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Reduction of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine by Zerovalent Iron: Product Distribution

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RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) are cyclic nitramines ($(CH_2NNO_2)_n$; $n = 3$ or 4, respectively) widely used as energetic chemicals. Their extensive use led to wide environmental contamination. In contrast to RDX, HMX tends to accumulate in soils due to its unique recalcitrance. In the present study, we investigated the potential of zerovalent iron (ZVI) to transform HMX under anoxic conditions. HMX underwent a rapid transformation when added in well-mixed anoxic ZVI−H_2O batch systems to ultimately produce formaldehyde (HCHO), ammonium (NH_4^+), hydrazine (NH_2NH_2), and nitrous oxide (N_2O). Time course experiments showed that the mechanism of HMX transformation occurred through at least two initial reactions. One reaction involved the sequential reduction of N−NO_2 groups to the five nitroso products (1NO−HMX, *cis*-2NO−HMX, *trans*-2NO−HMX, 3NO−HMX, and 4NO−HMX). Another implied ring cleavage from either HMX or 1NO−HMX as demonstrated by the observation of methylenedinitramine ($NH(NO_2)CH_2NH(NO_2)$) and another intermediate that was tentatively identified as ($NH(NO_2)CH_2N(NO)CH_2NH(NO_2)$) or its isomer ($NH(NO)CH_2N(NO_2)CH_2NH(NO_2)$). This is the first study that demonstrates transformation of HMX by ZVI to significant amounts of NH_2NH_2 and HCHO. Both toxic products seemed to persist under reductive conditions, thereby suggesting that the ultimate fate of these chemicals, particularly hydrazine, should be understood prior to using zerovalent iron to remediate cyclic nitramines.

Introduction

RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) are high-energy explosives used in a wide range of commercial and military applications (*1*). The large-scale manufacture, use, and disposal of these chemicals has resulted in high levels of soil and groundwater contamination (*2*). Although HMX has a chemical structure very similar to that of its analogue, RDX ($(CH_2NNO_2)_n$ with $n = 3$ for RDX and $n = 4$ for HMX), the former was often found to be more resistant to both abiotic and biotic degradation (*3*, *4*). As a consequence of its highly recalcitrant behavior, HMX was detected as the only principal soil contaminant in several anti-tank firing ranges where mixtures of explosives had been used (*5*, *6*). Besides being explosive, HMX was found to be toxic to various terrestrial organisms (*7*, *8*) so that its removal from contaminated environments is necessary.

Although aerobic biodegradability of HMX was recently demonstrated using the rot fungus, *Phanerochaete chrysosporium* (*9*), resistance of HMX to bacterial degradation under aerobic conditions was often observed (*10*). Most of the studies describing the biotransformation of HMX were conducted under anaerobic conditions (*11*, *12*), thus demonstrating the susceptibility of this oxidized molecule to transformation via reductive processes. Biotransformation of HMX under anaerobic conditions involves an initial reduction of the nitro groups to form nitroso derivatives (*11*) that further decompose to nitrous oxide (N_2O), formaldehyde (HCHO), and CO_2 via the intermediate formation of several ring cleavage products including methylenedinitramine (MEDINA) and the tentatively identified product, bis-(hydroxymethyl)nitramine (*12*).

In recent years, an increasing number of laboratory and field studies have demonstrated the potential of zerovalent iron (ZVI) for the degradation of species that are susceptible to reductive transformations (*13*). In particular, nitro organic compounds including TNT (2,4,6-trinitrotoluene), RDX, and the polycyclic nitramine, CL-20, appeared readily degradable by ZVI (*14*−*17*) or surface-associated Fe^{II} (*18*). Recently, Park et al. (*19*) showed that HMX could be transformed by ZVI and that cationic surfactants could facilitate the reaction by increasing the solubility of HMX in water and modifying the surface of iron, but no information was revealed on the degradation pathway(s). In the present study, we conducted experiments to transform HMX by ZVI. We determined products of transformation to help understand the degradation pathways of the energetic chemical. Such knowledge may contribute to the effective removal of HMX from contaminated environments.

