Reduction of Nitroglycerin with Elemental Iron: Pathway, Kinetics, and Mechanisms

SEOK-YOUNG OH,[†] DANIEL K. CHA,[†] BYUNG J. KIM,[‡] AND PEI C. CHIU^{*,†} Department of Civil and Environmental Engineering, University of Delaware, Newark, Delaware 19716, and U.S. Army Engineering Research and Development Center, Champaign, Illinois 61826-9005

Nitroglycerin (NG) is a nitrate ester used in dynamites, propellants, and medicines and is therefore a common constituent in propellant-manufacturing and pharmaceutical wastewaters. In this study we investigated the reduction of NG with cast iron as a potential treatment method. NG was reduced stepwise to alveerol via 1.2- and 1.3-dinitroalveerins (DNGs) and 1- and 2-mononitroglycerins (MNGs). Nitrite was released in each reduction step and was further reduced to NH₄⁺. Adsorption of NG and its reduction products to cast iron was minimal. A reaction pathway and a kinetic model for NG reduction with cast iron were proposed. The estimated surface area-normalized reaction rate constants for NG and NO₂⁻ were (1.65 \pm 0.30) \times 10⁻² (L·m⁻²·h⁻¹) and $(0.78 \pm 0.09) \times 10^{-2} (L \cdot m^{-2} \cdot h^{-1})$, respectively. Experiments using dialysis cell with iron and a graphite sheet showed that reduction of NG to glycerol can be mediated by graphite. However, reduction of NO₂⁻ mediated by graphite was very slow. NG and NO₂⁻ were also found to reduce to glycerol and NH_4^+ by Fe^{2+} in the presence of magnetite but not by aqueous Fe²⁺ or magnetite alone. These results indicate that in a cast iron-water system NG may be reduced via multiple mechanisms involving different reaction sites, whereas nitrite is reduced mainly by iron and/ or adsorbed Fe²⁺. The study demonstrates that iron can rapidly reduce NG to innocuous and biodegradable end products and represents a new approach to treat NGcontaining wastewaters.

Introduction

Nitroglycerin (NG, CH(ONO₂)(CH₂ONO₂)₂), or glycerol trinitrate, is a nitrate ester explosive that is used as the main component in dynamites and propellants (1). NG has also been used as a vasodilator for heart diseases, such as angina pectoris (2). Despite its medicinal use, NG is known to be toxic to microorganisms, fish, rats, and humans at high levels (2, 3). At concentrations of 30–1300 mg/kg, NG has been reported to be acutely toxic to mammalian species (2). Chronic human exposure to NG may cause headache, palpitations, nausea, and vomiting (4). Due to its toxicity, NG-containing wastewaters from pharmaceutical and propellant-manufacturing processes need to be treated before they are discharged to wastewater treatment plants (5, 6). High concentrations of NG in wastewaters have been reported, ranging from an average of 180 mg/L (β , 7) at the Badger Army ammunition plant (Baraboo, WI) to between 300 and 600 mg/L (β) from the Radford Army ammunition plant (Radford, VA).

Adsorption with granular activated carbon (GAC), alkaline hydrolysis, and chemical reduction processes have been suggested as treatment methods for NG-containing wastewaters (5, 8, 9). However, these methods are costly and have serious drawbacks. GAC adsorption is expensive and requires periodic regeneration of spent carbon and further treatment to degrade the adsorbed NG. For alkaline hydrolysis and chemical reduction processes, large amounts of chemicals, such as NaOH and Na₂SO₃, need to be added in stoichiometric excess on a continuous basis (5).

Biological treatment may be a more cost-effective alternative and has been increasingly studied (2, 7-10). However, NG is not readily degradable by aerobic mixed cultures (7). The degradation, which was proposed to occur via either reduction or hydrolysis, appeared to be cometabolic (9) and thus required an external carbon source such as ethanol. Meng et al. (8) observed sequential denitration of NG to 1,2and 1,3-dinitroglycerins (DNGs), 1- and 2-mononitroglycerins (MNGs), and glycerol by whole cells and cell extracts of Bacillus thuringiensis/cereus and Enterobacter agglomerans. These authors suggested that NG was denitrated hydrolytically to form nitrate, which was subsequently reduced to nitrite by nitrate reductase. Reductive biotransformation of NG to its reduction products and nitrite by mixed culture, pure bacteria, and fungi was also reported (9-15). Christodoulatos and co-workers (9, 11) reported that NG was transformed cometabolically to DNGs and MNGs under both aerobic and anaerobic conditions, with concomitant release of nitrite and nitrate. The transformation of NG to MNGs was slow and was not complete after 20 days. White et al. (10) observed that Agrobacterium radiobacter transformed NG to DNGs under aerobic and nitrogen-limiting conditions over several days. The DNGs were later transformed reductively to MNGs, which were not degraded further. Using cell extracts of Agrobacterium radiobacter, these authors showed the production of nitrite during NG reduction. Blehert et al. (12) observed the reductive denitration of NG to yield nitrite by nitroester reductase purified from Pseudomonas species. In contrast to cometabolic transformation, Accashian et al. (15) reported that NG could be biodegraded by an aerobic mixed culture as the sole carbon, nitrogen, and energy source. NG was denitrated stepwise to 1,2-DNG, 2-MNG, and nitrite as the major products. However, this transformation took 10 days, and complete denitration was not achieved. From these studies, it appears that microbial degradation of NG tends to be slow and incomplete and may result in the accumulation of DNGs and MNGs. Therefore, there remains a need to develop a rapid, robust, and cost-effective method for the treatment NG-containing wastewaters.

Elemental iron has been used since the mid-1990s as a reactive material in permeable reactive barriers (PRBs) for groundwater remediation (*16*, *17*). Because of its passive nature and potential cost-effectiveness, much work has been conducted to evaluate the feasibility of using iron to treat halogenated organics (*16–20*), nitroaromatics (*21–23*), nitramines (*23*, *24*), azo dyes (*25*, *26*), metals (*27–29*), radionuclides (*30*), and oxyanions (*31–33*). Effectiveness of iron PRBs was also demonstrated in many field sites (*34–36*). More recently, application of elemental iron for the treatment of wastewaters containing azo dyes and energetic compounds was proposed (*37–39*). It was shown that reductive pre-

VOL. 38, NO. 13, 2004 / ENVIRONMENTAL SCIENCE & TECHNOLOGY = 3723

^{*} Corresponding author phone: (302)831-3104; fax: (302)831-3640; e-mail: pei@ce.udel.edu.

