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EFFECT OF ADSORPTION TO ELEMENTAL IRON ON THE TRANSFORMATION OF 2,4,6-TRINITROTOLUENE AND HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE IN SOLUTION

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Abstract—The effect of adsorption to elemental iron on the reductive transformation of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (royal demolition explosive [RDX]) in aqueous solution was studied with scrap iron and high-purity iron. In batch experiments with the same total iron surface area and a mixing rate of 100 rpm, TNT and RDX were removed from the solution within 30 min. With high-purity iron, adsorbed TNT was reduced to 2,4,6-triaminotoluene (TAT) rapidly, with little accumulation of intermediates at the surface. With scrap iron, the extent of adsorption of TNT and its daughter products was more significant and reduction of these adsorbed molecules to TAT was slower. Distribution of the intermediates indicated that the reaction with scrap iron occurred primarily through reduction of the ortho nitro group. Kinetic analysis suggests that mass transfer or adsorption of TNT controlled the overall rate of TNT reduction to TAT with pure iron, whereas with scrap iron, the rate of TAT formation was probably limited by other processes. Compared to TNT, transformation of adsorbed RDX was more rapid and less affected by iron type. The RDX was reduced to an unidentified, water-soluble intermediate and NH_4^+, which accounted for approximately 50% of the RDX nitrogen. No total organic carbon reduction was observed before and after RDX transformation with scrap iron.

Keywords—Adsorption Reduction 2,4,6-Trinitrotoluene Hexahydro-1,3,5-trinitro-1,3,5-triazine Elemental iron

INTRODUCTION

2,4,6-Trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (royal demolition explosive [RDX]) are the most widely used explosives in the world [1]. 2,4,6-Trinitrotoluene is known to be carcinogenic and mutagenic and is acutely toxic to microbes, algae, fish, and other organisms [2–4]. Royal demolition explosive is a heterocyclic nitramine that, together with octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (high-melting explosive), is a persistent compound that is toxic to organisms, including humans [5,6]. Soil and groundwater in the proximity of munitions-manufacturing plants are often contaminated with TNT and RDX [7,8]. In addition, explosives-laden wastewater from munitions-manufacturing facilities is difficult to treat because TNT and RDX are resistant to aerobic biodegradation, because of the presence of electron-withdrawing nitro constituents that inhibit electrophilic attack by oxygenase enzymes [9]. Therefore, these energetic compounds are often removed from wastewater by costly physicochemical processes, including advanced oxidation, alkaline hydrolysis, carbon adsorption, and incineration [10–13].

Elemental iron, usually in the form of scrap iron, has been increasingly used in recent years in permeable reactive barriers for the remediation of contaminated groundwater [14]. Through reductive transformation or precipitation, iron has been shown to remove chlorinated solvents, nitrate, heavy metals, and radionuclides from water [15–20]. More recently, elemental iron was shown to be able to enhance the degradation of azo- and nitroaromatic pollutants in water by reductively transforming them to more biologically amenable compounds [21]. Use of elemental iron to pretreat wastewater containing TNT and RDX may also be possible, provided the reduction of these compounds with iron is sufficiently rapid. Studies have been conducted to investigate the reductive transformation of TNT, RDX, and other nitroaromatics and nitramines with elemental iron. In a batch study, Agrawal and Tratnyek [22] observed rapid removal of several mono-, di-, and tri-nitroaromatic compounds from aqueous solution with elemental iron. Based on the effect of mixing rate and the minimal influence of pH and ring substitution on the disappearance rate in solution, these authors proposed that reaction of nitroaromatic compounds was controlled by mass transfer from solution to iron surface. Devlin et al. [23] also concluded that electron transfer was not the rate-limiting step for the reduction of TNT and other nitroaromatic compounds with scrap iron in a recirculating batch experiment. These authors reported that only traces of 2,4,6-triaminotoluene (TAT) were recovered and that TNT and its daughter products were strongly or irreversibly adsorbed to iron. Singh et al. [24] studied RDX reduction with iron in a batch system and found that RDX was reduced to nitroso intermediates and ammonium. Oh et al. [25] recently reported that, in soil microcosms containing master builder iron, anaerobic sludge, or both, RDX was reduced to small quantities of nitroso intermediates and methylenedinitramine (MDNA), a water-soluble product. The RDX removal rate and the extent of mineralization both increased in the presence of iron.