Experimental Section

Chemicals. Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX, >99% purity), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX, 99% purity), hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX, 98% purity), and ring-labeled [^{15}N]HMX (98% purity) were obtained from Defence Research and Development Canada (Valcartier, PQ). Methylenedinitramine (MEDINA) was purchased from the Rare Chemicals Department of Aldrich (Oakville, ON). All other chemicals were of reagent grade.

Granular iron was purchased from Fisher Scientific (Nepean, ON, iron metal filings, fine, about 40 mesh), used as received, and stored under argon until use. Elemental analysis of the iron was carried out at the Institute for Chemical Process and Environmental Technology (NRC, Ottawa, ON) and showed the presence of 0.004% S, 0.01% N, 1.7% C, 0.02% H, and 1.5% O. Specific surface area was measured using a multipoint BET−N_2 gas adsorption isotherm (Micromeritics, Norcross, GA) and found equal to 0.8 ± 0.2 $m^2\ g^{-1}$.

Degradation of HMX with ZVI in Batch Experiments. Experiments were carried out in 60-mL serum bottles. Iron metal was weighed in dry bottles, which were then filled with deionized water (50 mL), and crimp-sealed with Teflon

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coated septa. The ZVI−H_2O suspensions were made anoxic by purging the headspace for 1 h with deoxygenated argon (using argon sparged water showed insignificant changes in the removal rates of HMX) then allowed to preequilibrate on a reciprocating thermostated shaker (250 rpm) in the dark at 25 °C for 24 h. Subsequently each bottle was spiked with 0.4−1.0 μmole (8−20 μmol L^{-1}) HMX from an acetonitrile stock solution, and kept on the shaker in the dark at 25 °C.

To determine the effect of ZVI amounts on the degradation of HMX in 24-h preequilibrated mixtures of ZVI and water, we kept HMX concentration at 8 μmol L^{-1} and varied the iron concentrations between 2 and 20 g L^{-1} (1.6−16 m^2 L^{-1}, respectively). For each set of conditions, samples of approximately 2 mL were periodically withdrawn with a syringe through the septa, filtered through a 0.02-μm Anotop filter (LABCOR, Montreal, PQ), and analyzed by HPLC as described below.

For products identification and quantification we added HMX (20 μmol L^{-1}) to a 24-h preequilibrated ZVI−H_2O (10 g L^{-1}) mixture. At a given time, gaseous products were sampled with a gastight syringe and analyzed as described below, and the aqueous supernatant was filtered through a 0.02-μm Anotop filter before HMX and products analysis. In another experiment HMX (20 μmol L^{-1}) was added to nonequilibrated ZVI−H_2O (10 g L^{-1}) sparged with Ar for 1 h as described above.

Chemical Analyses. HMX and its nitroso derivatives were analyzed by HPLC/UV (*6*). No standards were available for the five detected HMX nitroso-derivatives so their respective UV peak areas were used to follow their appearance and disappearance.

HMX nitroso intermediates and other ring cleavage products were identified by LC/MS using a Bruker Esquire 3000 plus ion trap mass detector (Bruker-Daltonics, Boston, MA) attached to a Hewlett-Packard 1100 series HPLC system equipped with a photodiode array detector (Agilent, Waldbronn, Germany). The samples were injected into a 5-μm pore size Zorbax SB-C18 capillary column (0.5 mm i.d. × 150 mm; Agilent, Germany) at 30 °C. The solvent system was composed of a CH_3CN/H_2O gradient (20% v/v to 70% v/v) at a flow rate of 12 μL min^{-1}. For mass analysis, negative electrospray ionization (ES−) was used to produce deprotonated molecular ions $[M - H]^-$ or adduct mass ions. The ES source was operated using nitrogen as drying gas (15.0 psi) at a flow rate of 5 L min^{-1} and at temperature of 170 °C. The capillary voltage was set at 4000 V with an end plate offset of −500 V. The mass range was scanned from m/z 40 to 550.