[†] University of Delaware.

[‡] U.S. Army Engineering Research and Development Center.

treatment of wastewaters containing azo dyes and explosives with iron greatly enhanced the rates and extents of mineralization of these refractory compounds in the subsequent biological or chemical oxidation processes (*38, 39*).

Many studies have been conducted to elucidate the mechanisms through which pollutants are transformed in an iron-water system (40-44). Except pollutants that are reducible by aqueous ferrous ion (e.g., hexavalent chromium), the reaction is believed to take place at the surface of iron or iron (hydr)oxides (25, 45, 46). CCl₄ was shown to reduce by direct electron transfer from iron through electronconducting (hydr)oxide layer (40, 47). PCE was also shown to be reduced mainly through electron transfer (41). Another possible reduction mechanism involves structural ferrous ion (e.g., in magnetite and green rust) and ferrous ion adsorbed on minerals such as goethite and magnetite. Green rust and magnetite were shown to reduce nitrate, Cr(VI), and CCl₄ (43, 48-50), whereas ferrous ion adsorbed on iron (hydr)oxides can reduce nitroaromatic compounds (42, 51, 52) and polyhalogenated methanes (53, 54). In addition to iron and iron oxides, graphite inclusions in cast iron may serve as both adsorption and reaction sites for nitroaromatic compounds, as suggested by our recent study (55). We observed complete reduction of aqueous 2,4-dinitrotoluene (DNT) to 2,4-diaminotoluene when DNT was physically separated from corroding iron by a graphite sheet (55).

While the reduction of many nitrogenous pollutants with elemental iron has been studied, the transformation of nitrate esters with iron has not been examined, to our knowledge. This study was conducted to investigate the transformation of NG with a commercial cast iron in batch reactors. If elemental iron can rapidly reduce NG to less toxic and/or more degradable compounds, iron may be a potential technology to treat wastewaters containing NG. In this study, we quantified the intermediates and products of NG reduction to establish the carbon and nitrogen balances. A pathway and a kinetic model were proposed for NG reduction with cast iron, and a surface area-normalized rate constant was obtained for each reaction step in the proposed pathway. Additional experiments were performed to examine the possible involvement of graphite inclusions and adsorbed Fe²⁺ on magnetite in the reduction of NG with cast iron.

Materials and Methods

Chemicals. NG dissolved in deionized water (497.3 \pm 0.7 mg/L) was provided by Redford Army ammunition plant (Redford, VA). NG standard solution in ethanol (0.1 mg/mL) was purchased from Accustandard (New Haven, CT). Standard solutions in acetonitrile (100 μ g/mL each) of 1,3-DNG, 1,2-DNG, 1-MNG, and 2-MNG were obtained from Cerilliant (Round Rock, TX). Glycerol (>99.5%) and HEPES (N-[2-hydroxyethyl]piperazine-N'-[2-ethanesulfonic acid], >99%) were acquired from Sigma (St. Louis, MO). Acetonitrile (HPLC grade) was purchased from Fisher (Pittsburgh, PA).

The cast iron used in this study was obtained from Master Builders, Inc. (Aurora, OH) and was used without pretreatment. Master Builders iron has been characterized in earlier studies (56-58). The specific surface area of the Master Builders iron we used was 1.29 m^2/g (38, 55), as measured using the BET method with N_2 (59). Graphite sheets (>98%, 0.38 mm thickness) were purchased from SGL Carbon (Wiesbaden, Germany). Dialysis cells, each with a capacity of 10 mL, were acquired from Bell-Art Products (Pequannock, NJ). The high-purity iron powder ($<10 \,\mu m$, >99.5%) used for dialysis cell experiments was obtained from Alfa Aesar (Ward Hill, MA). Magnetite (Ishpeming, MI) was acquired from Ward's Geology (Rochester, NY). The magnetite was pulverized and sieved to obtain fine particles of diameters less than 150 μ m. The specific surface area of the magnetite powder was 0.56 ± 0.02 m²/g, as determined by the BET method

with N_2 . Ferrous chloride (FeCl₂·4H₂O, 99%) was obtained from Aldrich (Milwaukee, WI).

Batch Reduction Experiments with Cast Iron. The procedures and conditions for the batch NG reduction experiments and for extraction of adsorbed molecules are described in detail in our previous papers (23, 55). Batch experiments were conducted in an anaerobic glovebox (95% N₂ + 5% H₂, Coy laboratory, Grass Lake, MI). Replicate 8-mL borosilicate vials were set up, each filled with 5 mL of deoxygenated solution containing NG and 0.1 M HEPES buffer (pH 7.4). The initial concentration of NG was 0.395 \pm 0.023 mM in all vials. One gram of cast iron was added to each vial to start the reaction, giving an initial surface area concentration of 258 m²/L. The vial was immediately capped with a Teflon-lined closure and shaken at 100 rpm in a horizontal position using an orbital shaker in the glovebox. After different elapsed times, replicate vials were sacrificed, and 4.5 mL of solution was taken from each vial and filtered through a 0.22- μ m cellulose filter (Millipore, MA) before analysis. Molecules adsorbed to the iron surface were extracted once using 2 mL of acetonitrile. Additional extractions of the iron did not recover any NG or its reduction products.

Dialysis Cell Experiments with Graphite Sheet. The procedures of the dialysis cell experiments with graphite are described in detail in our previous paper (55). The dialysis cells were prepared in replicates in the glovebox. The two 5-mL compartments of each cell were separated by a graphite sheet. A leak-tight seal between the graphite sheet and the two compartments was achieved by using stainless steel screws and two-sided tape. One compartment was filled with high-purity iron powder (approximately 32 g) and 0.1 M deoxygenated HEPES buffer, and the other compartment contained 4 mL of NG solution in deoxygenated deionized water (0.436 \pm 0.016 mM). The dialysis cells were placed on an orbital shaker at 60 rpm in the glovebox. At different times, two replicate cells were sacrificed for analysis of the NG solution. Extraction of the graphite sheet recovered negligible amounts (<0.01 μ mol) of adsorbed NG and none of the reduction products, in contrast to DNT, which adsorbed to a much greater extent (55). This is due to the high solubility of NG and its daughter products (60). Dialysis cell experiments were also performed to examine the possible reduction of nitrite on graphite, since nitrite was a major intermediate during NG reduction (see below) and is readily reduced with iron (33). These experiments were conducted under the same conditions, using an initial nitrite concentration of 1.227 \pm 0.015 mM. Control cells without iron powder were included in both NG and nitrite reduction experiments.