These studies on TNT and RDX reduction with elemental iron were based on analysis of aqueous samples. However, molecules that disappeared from the aqueous phase may simply have been adsorbed to the surface without being trans-

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formed. Transformation of adsorbed TNT and RDX is difficult to confirm where aqueous concentrations of intermediates and products are low [23]. Adsorption may play an important role in the reduction of organic compounds with iron. Burris et al. [26] and Allen-King et al. [27] showed that chlorinated ethenes were adsorbed to nonreactive sites of iron filings. These authors proposed that the adsorption of chlorinated ethenes was due to exposed graphite in scrap iron and that the extent of adsorption was related to the hydrophobicity of the adsorbate [28]. Because scrap iron is typically used for site remediation, adsorption of hydrophobic organic pollutants may be particularly important because of high carbon contents of scrap iron. However, to date, the extent of adsorption and its effect on the transformation rates of TNT and RDX with elemental iron have not been characterized.

This study was conducted to determine the extent of adsorption to iron during reductive transformation of TNT and RDX and the effect of adsorption on the transformation rates. In addition to extraction from aqueous samples, adsorbed molecules were extracted and analyzed at different times. The effect of iron type on adsorption and transformation was investigated by using high-purity iron powder and scrap iron having the same surface area. Data also were analyzed to examine whether TNT reduction and TAT formation rates were controlled by mass transfer.

MATERIALS AND METHODS

Chemicals

2,4,6-Trinitrotoluene (>99%) and RDX (>99%) were provided by Holston Army Ammunition Plant (Kingsport, TN, USA). 2-Amino-4,6-dinitrotoluene (2A46DNT; 99%) and 4-amino-2,6-dinitrotoluene (4A26DNT; 99.5%) were obtained from Chem Service (West Chester, PA, USA). 2,4-Diamino-6-nitrotoluene (24DA6NT; 0.1 mg/ml standard in acetonitrile), 2,6-diamino-4-nitrotoluene (26DA4NT; 0.1 mg/ml standard in acetonitrile), and 2,4,6-triaminotoluene trihydrochloride (~100%) were purchased from Accustandard (New Haven, CT, USA). *N*-(2-Hydroxyethyl)piperazine-*N*′-2-(ethanesulfonic acid) (HEPES) was obtained from Sigma (St. Louis, MO, USA). Acetonitrile (≥99.9%) was purchased from Fisher Scientific (Pittsburgh, PA, USA). All chemicals were used as received.

Two types of elemental iron were used for this study. Master builder iron was chosen as a representative scrap iron because it has been widely used in groundwater remediation work and its elemental composition has been determined [20,29,30]. High-purity iron powder (<10 μm, >99.5%) was purchased from Alfa Aesar (Ward Hill, MA, USA). These irons were used as received without pretreatment. Specific surface areas of master builder iron and the high-purity iron powder were 1.29 and 0.19 m^2/g, respectively, as determined by the Brunauer–Emmett–Teller method with N_2.

Batch reduction experiments

Batch reduction experiments were conducted in an anaerobic glove box (95% N_2 + 5% H_2, Coy, MI, USA) with 8-ml borosilicate vials containing 5 ml of aqueous solution and either 1 g of scrap iron or 6.8 g of high-purity iron powder. The different iron masses were used to give the same surface area of 1.29 m^2. Replicate vials were set up for each experiment. The TNT and RDX solutions contained 0.1 M HEPES buffer to maintain a constant pH of 7.4 throughout the experiments. The solutions were purged in a glove box to completely remove oxygen. Initial concentrations of TNT and RDX were 0.206 ± 0.003 mM and 0.202 ± 0.006 mM, respectively. After iron was added, the vials were shaken in a horizontal position by an orbital shaker at 100 rpm. At different elapsed times, one of the vials was sacrificed and 4.5 ml of the supernatant was filtered through a 0.22-μm mixed cellulose membrane filter (Millipore, Bedford, MA, USA) for analysis by high-performance liquid chromatography (HPLC). Acetonitrile extraction of used filters indicated that TNT and RDX did not adsorb to the filters.