Hydrazine (N_2H_4) was analyzed as described by Bailey and Medwick (*20*) with few modifications. Samples were derivatized with salicylaldehyde in the presence of acetic acid for 1 h at 40 °C. After identification by LC/MS (ES−) using the $[M - H]^-$ at m/z 239, the derivative was quantified using its UV peak area (λ = 300 nm). A Micromass Platform II benchtop single quadrupole mass detector fronted by a Hewlett-Packard 1100 series HPLC system was used, with a 5-μm Supelcosil LC-8 column (4.6 mm i.d. × 250 mm) (Supelco, Bellefonte, PA) maintained at 35 °C. The mobile phase consisted of 60% acetonitrile in water at a flow rate of 1.0 mL min^{-1}.

Nitrogen, O_2, and H_2 were measured on an Agilent 6890 gas chromatograph (Palo Alto, CA) coupled to a thermal conductivity detector (*4*). Nitrous oxide (N_2O and $^{15}N^{14}NO$) was measured as previously described (*21*).

Nitrite (NO_2^-), formate ($HCOO^-$), and ammonium (NH_4^+) were analyzed by ion chromatography (IC) as described earlier (*17*). Formaldehyde (HCHO) and formamide (NH_2-CHO) were analyzed after derivatization, as previously described (*22*).

TABLE 1. Physicochemical Parameters[a] of the ZVI−H_2O System (10 g L^{-1}) during Preequilibration Under Anaerobic Conditions

equilibration time (h)	dissolved Fe^{2+} (μmol)	H_2 in headspace (μmol)	pH
1	0.318 ± 0.091	0.077 ± 0.008	5.37 ± 0.11
4	0.472 ± 0.029	0.160 ± 0.031	5.65 ± 0.34
23	0.229 ± 0.064	0.245 ± 0.037	6.14 ± 0.16
47	0.249 ± 0.024	0.319 ± 0.047	5.56 ± 0.14
71	0.122 ± −	0.293± 0.032	5.55 ± 0.06
95	0.117 ± 0.058	0.382 ± 0.013	5.56 ± 0.21

[a] Values of triplicate measurements expressed as the mean ± standard deviation.

Methanol (CH_3OH) was analyzed on a Hewlett-Packard 6890 gas chromatograph coupled to an FID using a Hayesep Q micropacked column (2 m × 0.03 mm, Supelco) (detection limit, 0.1 mg L^{-1}).

Methylenedinitramine (MEDINA) was analyzed and quantified by HPLC using an ICSep ICE-ION-310 column (Transgenomic, San Jose, CA), as described earlier (*23*).

Ferrous iron was determined photometrically (λ 562 nm) after complexation with ferrozine (*24*) in the aqueous phase and in 0.5 N HCl extract of the metal. Ferric iron and 0.5 N HCl extractable $Fe(OH)_3$ were determined as the difference between total iron (measured as Fe^{II} after reduction with hydroxylamine) and ferrous iron.

Results and Discussion

Potential Species Initiating HMX Reduction. Zerovalent iron metal, Fe^0, is known to react with water according to eqs 1 and 2, depending on the presence of O_2 in the Fe^0-H_2O system. Consequently, Fe^0 (ZVI), Fe^{II} (dissolved or adsorbed), OH^-, and H_2 are all species that could contribute to the degradation of HMX.

$$Fe^0 + 2H_2O \rightleftharpoons Fe^{II} + H_2 + 2OH^- \quad (1)$$

$$2Fe^0 + O_2 + 2H_2O \rightleftharpoons 2Fe^{II} + 4OH^- \quad (2)$$

Prior to starting HMX transformation reactions, the ZVI−H_2O systems were preequilibrated. Reactivity of iron during the preequilibration step was thus followed by measuring Fe^{II}, H_2, and pH at different time intervals (Table 1). Dissolved Fe^{II} was detected after 1 h, but its concentration decreased after 4 h (Table 1). Extracting the metal surface with 0.5 N HCl showed the presence of Fe^{II} and ferric hydroxide ($Fe(OH)_3$) only in trace amounts (data not shown), suggesting the potential formation of other iron species at the metal surface. It has been reported that ferrous hydroxide ($Fe(OH)_2$) can be converted to magnetite (Fe_3O_4) (*25*).

