



Surface-promoted hydrolysis of 2,4,6-trinitrotoluene and 2,4-dinitroanisole on pyrogenic carbonaceous matter

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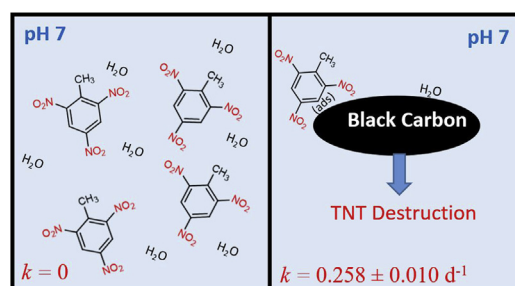
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HIGHLIGHTS

- Pyrogenic carbonaceous matter (PCM) fostered the decay of nitroaromatics at pH 7.
- A two-step surface-promoted hydrolysis was proposed for TNT decay with graphite powder at pH 7.
- Nitrite and a Meisenheimer complex were identified as products for TNT decay with graphite at pH 7.
- Soil samples amended with 4% biochar by weight can facilitate rapid TNT decay at pH 7.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the fate of sorbed nitroaromatics on the surface of pyrogenic carbonaceous matter (PCM) to assess the feasibility of a PCM-promoted hydrolysis. The degradation of two nitroaromatic compounds, 2,4,6-trinitrotoluene (TNT) and 2,4-dinitroanisole, was observed at pH 7 in the presence of graphite powder, a model PCM. By contrast, no decay occurred without graphite. Using TNT as a model compound, our results suggest that TNT decay demonstrated a strong pH dependence, with no reaction at pH 3–5 but rapid degradation at pH 6–10. Moreover, by fitting TNT decay at different pH conditions along with its sorption kinetics to the Langmuir Kinetic Model, our results suggest that the base-catalyzed hydrolysis was important. The activation energy for TNT decay was obtained by measuring reaction rates at different temperatures with or without graphite and no significant difference was observed. However, the addition of tetramethylammonium cation was able to promote TNT decay possibly due to its ability to attract more OH⁻ from the aqueous solution, leading to an increase in the sorbed OH⁻ concentrations. Nitrite and a Meisenheimer complex were identified as degradation products for TNT. Other PCM, such as biochar, also demonstrated a comparable ability in promoting TNT decay at pH 7. Furthermore, a rapid degradation of TNT at pH 7 was observed when biochar was used as a soil amendment (4% by weight). Our results suggest that PCM can facilitate TNT and 2,4-dinitroanisole decay via a surface-promoted hydrolysis at neutral pH conditions, suggesting a promising alternative for *in situ* soil remediation.

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1. Introduction

2,4,6-Trinitrotoluene (TNT) is one of the most widely used explosives of the past century and has entered the environment via

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military training and the disposal of outdated munitions (Boopathy and Manning, 1999; Spain et al., 2000). Due to its strong tendency to accumulate in soils, TNT has been detected at concentrations up to 12 g/kg in more than 95% of explosive-contaminated sites across the United States (Rodgers and Bunce, 2001; USEPA, 2014). According to the U.S. Environmental Protection Agency, TNT is a possible human carcinogen (Group C) with an associated cancer rate of 1×10^{-6} at a 1.0 $\mu\text{g/L}$ exposure concentration (USEPA, 2014). *Ex situ* remediation, such as dredging with subsequent composting, is the most frequently used remediation approach (Rodgers and Bunce, 2001). However, dredging is costly and could increase health risks by re-suspending buried contaminants back into the water column and, thereby, destroy habitats for benthic organisms (FRTR, 2007). Moreover, the dredging of soils contaminated with explosives at concentrations greater than 10% by weight poses safety concerns and requires additional protective measures (FRTR, 2007). *In situ* remediation technologies (e.g., bioremediation and phytoremediation), on the other hand, could be attractive alternatives. However, bioremediation often requires additional carbon sources to facilitate the growth of bacteria due to the slow uptake of TNT as the sole carbon source (Boopathy, 2000). Moreover, the nitro group ($-\text{NO}_2$) inhibits the complete mineralization of nitroaromatic compounds, posing additional challenges for the bioremediation of TNT (Rodgers and Bunce, 2001; Karasch et al., 2002; USEPA, 2014). Alternatively, phytoremediation utilizes plants to uptake or metabolize contaminants. However, the low solubility of TNT restricts its uptake by plants and, consequently, also limits further applications of phytoremediation in the field (Yu et al., 2012; Zhu et al., 2012).