Extraction of adsorbed compounds

After 4.5 ml of supernatant was removed, the iron (and 0.5 ml of solution) remaining in the vial was extracted once for high-purity iron powder and twice for scrap iron filings, each with 2 ml of acetonitrile, to recover adsorbed molecules. Additional extraction did not yield meaningful increases in recovery. For high-purity iron, after 2 ml of acetonitrile was added, the vial was vigorously shaken for 1.5 min by a vortex mixer, 2 ml of the supernatant was withdrawn and passed through a glass fiber filter, and the filtrate was analyzed by HPLC. Surface concentrations of adsorbates, defined as adsorbed mass divided by initial solution volume (5 ml), were calculated with Equation 1

$$C_S = (C_e \cdot V_e - C_a \cdot V_a)/V_T \tag{1}$$

where C_S is the surface concentration (mM; the adsorbed mass divided by the initial solution volume [V_T]), C_e is the concentration in the extract (mM), obtained from HPLC analysis, C_a is the aqueous concentration (mM), obtained from HPLC analysis, V_a is the volume of solution extracted by acetonitrile (0.5 ml), V_e is the extract volume (2.5 ml), and V_T is the initial solution volume (5 ml).

For scrap iron, the extraction was repeated with another 2 ml of acetonitrile. Total surface concentration was taken to be the sum of the two surface concentrations calculated based on the two extract concentrations, by using Equations 2 through 4. The first and second extraction efficiencies, defined as C_{S1}/C_S and C_{S2}/C_S, were 82.5 ± 0.3% and 17.5 ± 0.3%, respectively, for TNT.

$$C_{S1} = (C_{e1} \cdot V_e - C_a \cdot V_a)/V_T \tag{2}$$

$$C_{S2} = (C_{e2} \cdot V_e - C_{e1} \cdot V_a)/V_T \tag{3}$$

$$C_S = C_{S1} + C_{S2} \tag{4}$$

where C_{S1} and C_{S2} are surface concentrations based on first and second extractions (mM), respectively, and C_{e1} and C_{e2} are concentrations in the first and second extracts (mM), respectively.

Analytical methods

The TNT, 2A46DNT, 4A26DNT, 24DA6NT, 26DA4NT, RDX, and a soluble RDX reduction product (see Results and Discussion section) were analyzed with a Varian high-performance liquid chromatograph (Walnut Creek, CA, USA) equipped with a Supelguard guard column (20 × 4.6 mm, Supelco, Bellefonte, PA, USA), a Supelco LC-18 column (250 × 4.6 mm, 5-μm particle size), an ultraviolet (UV) detector (2510 Varian), and an isocratic pump (2550 Varian). A methanol:water mixture (55:45, v/v) was used as the mobile phase at a flow rate of 1.0 ml/min. 2,4,6-Triaminotoluene was analyzed by HPLC with an Alltima C_{18} column (250 × 4.6 mm, 5-μm particle size, Alltech, Deerfield, IL, USA) and an Alltima guard column (7.5 × 4.6 mm, Alltech). Acetonitrile:phosphate buffer (40 mM, pH 3.2, 10:90, v/v) was used as an eluent at 1.0 ml/min. The injection volume for all samples was 10 μl and the wavelength for the UV detector was 254 nm.

Total organic carbon (TOC) was analyzed with a TOC analyzer (DC-190 Dohrmann, Santa Clara, CA, USA). The NH_4^+ was analyzed by the salicylate method [31] with a UV-vis spectrophotometer (DR2010, HACH, Loveland, CO, USA). Nitrate and nitrite were analyzed with an ion chromatograph (Dionex, Sunnyvale, CA, USA) equipped with a Dionex Ionpac AS11 column.

RESULTS AND DISCUSSION

Reduction of TNT with scrap iron and high-purity iron powder

Figure 1 shows the aqueous, surface, and total concentrations of TNT and the major reduction intermediates (2A46DNT, 4A26DNT, 24DA6NT, and 26DA4NT) and end product (TAT) during reduction with scrap iron. Aqueous TNT concentration rapidly decreased to zero within 30 min, but only low quantities of the intermediates were detected in solution during this period (Fig. 1a). More than 75% of the initial TNT was recovered as TAT after 3 h. However, the surface concentrations of adsorbed compounds presented a very different picture. As shown in Figures 1a and 1b, almost one half of the TNT removed from water in the first 5 min (~0.13 mM) was adsorbed to scrap iron, and the amounts of intermediates adsorbed were greater than that found in solution. In comparison, TAT was only weakly adsorbed because of its relatively high water solubility. The dominant intermediate was 2A46DNT, indicating that reduction of the ortho nitro group was the principal reaction in the TNT reduction pathway with scrap iron. Reduction of the ortho nitro group was also a major reaction for 2A46DNT, as shown by the high yields of 26DA4NT. Figure 1c shows the total concentrations of TNT and its daughter products, which were obtained by adding the aqueous and surface concentrations. These profiles represent concentration changes due only to transformation. Complete reduction of TNT to TAT took more than 3 h, because the reaction rate decreased with decreasing number of nitro groups. Mass balance during the experiment ranged from 70.1 to 97.3%. The lower mass balance at early times might be ascribed to the TNT reduction products that were not measured (e.g., nitroso compounds).