Reduction by Fe²⁺ Associated with Magnetite. Batch experiments were performed in the glovebox using 250-mL flasks each containing 90 mL of 0.1 M deoxygenated HEPES buffer (pH 7.4). After addition of 1 g of magnetite powder and 0.2 g (1 mmol) of FeCl₂·4H₂O, the solution was vigorously shaken for 3 h using a magnetic stirrer. Reaction was initiated by introducing a 10-mL stock solution of either NG or nitrite to the flask. The initial concentrations of NG and nitrite were 0.226 \pm 0.013 mM and 0.372 \pm 0.01 mM, respectively. The shaking rate after NG addition was 950 \pm 50 rpm, as determined using a tachometer. At different reaction times, a 1.5-mL aliquot was withdrawn and filtered through a 0.22- μ m mixed cellulose filter for analysis.

Controls were set up under identical conditions, except either magnetite or ferrous ion was omitted. For the Fe²⁺only (oxide-free) control, after addition of 0.2 g of FeCl₂· 4H₂O the solution was filtered through a 0.22- μ m filter (Fisher, Pittsburgh, PA) once every hour for three consecutive hours in the glovebox, prior to introduction of NG or nitrite. This was necessary because at circumneutral pH ferrous ion is readily oxidized by dissolved oxygen to form ferric precipi-

TABLE 1. Reactions and Rate Laws for NG and Its Reduction Products in the Proposed Pathway (Figure 2)^a

compound	reaction(s) involved	rate law	correlation coefficient	
NG	(1), (2)	$-d[NG]/dt = k_1[NG] + k_2[NG]$	$R^2_{\rm NG} = 0.992$	
1,3-DNG	(1), (3)	$-d[1,3-DNG]/dt = k_3[1,3-DNG] - k_1[NG]$	$R^{2}_{1,3-DNG} = 0.905$	
1,2-DNG	(2), (4), (5)	$-d[1,2-DNG]/dt = k_4[1,3-DNG] + k_5[1,3-DNG] - k_2[NG]$	$R^{2}_{1,2-DNG} = 0.860$	
1-MNG	(3), (5), (6)	$-d[1-MNG]/dt = k_6[1-MNG] - k_3[1,3-DNG] - k_5[1,2-DNG]$	$R^{2}_{1-MNG} = 0.921$	
2-MNG	(4), (7)	$-d[2-MNG]/dt = k_7[2-MNG] - k_4[1,2-DNG]$	$R^{2}_{2-MNG} = 0.699$	
glycerol (G)	(6), (7)	$d[G]/dt = k_6[1-MNG] + k_7[2-MNG]$	$R^2_G = 0.956$	
NO_2^-	(1), (2), (3), (4), (5), (6), (7), (8)	$-d[NO_2^-]/dt = 1/3 k_1[NG-N] + 1/3 k_2[NG-N] +$	$R^2_{NO2-} = 0.923$	
		1/2 <i>k</i> ₃ [1,3-DNG-N] + 1/2 <i>k</i> ₄ [1,2-DNG-N] +		
		1/2 <i>k</i> ₅ [1,2-DNG-N] + <i>k</i> ₆ [1-MNG-N] +		
		k_7 [2-MNG-N] – k_8 [NO ₂ ⁻]		
$\rm NH_4^+$	(8)	$d[NH_4^+]/dt = k_8[NO_2^-]$	$R^2_{\rm NH4+} = 0.983$	
^a The correlation coefficient for each compound is also shown.				

tates, which might adsorb Fe^{2+} and initiate an autocatalytic oxidation of Fe^{2+} when an oxidant such as NG or nitrite was added. Thus it was crucial all oxygen and ferric colloids be removed before NG and nitrite addition to avoid a false positive result for the Fe^{2+} -only control.

Chemical Analysis. NG was analyzed using a Varian HPLC (Walnut Creek, CA) equipped with a Supelguard guard column (20×4.6 mm, Supelco, Bellefonte, PA), a SUPELCO LC-18 column (250×4.6 mm, 5 μ m, Supelco), a UV detector (Varian 2510, Walnut Creek, CA), and an isocratic pump (Varian 2550). Methanol–water mixture (70/30, v/v) was used as the mobile phase at a flow rate of 1.0 mL/min. 1,3-DNG, 1,2-DNG, 1-MNG, and 2-MNG were analyzed using the HPLC with an Alltima C18 column (250×4.6 mm, 5 μ m, Alltech, Deerfield, IL) and an Alltima guard column (7.5×4.6 mm, Alltech). Methanol–water mixtures were used as eluents for the DNGs (50/50, v/v) and MNGs (10/90, v/v) at 1.0 mL/min. The wavelength was set at 214 nm for the UV detector. The injection volume for all LC samples was 10 μ L.

Glycerol was analyzed using a gas chromatograph (GC, HP5890, Hewlett-Packard, Palo Alto, CA) equipped with a 25-m Ultra-2 capillary column (0.2 mm i.d., 0.33 μ m film thickness, J&W, Wilmington, DE) and a flame ionization detector (FID). Five-mL glass vials, each containing 1 mL of aqueous sample, were placed in a vacuum oven (Model 5821, Napco, Winchester, VA) at 40 °C and approximately -13.2 psig (0.1 atm). When water was completely removed (after about 15 h), 0.1 mL of acetone was added to each vial. The vials were shaken well, and the contents were analyzed by GC/FID. A five-point quadratic calibration curve was constructed following the same procedures using duplicate glycerol standards prepared in deionized water ($R^2 = 0.995$). A quadratic rather than linear fit was used because the recovery, which was determined by comparing the above calibration standards against glycerol standards prepared directly in acetone, increased with glycerol concentration from 57.0 \pm 3.9% at 5 mg/L to 79.0 \pm 8.5% at 100 mg/L. The detection limit of glycerol using this quantification method was 3 mg/L.