Although reaction of ZVI with H_2O (eq 1) is expected to increase pH no significant change in pH was observed (Table 1). Also Table 1 shows slow evolution of H_2 during the period investigated, suggesting the potential sorption of hydrogen on the metal surface before being transformed into gas (*25*).

When HMX was added to a 24-h preequilibrated ZVI−H_2O suspension (10 g L^{-1}), the nitramine (0.4 μmol) was fully removed within 3 h (Figure S1, see Supporting Information). As with the preequilibration step without HMX, the system remained slightly acidic in all reactions containing the energetic chemical (final pH 5.5), excluding alkaline hydrolysis as a potential degradation route for the nitramine. In addition neither H_2 (2.23 μmol) nor dissolved Fe^{II} ($FeCl_2$, 5 μmol) led to any noticeable HMX transformation in the absence of metallic iron, thereby excluding their direct role in the degradation of HMX. It has been recently reported

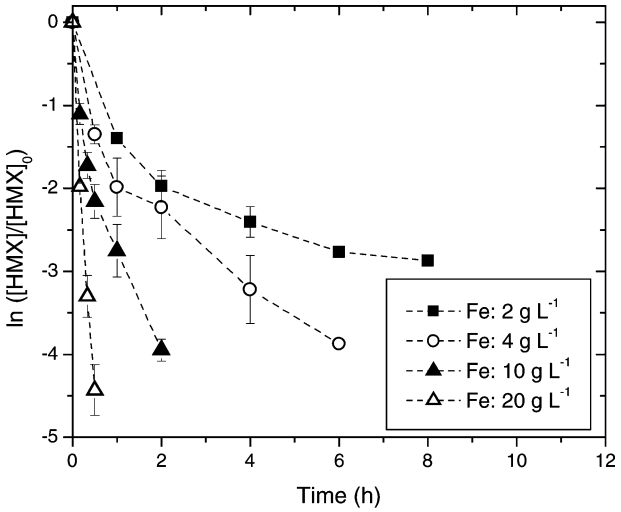

FIGURE 1. Time course showing effect of iron amounts on the transformation of HMX (0.4 μmol) in 24-h preequilibrated ZVI−H_2O mixtures. Data points are the mean of triplicate experiments and error bars are the standard deviation.

that hydrogen atom species sorbed on ZVI are responsible for the metal corrosion in water (*25*) and also for the reduction of *N*-nitrosodimethylamine to dimethylamine and ammonia (*26*). The sequential reduction of HMX to the corresponding nitroso derivatives and the eventual formation of hydrazine (discussed below) might also suggest the involvement of sorbed reactive hydrogen species in addition to sorbed Fe^{II} in the reductive degradation of HMX.

Ferrous ion associated with solid phases is reportedly much more reactive than the dissolved form in reducing many organic and inorganic contaminants (*27*). In particular, RDX was reported to undergo transformation by Fe^{II} associated with magnetite (*18*) or biologically reduced ferrihydrite (*28*) despite the lack of transformation observed in the presence of dissolved Fe^{II} alone.