Figure 2 shows the aqueous, surface, and total concentration profiles during TNT reduction with high-purity iron powder. Similar to the data in Figure 1a, TNT was completely removed from solution within 30 min (Fig. 2a). The intermediates found in the aqueous phase were 24DA6NT and 4A26DNT, but only in minute quantities (Fig. 2a, insert). In contrast to Figure 1a, aqueous TAT appeared very early and its concentration quickly approached the initial TNT concentration. This suggested that TNT and intermediates adsorbed on high-purity iron were transformed much faster than those adsorbed on scrap iron. Indeed, Figure 2b shows that all adsorbed TNT reacted within 30 min, adsorbed TAT appeared immediately, and no intermediates accumulated at the surface. These observations are in sharp contrast to those in Figure 1b. All TNT was fully reduced and recovered as TAT in solution and the mass balance ranged from 82 to 108% during the experiment (Fig. 2c).

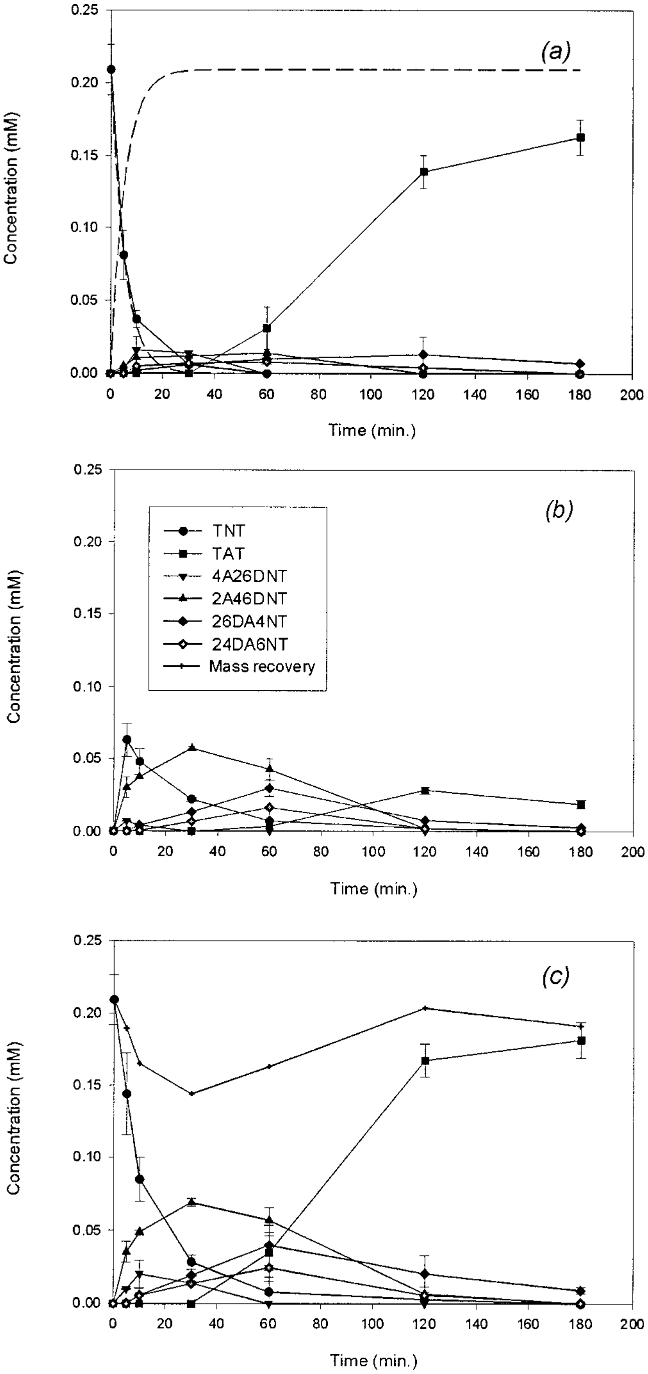

Fig. 1. Aqueous (**a**), surface (**b**), and total (**c**) concentrations of 2,4,6-trinitrotoluene (TNT), 2,4,6-triaminotoluene (TAT), and four intermediates during TNT reduction with scrap iron. The dashed lines in Figure 1**a** represent the aqueous TNT and TAT concentration profiles based on the fitted first-order rate constant ± standard deviation of 0.190 ± 0.013/min ($r^2 = 0.993$) for the disappearance of TNT in solution. 4A26DNT = 4-amino-2,6-dinitrotoluene; 2A46DNT = 2-amino-4,6-dinitrotoluene; 26DA4NT = 2,6-diamino-4-nitrotoluene; 24DA6NT = 2,4-diamino-6-nitrotoluene.