Nitrite and nitrate were analyzed based on a modified EPA method B-1011 (*61*) using a Varian HPLC with a UV detector and an OmniPac Pax-100 column (Dionex, Sunnyvale, CA). A solution containing Na₂CO₃ (1.8 mM) and NaHCO₃ (1.7 mM) was used as eluent at 1.0 mL/min. The injection volume was 10 μ L, and the wavelength for the UV detector was 214 nm. NH₄⁺ was analyzed using the salicylate method (*62*) and a UV–visible spectrophotometer (DR2010, HACH, Loveland, CO). Solution pH was measured using a pH-30 pH sensor (Corning, Big Flats, NY).

Kinetic Data Analysis. A kinetic model was formulated based on the proposed NG reaction pathway, in which the disappearance of each reactive species was assumed to be pseudo-first-order. This was assumed because reactions of low-concentration oxidants, including chlorinated (45, 63) and nitroaromatic (64) compounds and inorganic ions (33), in iron–water systems have been shown to be first-order with respect to the oxidant concentration per unit iron surface area. While deviation from first-order behavior can occur when surface area is limiting (65), this limitation was unlikely in our study since the iron surface area-to-solution volume ratio was high (258 m²/L, compared to 0.1–4.5 m²/L in ref 65).

The kinetic model consists of a set of ordinary differential equations (Table 1), each of which represents a reduction reaction in the pathway. The pseudo-first-order rate constants were estimated from two sets of raw data (i.e., duplicate experiments) using the software Scientist (Micro-Math, Salt Lake City, UT). The ordinary differential equations were solved by numerical integration using EPISODE, a differential equation solver provided by Scientist.

Results and Discussion

Reduction Pathway of Nitroglycerin. The masses of NG, 1,2- and 1,3-DNG, 1- and 2-MNG, and glycerol during NG reduction with cast iron are shown in Figure 1(a). Each mass is the sum of aqueous and surface masses, and thus the mass changes represent transformation rather than sorption. Despite the significant carbon content of Master Builders iron (2-4 wt % (56-58)), adsorption of NG and its reduction products was minimal. This is presumably due to their high water solubility: 1.5, 80, and 700 g/L for NG, 1,2- and 1,3-DNG, and 1- and 2-MNG, respectively (60). The adsorbed mass of NG and its daughter products was consistently below $0.05 \,\mu mol$ (2.5% of the total mass) throughout the experiment. This is in contrast to nitroaromatic compounds which adsorb to cast iron to a much greater extent (23, 55). As NG was transformed, 1,2- and 1,3-DNG were produced concurrently. This was followed shortly by the appearance of 1- and 2-MNG, with 1-MNG being the dominant isomer (up to 0.70 μ mol, or 10 times the 2-MNG concentration, at 60 min). NG and the intermediates were transformed completely within 2 h, and the amount of glycerol recovered at 2 h was 1.78 μ mol, or 90.2% of the initial of NG. The carbon balance during the reaction was 77.4%-97.2%. The incomplete recovery was most likely due to errors associated with glycerol analysis, particularly at low concentrations.

In addition to the nitrate esters, we also measured NH_{4^+} , NO_2^- , and NO_3^- in the aqueous phase to establish a nitrogen balance. As shown in Figure 1(b), NO_2^- was released as NG was reduced to DNGs and MNGs, suggesting that reduction of the nitrate function (+V) of NG to NO_2^- (+III) was the first step in NG reduction with cast iron. It is also possible, albeit not probable in a buffered solution, that NG was transformed



FIGURE 1. Masses of the (a) carbonaceous and (b) nitrogenous compounds during NG reduction in batch reactors containing cast iron. The error bars are based on samples from duplicate reactors.

through hydrolysis to form NO_3^- (+V), which was subsequently reduced to NO2- by cast iron. However, NO3- was never detected during our experiments. Our control experiments further showed that NG was stable at pH 7.4 without iron and that NO3⁻ was reduced only very slowly in an ironwater system under identical conditions (data not shown). Therefore, it appears that NO_2^- rather than NO_3^- was a product of NG transformation with cast iron and that the reaction was reductive rather than hydrolytic. The reaction of NG with iron is thus similar to its reductive transformation in some biological systems (9). The amount of NO₂⁻ started to decrease after 30 min as NO_2^- was further reduced to NH4⁺. After 2 h, 96.5% of the initial nitrogen was recovered as NH4⁺, indicating that the NO2⁻ produced was completely converted to NH4⁺ as the dominant nitrogen-bearing end product of NG. The nitrogen recovery during the experiment ranged from 83.0% to 101.4%.

From the data in Figure 1, it appears that NG was reductively denitrated stepwise to glycerol with concomitant release of NO_2^- , which was further reduced quantitatively to NH_4^+ . Based on this result, a pathway for NG reduction with cast iron was proposed (Figure 2). In an iron–water system, NG may be reduced to glycerol following one of the three reduction paths: (1) NG \rightarrow 1,3-DNG \rightarrow 1-MNG \rightarrow glycerol, (2) NG \rightarrow 1,2-DNG \rightarrow 1-MNG \rightarrow glycerol, and (3) NG \rightarrow 1,2-DNG \rightarrow 2-MNG \rightarrow glycerol. All the compounds in the pathway were detected in our batch experiments. Each step involves transfer of two electrons and release of a NO_2^- ion (eqs 1–3), which was further reduced to NH₄⁺ (eq 4). The complete reduction of 1 mol of NG to glycerol and ammonium ion



FIGURE 2. Proposed pathway of NG reduction with cast iron.

requires 24 mol of electrons (eq 5).

$$C_{3}H_{5}(ONO_{2})_{3} + 2e^{-} + H_{2}O \rightarrow C_{3}H_{5}(ONO_{2})_{2}(OH) + NO_{2}^{-} + OH^{-} (1)$$

 $C_{3}H_{5}(ONO_{2})_{2}(OH) + 2e^{-} + H_{2}O \rightarrow C_{3}H_{5}(ONO_{2})(OH)_{2} + NO_{2}^{-} + OH^{-} (2)$

$$C_{3}H_{5}(ONO_{2})(OH)_{2} + 2e^{-} + H_{2}O \rightarrow C_{3}H_{5}(OH)_{3} + NO_{2}^{-} + OH^{-}$$
 (3)

$$NO_2^{-} + 6e^{-} + 6H_2O \rightarrow NH_4^{+} + 8OH^{-}$$
 (4)

$$C_{3}H_{5}(ONO_{2})_{3} + 24e^{-} + 21H_{2}O \rightarrow C_{3}H_{5}(OH)_{3} + 3NH_{4}^{+} + 27OH^{-}$$
 (5)