Effect of Iron Amount on HMX Degradation. Figure 1 is a typical time course for the reaction of HMX (0.4 μmol) with ZVI (2−20 g L^{-1}, corresponding to 1.6−16 m^2 L^{-1}, respectively). Figure 1 shows a noticeable increase in the initial removal rate of HMX with the amount of ZVI employed followed by a slower rate except when using a high concentration of ZVI (20 g L^{-1}). In the latter case HMX disappearance was very rapid possibly caused by the availability of a larger surface area at the metal surface. The slow phase in HMX removal could be attributed to the potential sorption of HMX degradation products on the metal surface. Products accumulation has been suggested previously to explain the decreasing rate of nitroaromatics reduction by ZVI. Indeed, reduction of nitroaromatics by ZVI was shown to produce aromatic aminated compounds (*16*, *29*) that can adsorb on iron and therefore decrease the number of available sites. For instance, reduction of nitrobenzene by ZVI was inhibited in the presence of aniline (*29*). However, when [^{14}C]RDX is treated with either ZVI (*30*) or Fe^{II} bound to magnetite (*18*), mostly water-soluble carbon-containing products are formed. Assuming that RDX reacts in a way similar to that of HMX, both are cyclic nitramines, then we should expect that in the present study HMX reacts with ZVI to produce water-soluble C-containing products. Acetonitrile extracts of iron (after aqueous phase removal) at the end of the reaction (>98% of HMX reacted) did not show any C-containing products as determined by either LC/UV or LC/MS using either negative (ES−) or positive (ES+) chemical ionization. However, the diamine product NH_2NH_2, an important HMX product in the present study (discussed below), can form complexes with species resulting from ZVI such as Fe^{III} (*31*).

Products of HMX Transformation in Preequilibrated and Nonequilibrated ZVI−Water Mixtures. *HMX Nitroso Derivatives.* In preequilibrated ZVI−water systems the disappearance of HMX (1.0 μmol) in the presence of ZVI (10 g L^{-1}) was accompanied with the rapid formation of five UV-absorbing products (**I**, **IIa**, **IIb**, **III**, **and IV**) (Figure 2A). LC/MS (ES−) analysis of HMX and its five intermediates showed a constant mass difference of 16 Da representing the loss of 1 O from one compound (peak) to the subsequent one. These regular shifts were attributed to the stepwise reduction of the NO_2 groups to the corresponding NO groups, resulting in the formation of the five nitroso-derivatives, octahydro-1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine (1NO−HMX, **I**), octahydro-1,5-dinitroso-3,7-dinitro-1,3,5,7-tetrazocine (*trans*-2NO−HMX, **IIa**) or octahydro-1,3-dinitroso-5,7-dinitro-1,3,5,7-tetrazocine (*cis*-2NO−HMX, **IIb**), octahydro-1,3,5-trinitroso-7-nitro-1,3,5,7-tetrazocine (3NO−HMX, **III**), and octahydro-1,3,5,7-tetranitroso-1,3,5,7-tetrazocine (4NO−HMX, **IV**). These intermediate products could not be quantified due to the lack of commercial products, however, a time-course, constructed of the relative HPLC−UV peak areas, showed that all five intermediates were transient (Figure 2C). The tetranitroso compound **IV**, which was the only intermediate remaining in the supernatant after 6 h, also disappeared after 24 h (result not shown). A similar behavior has been recently observed for the transformation of RDX by adsorbed Fe^{II}, where the three nitroso derivatives were transiently formed (*18*).

In the nonequilibrated ZVI−water mixture, HMX removal rate was twice lower than that of the 24-h preequilibrated mixtures. In addition the five nitroso intermediates of HMX were formed with different relative yields in both the preequilibrated and the nonequilibrated systems (Figure 2C and E). For example, 1NO−HMX seemed to persist longer in the nonequilibrated mixture with the yield of 4NO−HMX higher in the preequilibrated one (Figure 2C and E), indicating that the preequilibrated medium is more reductive.