From the results shown in Figures 1 and 2, adsorption of TNT and its daughter products clearly was more pronounced with scrap iron. This may be attributed to the carbon in scrap iron. Master builder iron is known to contain 2 to 4% carbon and other elements [28–30]. Adsorption of chlorinated ethenes to scrap iron has been proposed to occur at nonreactive sites, such as graphite inclusions [28]. However, in contrast to the studies with chlorinated ethenes [26–28], adsorbed TNT on scrap iron was reduced much more rapidly. If most TNT was

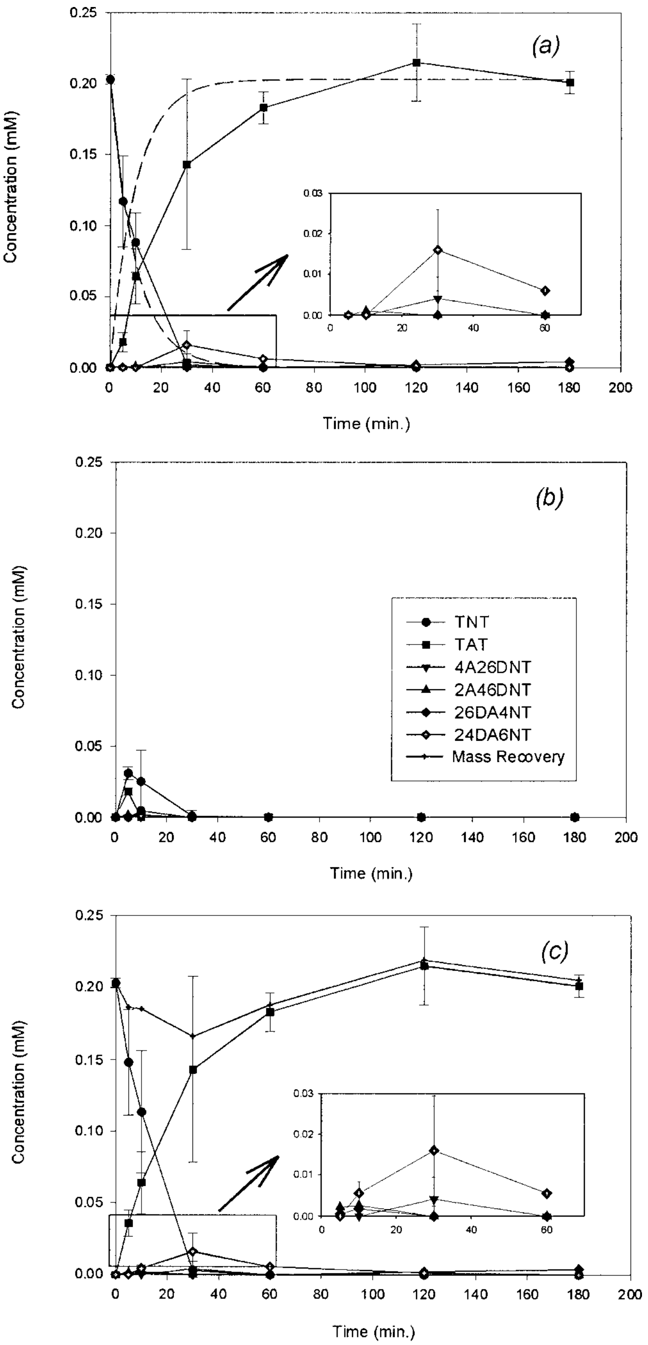

Fig. 2. Aqueous (**a**), surface (**b**), and total (**c**) concentrations of 2,4,6-trinitrotoluene (TNT), 2,4,6-triaminotoluene (TAT), and four intermediates during TNT reduction with high-purity iron powder. The dashed lines in Figure 2**a** represent the aqueous TNT and TAT concentration profiles based on the fitted first-order rate constant of 0.096 ± 0.009/min ($r^2 = 0.990$) for the disappearance of TNT in solution. 4A26DNT = 4-amino-2,6-dinitrotoluene; 2A46DNT = 2-amino-4,6-dinitrotoluene; 26DA4NT = 2,6-diamino-4-nitrotoluene; 24DA6NT = 2,4-diamino-6-nitrotoluene.

also adsorbed to nonreactive sites (e.g., graphite), then the faster removal of TNT may be explained by the high reactivity of TNT. Rapid consumption of aqueous TNT could have shifted the equilibrium and caused TNT to desorb from the nonreactive sites. Alternatively, the more pronounced adsorption of TNT with scrap iron could be due to adsorption to other types of reactive sites, which were different from and less reactive than those found in pure iron. The mechanism through which adsorbed TNT is transformed is currently under investigation.