Reduction Kinetics of Nitroglycerin. Based on the proposed NG reduction pathway and assuming that each step in the pathway is a pseudo-first-order process, the reactions can be described by a kinetic model consisting of a series of differential equations (i.e., rate laws), which can be solved to obtain a rate constant for each reaction step. Table 1 summarizes the rate law and the reactions involved in the formation and transformation of each of the eight compounds shown in Figure 2. The pseudo-first-order rate constants for the eight reactions in the pathway, obtained though least-squares fitting, are shown in Table 2, along with the corresponding surface area-normalized rate constants. The kinetic model fits the data rather well, as indicated by the R^2 values in Table 1 and the fitted curves of NG and its daughter products in Figure S1(a). The overall correlation coefficient for the model fit is 0.975. The error associated with the curve fit for 2-MNG was greater than that for the other compounds due to the low concentrations of 2-MNG.

Using the fitted values of k_1 to k_7 , we also estimated the pseudo-first-order rate constant for NO₂⁻ reduction to NH₄⁺ ($k_8 = 2.014 \pm 0.239 \text{ h}^{-1}$, Table 2). The surface area-normalized rate constant (7.8 \pm 0.9 \times 10⁻³ L·m⁻²·h⁻¹) obtained from modeling is comparable to the measured rate constants for

TABLE 2. Fitted Pseudo-First-Order Rate Constants $[h^{-1}]$ for the Reactions Shown in Figure 2^a

reaction	fitted pseudo-first-order rate constant [h ⁻¹]	surface area-normalized rate constant [L·m ⁻² ·h ⁻¹]
$\begin{array}{l} (1) \ NG \rightarrow 1,3\text{-}DNG \\ (2) \ NG \rightarrow 1,2\text{-}DNG \\ (3) \ 1,3\text{-}DNG \rightarrow 1\text{-}MNG \\ (4) \ 1,2\text{-}DNG \rightarrow 2\text{-}MNG \\ (5) \ 1,2\text{-}DNG \rightarrow 1\text{-}MNG \\ (6) \ 1,\text{-}MNG \rightarrow glycerol \\ (7) \ 2\text{-}MNG \rightarrow glycerol \\ (8) \ NO_2^{-} \rightarrow NH_4^{+} \end{array}$	$\begin{array}{c} 2.238 \pm 0.390 \\ 2.022 \pm 0.378 \\ 4.074 \pm 1.110 \\ 0.546 \pm 0.246 \\ 2.074 \pm 0.852 \\ 2.381 \pm 0.292 \\ 0.752 \pm 0.363 \\ 2.014 \pm 0.239 \end{array}$	$\begin{array}{c} (0.87\pm 0.15)\times 10^{-2}\\ (0.78\pm 0.15)\times 10^{-2}\\ (1.58\pm 0.43)\times 10^{-2}\\ (0.21\pm 0.10)\times 10^{-2}\\ (0.80\pm 0.33)\times 10^{-2}\\ (0.92\pm 0.11)\times 10^{-2}\\ (0.29\pm 0.14)\times 10^{-2}\\ (0.78\pm 0.09)\times 10^{-2} \end{array}$

 a The corresponding surface area-normalized rate constants [L-m^-2-h^-1] were calculated based on the BET surface area concentration of 258 [m²/L]. The errors are two standard deviations obtained from the model fit.

 NO_2^- reduction with Fisher, Connelly, and Peerless irons at pH 7.0 (8.8 × 10⁻³-9.1 × 10⁻³ L·m⁻²·h⁻¹ (*33*)). The model curves for NO_2^- and NH_4^+ using the estimated k_8 value fit the experimental data well, as shown in Figure S1(b).

Although the fitted pseudo-first-order rate constants describe the profiles of NG and its daughter products satisfactorily, it is not clear to what physical or chemical process these rate constants correspond. The possible ratelimiting processes may include external mass transfer from the bulk solution to the iron particle surface, intraparticle diffusion, adsorption to a reactive site, and reduction of the adsorbed molecule. While there is insufficient information to ascertain the rate-limiting step, it is possible to independently estimate the external mass transfer coefficient in batch reactors using the method employed by Arnold et al. (66). Using an assumed iron particle diameter of 1 mm and an estimated molecular diffusivity for NG of 5.4×10^{-6} cm²/s, the external mass transfer coefficient for the reaction vials was calculated to be 72 h^{-1} . This value is 1 to 2 orders of magnitude larger than all the fitted pseudo-first-order rate constants in Table 2, suggesting that external mass transfer was not the rate-limiting step for NG reduction in our batch system. Therefore, the fitted pseudo-first-order rate constants may correspond to diffusion within iron particles, adsorption, or surface reaction. Which of these processes controls the overall rate of NG reduction remains to be elucidated.

The fitted pseudo-first-order rate constant for 1,3-DNG production ($\hat{k_1} = 2.238 \pm 0.390 \text{ h}^{-1}$) is similar to that for 1,2-DNG formation ($k_2 = 2.022 \pm 0.378 \text{ h}^{-1}$). Since NG contains two identical terminal nitrate groups, the result suggests that the nitrate group at the 2-position is about two times as likely to be reduced as each terminal nitrate group. This regioselectivity, which cannot be explained by physical processes such as intraparticle diffusion, suggests that the rate-limiting step for NG reduction is probably a chemical process, such as adsorption or redox reaction. One possible explanation for this selectivity is that the nitrate group at the 2-position of NG is more susceptible to reduction than the terminal nitrate groups. Consistent with this explanation, 1,2-DNG was reduced faster to 1-DNG ($k_5 = 2.074 \pm 0.852$ h^-1) than to 2-DNG (k_4 = 0.546 \pm 0.246 h^-1), again indicating the central nitrate group is more likely to be reduced by cast iron. This regioselectivity might be related to the electrondeficient (and thus electron-withdrawing) nature of the carbon atom at the 2-position relative to the terminal carbon atoms.