Ring Cleavage Intermediates. Analysis of the preequilibrated reaction medium by HPLC/UV using an ICSep ICE-ION-310 column allowed detecting methylenedinitramine, $NH(NO_2)CH_2NH(NO_2)$, (MEDINA, **V**, rt 6.5 min) as a transient intermediate, which was identified and quantified by comparison with an authentic reference standard (Figure 2B and D). Maximum amount of MEDINA (0.1 μmol) was reached after 0.5 h which completely disappeared after 24 h of reaction (result not shown). MEDINA (**V**) has been previously detected as a transient ring cleavage product during biodegradation of RDX (*32*) or HMX (*12*) with anaerobic sludge and during transformation of RDX by ZVI and anaerobic cultures (*15*). Besides MEDINA, another compound, **VI**, was detected at 8.4 min, with a UV spectrum closely related to that of MEDINA. LC/MS (ES−) of compound **VI** showed a $[M - H]^-$ ion at 193 Da, matching a molecular formula of $C_2H_6N_6O_5$ (Figure 3A). Using ring labeled [^{15}N]HMX the previously detected mass ion was observed at 196 Da (an increase of 3 amu), suggesting the involvement of three ring ^{15}N atoms in intermediate **VI** (Figure 3B). Mass spectra of compound **VI** resulting from HMX (and its ring labeled [^{15}N]HMX) gave fragments ions at 61 (62), and 162 (165) Da, corresponding to $[NHNO_2]^-$ and $[M - H - HNO]^-$, respectively. Given the similar chemical behavior of compounds **V** (MEDINA) and **VI**, and the data provided by LC/MS, we tentatively identified compound **VI** as $NH(NO_2)CH_2N(NO)CH_2NH(NO_2)$ or its isomer, $NH(NO)CH_2N(NO_2)CH_2NH(NO_2)$. Formation of MEDINA and compound **VI** implies the occurrence of ring cleavage from either HMX or its nitroso intermediates **I** or **II**. The reduction of a nitro group to a nitroso group in both RDX (*33*) and HMX (*9*) has been shown previously to lead to cleavage of the ring in water.