The results also suggest that, for pure iron powder, the overall rate of TNT reduction to TAT was controlled by either mass transfer or adsorption of TNT in solution. Equation 5 shows a simplified reaction sequence of TNT reduction to TAT. Note that all steps were assumed to be first-order and desorption of the intermediates was omitted for simplicity. If the removal of TNT from solution controlled the overall rate of the reaction, then either the TNT mass transfer rate constant ($k_{\mathrm{MT,TNT}}$) or the adsorption rate constant (k_{ads}) would be approximately equal to the overall rate constant (k_{overall}, Eqn. 6). In that case, the sequence can be modeled as a single-step, first-order reaction (Eqn. 6) and the aqueous concentrations of TNT and TAT can be calculated with Equations 7 and 8. The predicted concentration profiles of aqueous TAT with scrap iron and pure iron are shown in Figures 1a and 2a (dashed lines), by using the fitted pseudo–first-order rate constants for the disappearance of aqueous TNT (fitted curves also shown in the figures). Note that these empirical rate constants may correspond to either $k_{\mathrm{MT,TNT}}$ or k_{ads}, because mass transfer and adsorption could not be differentiated in our experiments. For scrap iron, the model prediction differs greatly from the actual aqueous concentrations of TAT, suggesting that TAT formation was controlled not by TNT removal from solution but by subsequent steps in the sequence. For high-purity iron, the model fits the observed TAT data quite well, which suggests that either mass transfer or adsorption of aqueous TNT was the rate-limiting step in the sequence (Eqn. 5).

$$\mathrm{TNT}_{(\mathrm{aq})} \xrightarrow{k_{\mathrm{MT,TNT}}} \xrightarrow{k_{\mathrm{ads}}} \xrightarrow{k_{\mathrm{R1}}} \xrightarrow{k_{\mathrm{R2}}}$$

$$\rightarrow \rightarrow \xrightarrow{k_{\mathrm{Rn}}} \xrightarrow{k_{\mathrm{des}}} \xrightarrow{k_{\mathrm{MT,TAT}}} \mathrm{TAT}_{(\mathrm{aq})} \qquad (5)$$

$$\mathrm{TNT}_{(\mathrm{aq})} \xrightarrow{k_{\mathrm{overall}}} \mathrm{TAT}_{(\mathrm{aq})} \qquad (6)$$

$$[\mathrm{TNT}]_{(\mathrm{aq})} = [\mathrm{TNT}]_{\mathrm{o(aq)}} \cdot e^{-k_{\mathrm{overall}}t} \qquad (7)$$

$$[\mathrm{TAT}]_{(\mathrm{aq})} = [\mathrm{TNT}]_{\mathrm{o(aq)}} \cdot (1 - e^{-k_{\mathrm{overall}}t}) \qquad (8)$$

where k_{R1} k_{R2} and k_{Rn} are the rate constants of sequential reactions, k_{des} is the desorption rate constant, and t is time.

Reduction of RDX with scrap iron and high-purity iron powder

Figures 3 and 4 show the changes of aqueous, surface, and total concentrations of RDX during its reduction with scrap iron and high-purity iron, respectively. The RDX disappeared from the aqueous phase within 30 min regardless of the iron type, as was observed for TNT. However, in contrast to the TNT data with scrap iron (Fig. 1b), adsorbed RDX was transformed within 30 min with both pure iron and scrap iron (although slightly faster with pure iron). Thus, the RDX adsorbed to scrap iron apparently either desorbed or reacted more rapidly than adsorbed TNT.