Graphite-Mediated Reduction of Nitroglycerin. Result of the NG reduction experiment in two-compartment dialysis cells with graphite sheet and iron powder is given in Figure 3. The data in Figure 3(a) show that NG was reduced sequentially to DNGs, MNGs, and glycerol when these compounds were separated from iron by graphite. In control



FIGURE 3. Masses of the (a) carbonaceous and (b) nitrogenous compounds during NG reduction in dialysis cells containing iron powder and a graphite sheet. The error bars are based on samples from duplicate reactors.

cells where iron powder was omitted, no NG reduction was observed during the same period. This result is similar to that observed previously for the reduction of DNT on graphite (55) and strongly suggests that, in a cast iron-water system, reduction of nitrate esters may be mediated by the graphite inclusions in cast iron. The mass recovery ranged from 83.1 to 103.0% during the experiment.

Compared to the batch experiment with cast iron (Figure 1), the amounts of 1,3-DNG observed in the dialysis cells were more than two times higher than that of 1,2-DNG. This implies that 1,3-DNG was either formed more rapidly or transformed more slowly than 1,2-DNG when NG was reduced on graphite than with cast iron. By using the same kinetic model to fit the dialysis cell data, it appears that the latter was the reason (Table S1). NG was reduced to 1,3-DNG $(k = 0.084 \pm 0.021 \text{ h}^{-1})$ only slightly faster than to 1,2-DNG $(k = 0.072 \pm 0.022 \text{ h}^{-1})$, as was found in the batch cast iron experiment (Table 2). In contrast to the cast iron experiment, however, 1,3-DNG was transformed ($k = 0.209 \pm 0.076 \text{ h}^{-1}$) more slowly than 1.2-DNG ($k = 0.643 \pm 0.286 \text{ h}^{-1}$) resulting in higher concentrations of 1,3-DNG. This suggests that reduction of nitrate esters mediated by graphite may exhibit a different kinetic selectivity than that with iron, as has been observed for nitroaromatic compounds (55, 67).

A more striking difference between the results with cast iron and dialysis cells, however, is the reactivity of nitrite. As shown in Figure 3(b), NO₂⁻ was the dominant nitrogenous product at the end of NG reduction, in sharp contrast to Figure 1(b). NO₂⁻ did reduce further to NH₄⁺ but only at a very slow rate. The NH₄⁺ formed at 72 h was 0.49 μ mol or 9.3% of the initial nitrogen. To verify this result, we conducted a separate dialysis cell experiment under the same conditions



FIGURE 4. Masses of the (a) carbonaceous and (b) nitrogenous compounds during NG reduction in batch reactors containing Fe^{2+} and magnetite suspension. The Fe^{2+} -only and magnetite-only controls are also shown. The error bars are based on duplicate samples.

using NO₂⁻ (4.95 μ mol) instead of NG as an initial reactant. The reduction of NO₂⁻ mediated by graphite was minimal, and only 4.0% of the initial NO₂⁻ was converted to NH₄⁺ after 72 h (Figure S2). It therefore appears that, in contrast to nitrate esters and nitroaromatic compounds, graphite inclusions are probably not significantly involved in the reduction of NO₂⁻ with cast iron.

Reduction by Fe²⁺ Adsorbed to Magnetite. Magnetite was chosen as a model iron oxide to test the potential involvement of adsorbed ferrous ion in the reduction of NG with cast iron, because it is known to be the dominant mineral formed on the iron surface under anaerobic conditions (47). The result of this experiment is shown in Figure 4. Little losses of NG occurred over 3 h in the Fe2+-only and magnetiteonly controls (4% and 11%, respectively), indicating that NG was relatively stable in the absence of added Fe²⁺ or magnetite. In the presence of magnetite suspension preequilibrated with Fe2+, NG was reduced completely to glycerol, which appeared after 20 min and accounted for 87.5% of the initial NG after 3 h (Figure 4(a)). In contrast to the cast iron and dialysis cell experiments (Figures 1 and 3), only small amounts of 1,3-DNG and 1-MNG were found during NG reduction, suggesting that the intermediates were either adsorbed more strongly to magnetite or reduced more rapidly by surface-bound Fe²⁺ than NG. The data in Figure 4(a) show that NG was fully denitrated by Fe²⁺ adsorbed to magnetite, as observed with cast iron (Figure 1(a)). Therefore, the Fe²⁺ mechanism may be involved in the reduction of NG with cast iron, although its importance relative to other mechanisms remains to be determined.

Figure 4(b) shows that NO_2^- was produced during NG reduction and was further reduced to NH_4^+ by Fe^{2+} associated with magnetite, similar to the reaction with cast iron in Figure



FIGURE 5. Amounts of NO_2^- and NH_4^+ during NO_2^- reduction in batch reactors containing Fe^{2+} and magnetite. The Fe^{2+} -only and magnetite-only controls are also shown. The error bars are based on duplicate samples.

1 (b). However, the final nitrogen recovery was different. After 3 h, only 78.9% of the initial nitrogen was recovered as NH_4^+ , approximately 20% lower than that in the cast iron system (Figure 1(b)). The lower NH_4^+ yield in Figure 4(b) suggests that either a portion of the NH_4^+ produced was removed from the solution due to volatilization (as NH_3) or adsorption to magnetite or a product(s) other than NH_4^+ was formed during NO_2^- reduction by adsorbed Fe^{2+} . To assess the extent of NH_4^+ losses due to volatilization and adsorption, we conducted a control experiment with NH_4^+ as a starting material under the same conditions as the NG reduction experiment with magnetite and Fe^{2+} . The result indicated that, after an equilibration time of 3 h at pH 7.4, losses of NH_4^+ due to volatilization and adsorption to magnetite were negligible (data not shown).

To confirm the lower NH_4^+ yield, a parallel experiment was performed under identical conditions to investigate the reduction of NO_2^- by Fe^{2+} associated with magnetite. As shown in Figure 5, NO_2^- was removed completely within 1 h, but only 72% of the NO_2^- was recovered as NH_4^+ after 3 h. Controls without Fe^{2+} or magnetite did not show meaningful removal of NO_2^- over the same time period, indicating NO_2^- was indeed reduced by Fe^{2+} adsorbed to magnetite. The data in Figure 5 also suggest that a portion of the $NO_2^$ was converted to a stable product(s) that was not further reduced to NH_4^+ . Such products may include N_2O , which has been observed during NO_2^- reduction by Fe^{2+} adsorbed to iron (hyd)roxide (*68*). However, formation of N_2O in our experiment could not be confirmed because open reactors were used and gaseous products were not collected.

