiple analytical techniques, including reverse-phase high-performance liquid chromatography (RP-HPLC), ion chromatography (IC), UV–visible spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and liquid chromatography electrospray ion mass spectrometry (LC–ESI-MS).

2. Materials and methods

Reagent grade DNAN ($C_7H_6N_2O_5$, 98% purity, Sigma Aldrich) was used for the preparation of aqueous DNAN stock solutions in distilled deionized water (purity > 18 Ω cm^{-1}, Milli-Q$_{PLUS}$, Siemens, MA). All chemicals used for the pH adjustments (0.1 N NaOH) and for preparation of the phosphate buffer (0.01 M Na_2HPO_4 and 2×10^{-3} M KH_2PO_4) were of reagent grade or better.

2.1. Photolysis in the ultraviolet (UV) reactor

Photolysis of DNAN in the ultraviolet light region (250–400 nm) was performed separately with two sets of lamps (Luzchem Research, Canada) operating at predominantly UV-A (316–400 nm) and UV-B (280–315 nm) wavelength regimes with peak intensities ~ 350 and 312 nm, respectively (Fig. 1 and Table 1). A total of 8 lamps (either UV-A or UV-B) were arranged in the overhead slots of a closed UV reactor (Model ICH2, Luzchem Research) about 18 cm from the bottom of the reactor. The inside surface of the reactor was made of unpolished aluminum to enhance diffuse scattering of light. Sample containers were placed upright at the bottom center region of the reactor. A modified ferrioxalate actinometer method (Goldstein and Rabani, 2008) was used to determine the photon flux into the quartz reactor during UV-B and UV-A irradiations. Briefly, 1.5 mL of 0.02 M ammonium ferric sulfate dodecahydrate and 1.5 mL of 0.06 M potassium oxalate monohydrate both in 0.1 N H_2SO_4 were mixed in the dark to form the actinometry solution. After illumination of samples for a predetermined time period, the product Fe^{2+} was analyzed by adding 65 μL of Ferrozine (50 g/L in 0.05 M HEPES buffer) to 3 mL of the actinometry solution (Zepp et al., 1998). The absorbance of the Ferrozine–ferrous complex was measured at a wavelength of 565 nm after a 2-min incubation in the dark. Using the production rate of Fe^{2+} and the surface area to volume ratio of the reaction solution, the photon flux was calculated as 1.4×10^{-5} and 1.1×10^{-5} milli-Einstein cm^{-2} s^{-1} for UV-B and UV-A irradiations, respectively. The temperature inside the reactor was maintained at the set point (ranging from 25 to 35 °C) using a control system connected to a set of internal heating and cooling fans. Quartz cuvettes (3.5 mL) with Teflon caps were filled with solutions of known DNAN concentrations and used for all the kinetic experiments. Samples after irradiation were sacrificed at different time intervals and stored in amber glass containers at 4 °C prior to analysis. Dark control (DC) experiments were conducted in parallel by covering the sample cuvettes with aluminum foil and placing alongside the irradiated samples.

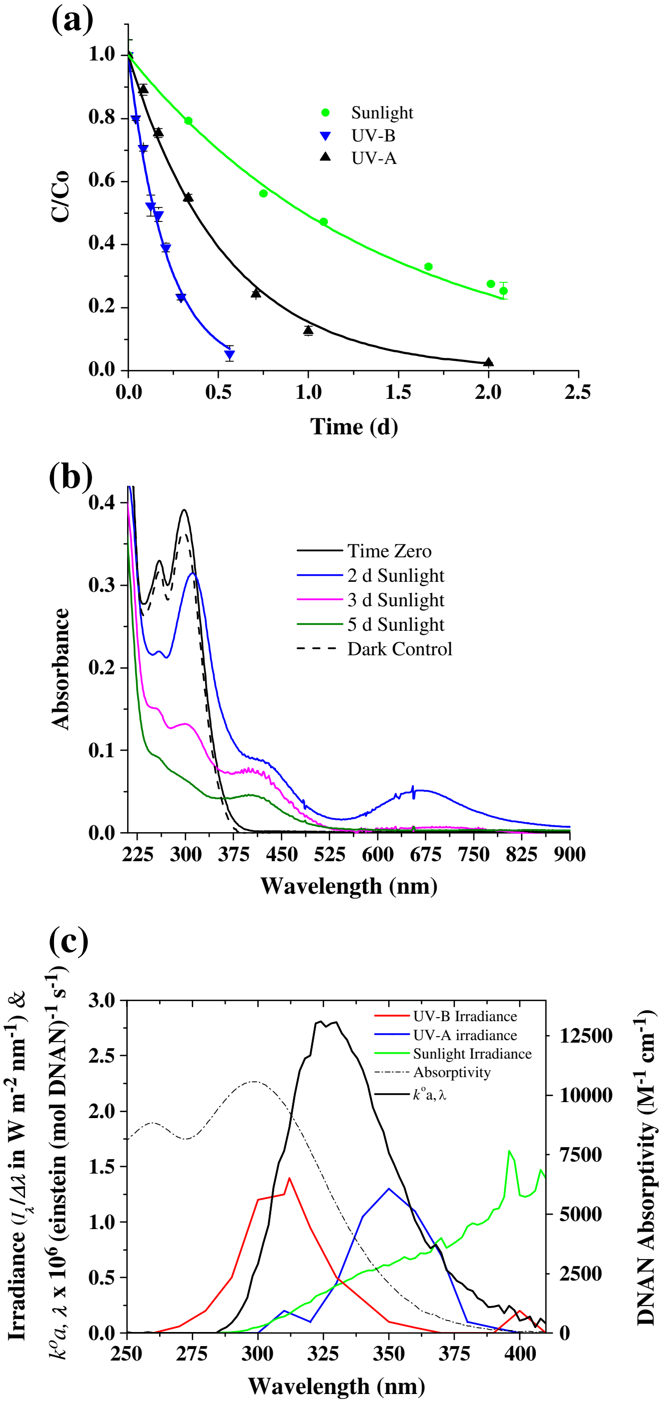

Fig. 1. a) Experimental (symbols) and first-order fitting (lines) results of DNAN photo-transformation under UV-A, UV-B, and solar irradiation normalized to the initial DNAN concentration (C/C$_o$) (see Table 1 for details). b) UV–visible spectra of DNAN (10 mg L^{-1}) after sunlight photolysis ($\Sigma I_{300\text{–}400\text{nm}}$ = 38 W m^{-2}) at times of 0, 2, 3, and 5 d. c) Spectral irradiance ($I_{\lambda/\Delta\lambda}$) of the lamps used for the photo-transformation experiments and calculated near-surface specific light absorption rate ($k^o_{a,\lambda}$) for the sunlight photolysis of DNAN (right y-axis) and plotted along with molar absorptivity of DNAN (left y-axis).

2.2. Photolysis in a solar simulator

Experiments were also performed under simulated sunlight using a bench-scale solar simulator (SUN TEST XLS+, Atlas-MTS, Germany)