By using the same liquid chromatography (LC) conditions as for RDX analysis, we detected a large peak with a retention time of 2.2 ± 0.1 min during RDX reduction with both irons. The area of the peak increased with time initially and then slowly decreased (Figs. 3a and 4a), suggesting that it was an RDX reduction intermediate. This compound was water-soluble and could not be solvent-extracted for analysis by gas chromatography–mass spectrometry (GC-MS). In soil microcosms containing elemental iron, Oh et al. [25] recently iden-

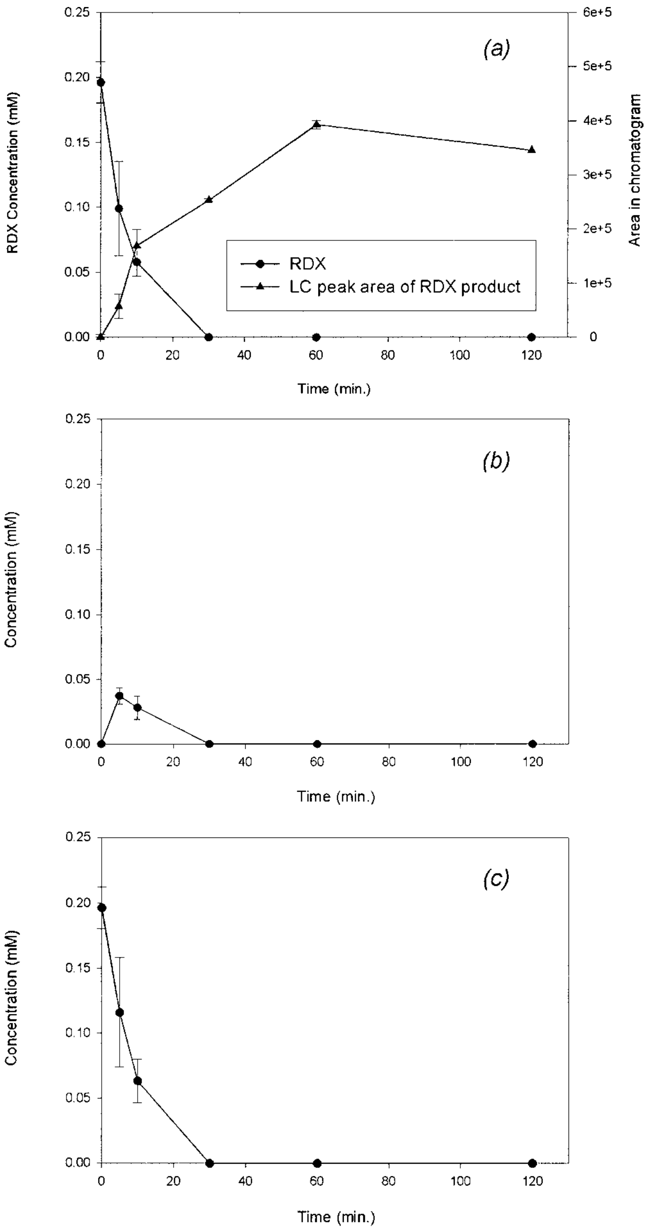

Fig. 3. Aqueous (**a**), surface (**b**), and total (**c**) concentrations of hexahydro-1,3,5-trinitro-1,3,5-triazine (royal demolition explosive [RDX]) during its reduction with scrap iron. Figure 3**a** also shows the liquid chromatography (LC) peak area of a possible RDX reduction product.