If one assumes that NO_2^- was reduced by adsorbed Fe^{2+} through two parallel, competing pseudo-first-order reactions, one producing NH_4^+ and the other yielding an unknown product(s), then the data in Figure 5 can be modeled to obtain the rate constants and the relative importance of the two NO_2^- reduction reactions. Based on this assumption, the first-order rate constants for NO_2^- reduction, NH_4^+ production, and formation of the unknown product(s) were estimated to be $3.704\pm0.301, 2.517\pm0.186$, and 1.187 ± 0.115 h⁻¹, respectively. These fitted rate constants suggest that 68.0% of the NO_2^- was reduced to NH_4^+ , while the remaining was converted to an unknown product(s). The fitted curves of NO_2^- and NH_4^+ match the observed data well (R^2 = 0.988), as shown in Figure S3 along with the predicted concentration of the unidentified product(s).

In summary, our results demonstrate that cast iron can rapidly reduce NG to relatively benign end products, glycerol and NH_4^+ , and thus represents a promising new approach to treat NG-laden wastewaters. Cast iron may be used, for example, as a reactive component in a packed column to treat pharmaceutical or ammunition wastewater, as has been suggested for the treatment of wastewater containing other energetic compounds (*39*). Our results also show that reduction of NG with cast iron may occur at different reaction sites and through multiple mechanisms involving adsorbed Fe^{2+} and graphite inclusions. In contrast, NO_2^{-} is most likely reduced on iron surface and by Fe^{2+} adsorbed to oxides, whereas graphite inclusions are probably less important. Further studies are needed to understand how hydrophobicity or other properties of an oxidant can influence the importance of its graphite-mediated reduction in a cast iron—water system.

Acknowledgments

This study was supported in part by the National Science Foundation (Award #9984669).

Supporting Information Available

Experimental and/or modeling results of (1) NG reduction with cast iron, (2) NG and NO_2^- reduction in dialysis cells with graphite, and (3) NO_2^- reduction by Fe²⁺ and magnetite. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

- Yinon, J.; Zitrin, S. Modern Methods and Applications in Analysis of Explosives; John Wiley & Sons: New York, 1993.
- (2) Wendt, T. M.; Cornell, J. H.; Kaplan, A. M. Appl. Environ. Microbiol. 1978, 36, 693-699.
- (3) Urbański, T. *Chemistry and Technology of Explosives*; Pergamon Press: New York, 1984; Vol. 4.
- (4) Yinon, J. Toxicity and Metabolism of Explosives; CRC Press: Boca Raton, FL, 1990.
- (5) Smith, L. L.; Carrazza, J.; Wong, K. J. Hazard. Mater. 1983, 7, 303–316.
- (6) United States Army Toxic and Hazardous Materials Agency. Ball powder production wastewater biodegradation support studies; Report No. CETHA-TE-CR-88344; USATHMA: Aberdeen, MD, 1989.
- (7) Pesari, H.; Grasso, D. Biotech. Bioeng. 1993, 41, 79-87.
- (8) Meng, M.; Sun, W. Q.; Geelhaar, L. A.; Kumar, G.; Patel, A. R.; Payne, G. F.; Speedie, M. K.; Stacy, J. R. *Appl. Environ. Microbiol.* 1995, *61*, 2548–2553.
- (9) Christodoulatos, C.; Bhaumik, S.; Broadman, B. W. Water Res. 1997, 31, 1462–1470.
- (10) White, G. F.; Snape J. R.; Nicklin, S. Appl. Environ. Microbiol. 1996, 62, 637–642.
- Bhaumik, S.; Christodoulatos, C.; Korfiatis, G. P.; Brodman, B. W. Water Sci. Technol. 1997, 36, 139–146.
- (12) Blehert, D. S.; Knoke, K. L.; Fox, B. G.; Chambliss, G. H. J. Bacteriol. 1997, 179, 6912–6920.
- (13) French, C. E.; Nicklin, S.; Bruce, N. C. J. Bacteriol. 1996, 178, 6623-6627.
- (14) Zhang, Y. Z.; Sundaram S. T.; Sharma, A.; Brodman, B. W. Appl. Environ. Microbiol. 1997, 63, 1712–1714.
- (15) Accashian, J. V.; Vinopal, R. T.; Kim, B. J.; Smets, B. F. Appl. Environ. Microbiol. 1998, 64, 3300–3304.
- (16) Gillham, R. W.; O'Hannesin, S. F. Ground Water 1994, 32, 958– 967.
- (17) Matheson, L. J.; Tratnyek, P. G. *Environ. Sci. Technol.* **1994**, *28*, 2045–2053.
- (18) Orth, W. S.; Gillham, R. W. Environ. Sci. Technol. **1996**, 30, 66–71.
- (19) Roberts, A. L.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. Environ. Sci. Technol. 1996, 30, 2654–2659.
- (20) Deng, B.; Burris, D. R.; Campbell, T. J. Environ. Sci. Technol. 1999, 33, 2651–2656.
- (21) Agrawal, A.; Tratnyek, P. G. Environ. Sci. Technol. 1996, 30, 153– 160.
- (22) Devlin, J. F.; Klausen, J.; Schwarzenbach, R. P. Environ. Sci. Technol. 1998, 32, 1941–1947.
- (23) Oh, S. Y.; Cha, D. K.; Kim, B. J.; Chiu, P. C. Environ. Toxicol. Chem. 2002, 21, 1384–1389.
- (24) Singh, J.; Comfort, S. D.; Shea, P. J. J. Environ. Qual. 1998, 27, 1240–1245.
- (25) Webber, E. J. Environ Sci. Technol. 1996, 30, 716-719.