Previous research has suggested that TNT is recalcitrant to hydrolysis in the homogeneous solution at pH 10 or below (Emmrich, 1999; Schwarzenbach et al., 2005). By contrast, TNT undergoes rapid hydrolysis within minutes to hours at pH 11–13, indicating that alkaline hydrolysis is effective at TNT degradation and could be used to treat TNT-contaminated soils off-site (Emmrich, 2001; Thorne et al., 2004; Hwang et al., 2005). However, alkaline hydrolysis often requires the addition of a large volume of chemicals, such as lime, to increase soil pH to a desirable range. Moreover, treated soils are often classified as hazardous materials and require special handling (Thorne et al., 2004). Interestingly, little is known regarding TNT hydrolysis in soils where black carbon, a naturally occurring PCM, constitutes 5–30% of the organic carbon content (Middelburg et al., 1999). Most previous studies have focused on TNT adsorption by black carbon (Schwarzenbach et al., 2005; Zhu and Pignatello, 2005). It was assumed that TNT does not undergo any environmental processes (e.g., abiotic and biotic degradation) once sorbed to PCM surfaces. However, recent research has revealed that PCM could catalyze the hydrolysis of chlorinated compounds (e.g., lindane and 1,1,2,2-tetrachloroethane) and lead to the dechlorination of contaminants under basic conditions (Mackenzie et al., 2005a, 2005b; Chen et al., 2014). Little is known with respect to nitroaromatic compounds in this context. Previous research on PCM and nitroaromatic compounds all involve sulfide and has focused on the surface-promoted reduction (Xu et al., 2010, 2013; Oh et al., 2014; Xu et al., 2015; Ding and Xu, 2016; Saquing et al., 2016; Pignatello et al., 2017).

The main objective of the present study, therefore, was to investigate the fate of sorbed nitroaromatic compounds on the surface of PCM in order to assess the feasibility of extending the surface-promoted hydrolysis pathway from chlorinated hydrocarbons to nitroaromatics. 2,4-dinitroanisole (DNAN) was also evaluated as a structural analog for TNT. DNAN has been widely used in insensitive munitions, which has gained increasing popularity due to its insensitivity to handling during use, storage, and transport (Badgujar et al., 2008). The second objective of the present study

was to understand the reaction mechanism for the observed TNT decay with PCM. Experiments on pH dependence, product identification, temperature dependence, and co-ion effects were carried out. This study demonstrates, for the first time, that nitroaromatic compounds can undergo surface-promoted hydrolysis in the presence of PCM under neutral pH conditions. As such, this study reveals a novel reaction pathway and advances our understanding of the reactivity of PCM.

2. Materials and methods

2.1. Chemicals

Alfa Aesar (Ward Hill, MA): graphite power (300 mesh, 99%), 2,4-dinitroanisole (DNAN, 98%); Sigma-Aldrich (St. Louis, MO): 2,4,6-trinitrotoluene solution (TNT, 1000 $\mu\text{g/mL}$ in acetonitrile), sodium azide (99.5%), tetramethylammonium chloride (98%), methanol (HPLC grade); Acros (Fair Lawn, NJ): sodium phosphate dibasic anhydrous and sodium phosphate monobasic monohydrate (>99%); Scientific Equipment Company (Aston, PA): sodium carbonate anhydrous (99.5%); Ricca Chemical Company (Arlington, TX): sodium bicarbonate (99.7%), sulfanilamide/*N*-(1-Naphthyl) ethylenediamine dihydrochloride solution (color reagent, for nitrite measurements); JT Baker (Phillipsburg, NJ): acetonitrile (HPLC grade). Deionized water (>18.2 M Ω cm) was produced with a Millipore Elix 10/Gradient A10 water purification system. All chemicals were used without further purification.

2.2. Black carbon preparation and characterization

Oak wood was used as the feedstock for biochar production via slow pyrolysis in a CM tube furnace (Model 1600 serial) at different temperatures (550 °C, 700 °C and 900 °C) under a N_2 flow of 1.5 L/min for 2 h. Elemental analysis of different PCM was carried out by Galbraith Laboratories (Knoxville, TN) using a Flash 2000 Elemental Analyzer. The surface areas of biochar and graphite powder were characterized by N_2 sorption (Autosorb-3B, Quantachrome Instruments).

2.3. Batch reactor experiments

A stock solution of TNT or DNAN was introduced into a borosilicate glass reactor containing 21 g/L of pre-weighed graphite powder buffered at a specific pH in order to achieve an initial concentration of 50 μM . 100 mg/L sodium azide was added to the buffer as an aerobic metabolic inhibitor. The vials were capped with Teflon-lined septa, placed on an end-to-end rotator at 30 rpm, and incubated in the dark at 25 °C. Controls without graphite powder were prepared at the same time. All experiments were conducted in triplicate. Samples were periodically collected and centrifuged at 3000 rpm for 15 min to separate the aqueous and solid phases. To ensure sufficient mass recovery, the solid phase was extracted with 10 mL of methanol for three consecutive times. The overall solid phase extraction efficiencies for TNT were $99.6 \pm 1.4\%$, $81.2 \pm 2.7\%$, $75.2 \pm 1.5\%$, and $71.8 \pm 1.6\%$ in the presence of graphite powder, 550 °C biochar, 700 °C biochar, and 900 °C biochar, respectively. The overall solid phase extraction efficiency for DNAN was $94.8 \pm 2.2\%$ in the presence of graphite. Both aqueous and solid phase extracts were analyzed by a Shimadzu HPLC-UV on a Phenomenex C18 column (15 cm \times 4.6 mm, $S = 5 \mu\text{m}$) with an isocratic mixture (70:30) of methanol and water at a flow rate of 1.0 mL/min at 254 nm.

2.4. Product identification

To obtain high concentrations of products for subsequent

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