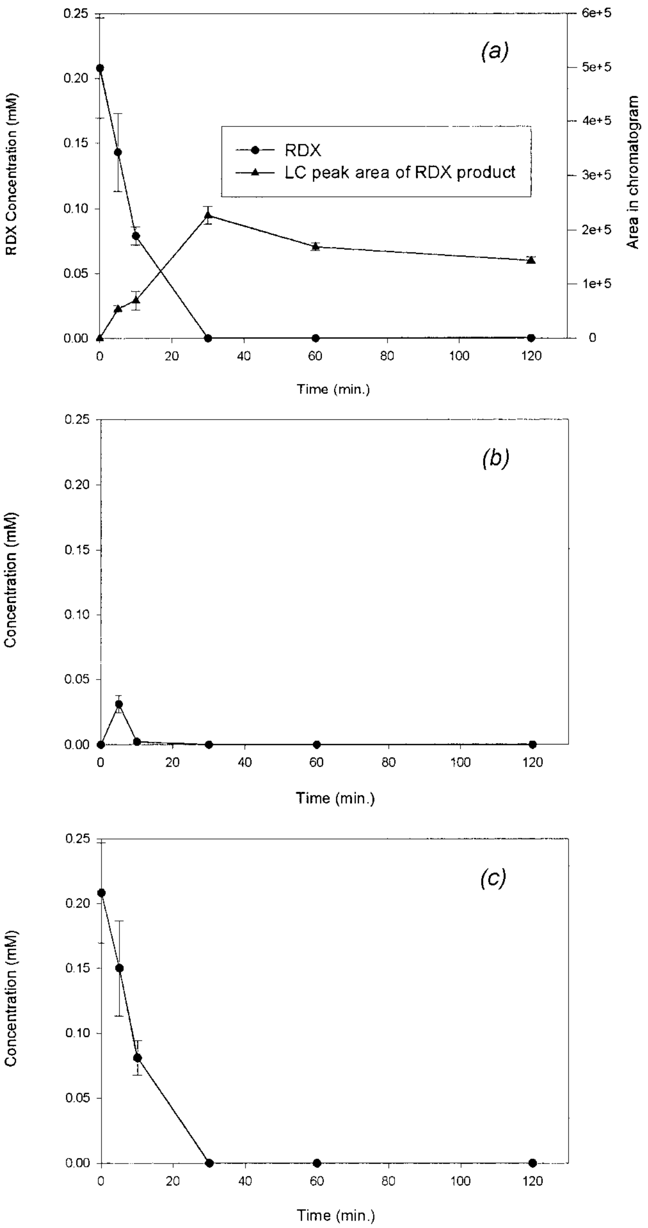

Fig. 4. Aqueous (**a**), surface (**b**), and total (**c**) concentrations of hexahydro-1,3,5-trinitro-1,3,5-triazine (royal demolition explosive [RDX]) during its reduction with high-purity iron powder. Figure 4**a** also shows the liquid chromatography (LC) peak area of an unidentified reduction product of RDX.

tified MDNA to be a soluble RDX reduction product by using LC-MS-MS. Whether the LC peak we observed corresponds to MDNA remains to be determined.

Although the pathway for RDX reduction with elemental iron is not resolved, a pathway for biological RDX reduction has been proposed. Under anaerobic conditions, RDX was shown by McCormick and coworkers [32] to transform in a stepwise fashion to hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine, hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine, and hexahydro-1,3,5-trinitroso-1,3,5-triazine. Further degradation involved cleavage of the triazine ring and formation of hydrazine, 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, formaldehyde, and methanol. Another possible reduction pathway was shown in anaerobic sludge by Hawari and coworkers [33], who proposed that the triazine ring of RDX was cleaved through enzymatic hydrolysis to form MDNA and bis(hydroxymethyl)nitramine. These compounds were further degraded abiotically to give formaldehyde, methanol, nitrous oxide (N_2O), and water. Formaldehyde and methanol were eventually converted to CO_2 and CH_4.

In an experiment conducted in deionized water (i.e., the HEPES buffer was omitted), we found that the TOC remained constant before (12.4 mg/L) and after (12.2 mg/L) complete RDX transformation with scrap iron. This indicates that the carbon in the triazine ring was not mineralized. By using liquid–liquid extraction with hexane or ether followed by GC-MS analysis, we did not detect either formaldehyde or methanol. In fact, no MS peaks were observed, suggesting that the carbonaceous products were highly polar or charged.

Attempts were also made to establish nitrogen balance by measuring NH_4^+, NO_2^-, and NO_3^- in solution during RDX transformation. The NH_4^+ appeared immediately and, within 1 h, its concentration reached a plateau, which corresponded to approximately 50% of the total RDX nitrogen (data not shown). The rapid formation of NH_4^+ indicated that the nitrogen–nitrogen bonds in RDX were cleaved early in the reaction. No NO_2^- or NO_3^- was detected during the experiment. These ions either were not formed during RDX reduction or were rapidly reduced with iron to NH_4^+ and did not accumulate [18,34].

In summary, our results show that TNT molecules removed from water may persist for hours at the scrap iron surface, although all adsorbed TNT was eventually reduced to TAT. The ortho nitro group of TNT seemed to be preferentially reduced with scrap iron. Mass transfer seems to be the rate-limiting step for both TNT reduction and TAT formation with high-purity iron, but not with scrap iron. In contrast to TNT, reduction of adsorbed RDX was faster and less affected by iron type. Approximately one half of the nitrogen in RDX was recovered as NH_4^+. No TOC removal was observed during RDX reduction with scrap iron and the carbonaceous products remain to be identified. The rapid reduction of adsorbed TNT and RDX suggests that elemental iron may be useful for treating munitions-manufacturing wastewater if combined with a subsequent treatment process to achieve complete mineralization of these energetic compounds.

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