- (26) Nam, S.; Tratnyek, P. G. Water Res. 2000, 34, 1837-1845.
- (27) Blowes, D. W.; Ptacek, C. J.; Jambor, J. L. Environ. Sci. Technol. 1997, 31, 3348–3357.
- (28) Su, C.; Puls, R. W. Environ. Sci. Technol. 2001, 35, 1487– 1492.
- (29) Melitas, N.; Wang, J.; Conklin, M.; O'Day, P.; Farrell, J. Environ. Sci. Technol. 2002, 36, 2074–2081.
- (30) Gu, B.; Liang, L.; Dickey, M. J.; Yin, X.; Dai, S. Environ. Sci. Technol. 1998, 32, 3366–3373.
- (31) Huang, C. P.; Wang, H. W.; Chiu, P. C. Water Res. 1998, 32, 2257–2264.
- (32) Blowes, D. W.; Ptacek, C. J.; Benner, S. G.; McRae, C. W. T.; Bennett, T. A.; Puls, R. W. J. Contam. Hydrol. 2000, 45, 123– 137.
- (33) Alowitz, M. J.; Scherer, M. M. Environ. Sci. Technol. 2002, 36, 299–306.
- (34) O'Hannesin, S. F.; Gillham, R. W. Ground Water 1998, 36, 164– 170.
- (35) McMahon, P. B.; Dennehy, K. F.; Sandstrom, M. W. Ground Water **1999**, 37, 396-404.
- (36) United States Environmental Protection Agency. Field application of in situ remediation technologies: Permeable reactive barriers; EPA 542-R-99-002; U.S. EPA: Washington, DC, 1999.
- (37) Mantha, R.; Taylor, K. E.; Biswas, N.; Bewtra, J. K. Environ. Sci. Technol. 2001, 35, 3231–3236.
- (38) Perey, J. R.; Chiu, P. C.; Huang, C. P.; Cha, D. K. Water Environ. Res. 2002, 74, 221–225.
- (39) Oh, S. Y.; Chiu, P. C.; Kim, B. J.; Cha, D. K. Water Res. 2003, 37, 4275–4283.
- (40) Balko, B. A.; Tratnyek, P. G. J. Phys. Chem. 1998, 102, 1459– 1465.
- (41) Li, T.; Farrell, J. Environ. Sci. Technol. 2000, 34, 173-179.
- (42) Heijman, C. G.; Grieder, E.; Holliger, C.; Schwarzenbach, R. P. Environ. Sci. Technol. 1995, 29, 775–783.
- (43) Williams, A. G. B.; Scherer, M. M. Environ. Sci. Technol. 2001, 35, 3488–3494.
- (44) Gui, L.; Gillham, R. W.; Odziemkowski, M. S. Environ. Sci. Technol. 2000, 34, 3489–3494.
- (45) Johnson, T. L.; Scherer, M. M.; Tratnyek, P. G. Environ. Sci. Technol. 1996, 30, 2634–2640.
- (46) Tratnyek, P. G.; Johnson, T. L.; Scherer, M. M.; Eykholt, G. R. Ground Water Monit. Rem. 1997, 17, 108–114.
- (47) Bonin, P. M. L.; Odziemkowski, M. S.; Gilham, R. W. Corros. Sci. 1998, 40, 1391–1409.
- (48) Hansen, H. C. B.; Koch, C. B.; Nancke-Krogh, H.; Borggaard, O. K.; Sorensen, J. *Environ. Sci. Technol.* **1996**, *30*, 2053– 2056.
- (49) Erbs, M.; Hansen, H. C. B.; Olsen, C. E. Environ. Sci. Technol. 1999, 33, 307–311.
- (50) Sivavec, T. M.; Horney, D. P. Natl. Mtg.-Am. Chem. Soc., Div. Environ. Chem. 1997, 37, 115–117 (Abstr.).
- (51) Klausen, J.; Tröber, S. P.; Haderlein, S. B.; Schwarzenbach, R. P. Environ. Sci. Technol. 1995, 29, 2396–2404.
- (52) Hofstetter, T. B.; Heijman, C. G.; Haderlein, S. B.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1999**, *33*, 1479– 1487.
- (53) McCormick, M. L.; Bouwer, E. J.; Adriaens, P. Environ. Sci. Technol. 2002, 36, 403–410.
- (54) Pecher, K.; Haderlein, S. B.; Schwarzenbach, R. P. Environ. Sci. Technol. 2002, 36, 1734–1741.
- (55) Oh, S. Y.; Cha, D. K.; Chiu, P. C. Environ. Sci. Technol. 2002, 36, 2178–2184.
- (56) Burris, D. R.; Campbell, T. J.; Manoranjan, V. S. Environ. Sci. Technol. 1995, 29, 2850–2855.
- (57) Allen-King, R. M.; Halket, R. M.; Burris, D. R. Environ. Toxicol. Chem. 1997, 16, 424–429.
- (58) Burris, D. R.; Allen-King, R. M.; Manoranjan, V. S.; Campbell, T. J.; Loraine, G. A.; Deng, B. *J. Environ. Eng. ASCE* **1998**, *124*, 1012–1019.
- (59) Brunauer, S.; Emmett, P. H.; Teller, E. J. Am. Chem. Soc. 1938, 60, 309–319.
- (60) Spain, J. C.; Hughes, J. B.; Knackmuss, H. J. Biodegradation of Nitroaromatic Compounds and Explosives; Lewis: Boca Raton, FL, 2000.
- (61) Waters Corporation. Waters Test Method for Determination of Nitrite/Nitrate in Water Using Single Column Ion Chromatography, Waters Corporation: Milford, MA, 1987.
- (62) Hach Co. *DR/2010 Spectrophotometer Handbook*; Hach Co.: Loveland, CO, 1998.
- (63) Scherer, M. M.; Westall, J. C.; Ziomek-Moroz, M.; Tratnyek, P. G. Environ. Sci. Technol. 1997, 31, 2385–2391.

- (64) Scherer, M. M.; Johnson, K. M.; Westall, J. C.; Tratnyek, P. G.
- 1794-1805.
- (66) Arnold, W. A.; Ball, W. P.; Roberts, A. L. J. Contam. Hydrol. 1999, 40, 183-200.
- (67) Jafarpour, Y.; Imhoff, P. T.; Chiu, P. C. J. Contam. Hydrol. accepted.
- (68) Cooper, D. C.; Picardal, F. W.; Schimmelmann, A.; Coby, A. J. Appl. Environ. Microbiol. 2003, 69, 3517-3525.

Received for review December 29, 2003. Revised manuscript received March 10, 2004. Accepted April 12, 2004.

ES0354667