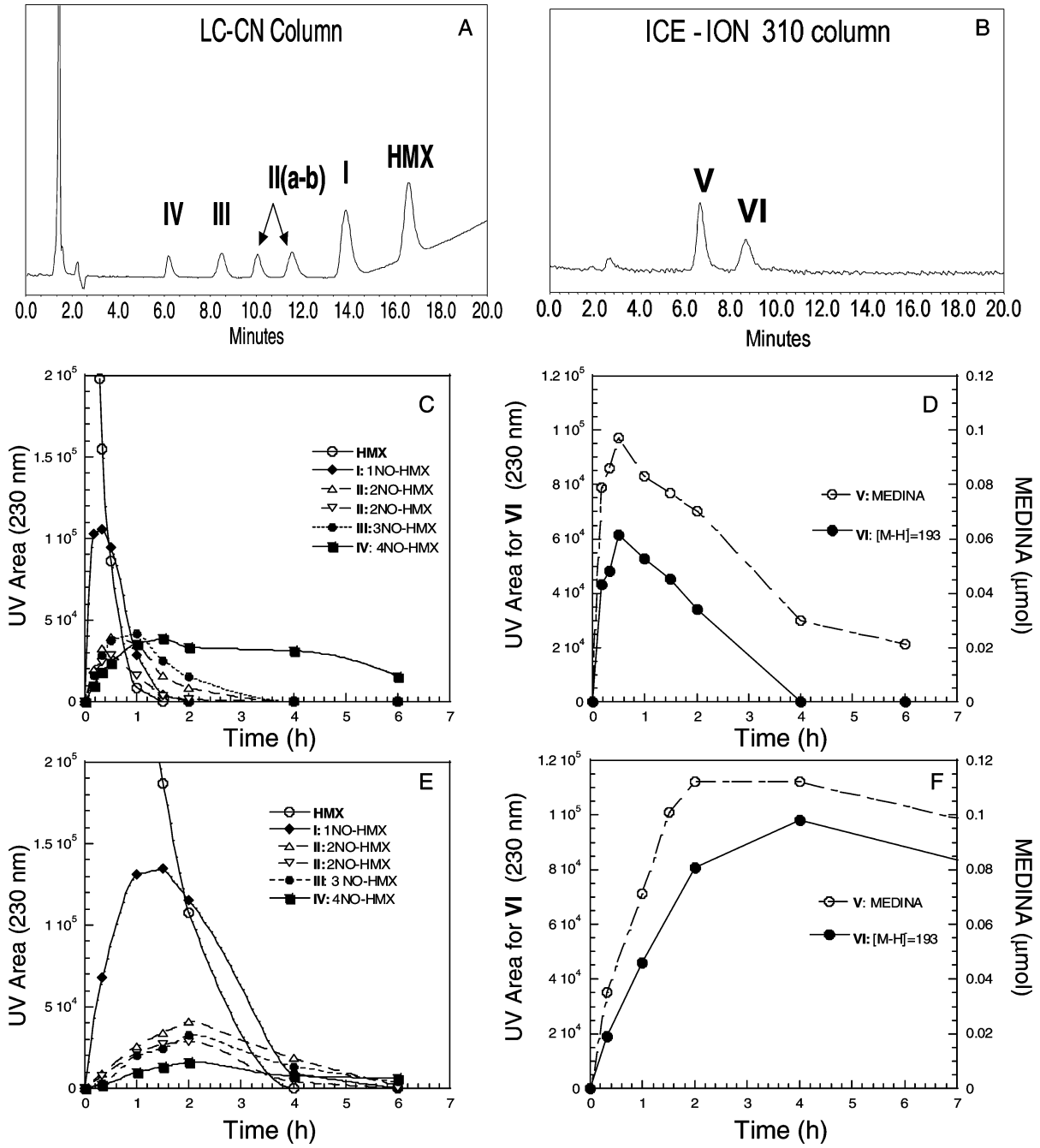

FIGURE 2. Transformation of HMX (1 μmol) in ZVI−H_2O mixtures: (A) a typical HPLC/UV chromatogram obtained using LC−CN column; (B) a typical HPLC/UV chromatogram obtained using ICE-ION-310 column; (C) a time course of the nitroso products (I−IV) determined in preequilibrated ZVI−water; (D) a time course of MEDINA (V) and the *m/z* 193 Da product (VI) determined in preequilibrated ZVI−water; (E) a time course of the nitroso products (I−IV) determined in nonequilibrated ZVI−water; and (F) a time course of MEDINA (V) and the *m/z* 193 Da product (VI) determined in nonequilibrated ZVI−water.

In the nonequilibrated ZVI−H_2O mixture we observed both MEDINA and the m/z 193 Da product but once again the two products seemed to persist longer than when obtained in the preequilibrated one (Figure 2D and F). Interestingly the time course of both MEDINA (**V**) and the mononitroso product (**I**) are similar in both the pre- and nonequilibrated ZVI−H_2O systems, suggesting that **I** might act as a precursor to **V**.

End-Products and Reaction Stoichiometry. The disappearance of HMX (1.02 μmol) with ZVI (10 g L^{-1}) in the preequilibrated mixture was accompanied with the formation of HCHO, NH_4^+, N_2O, and NH_2NH_2 (Figure 4), the amounts of which after 24 h reached 3.24, 2.15, 0.59, and 0.26 μmol, respectively (Table 2). Formaldehyde accounts for 79.5% of the total C content in HMX, while ammonium, nitrous oxide, and hydrazine account for 26.3, 14.5, and 6.4% of the total N, respectively. Both HCHO (24% of C) and NH_4^+ (17% of N) have been detected previously during RDX treatment with surface-bound Fe^{II} (*18*). Interestingly, the yields of the two end products HCHO and NH_2NH_2 were closely similar in both the preequilibrated and the nonequilibrated experiments: 3.24 and 3.66 μmol and 0.26 and 0.34 μmol, respectively (Table 2).

Although there is only one possible source of carbon for HCHO in HMX, the nitrogen-containing products could originate from either the peripheral $-NO_2$ groups or the inner aza Ns in the ring. The transient detection of nitrite ion (NO_2^-) in samples analyzed between 10 min and 4 h suggested the

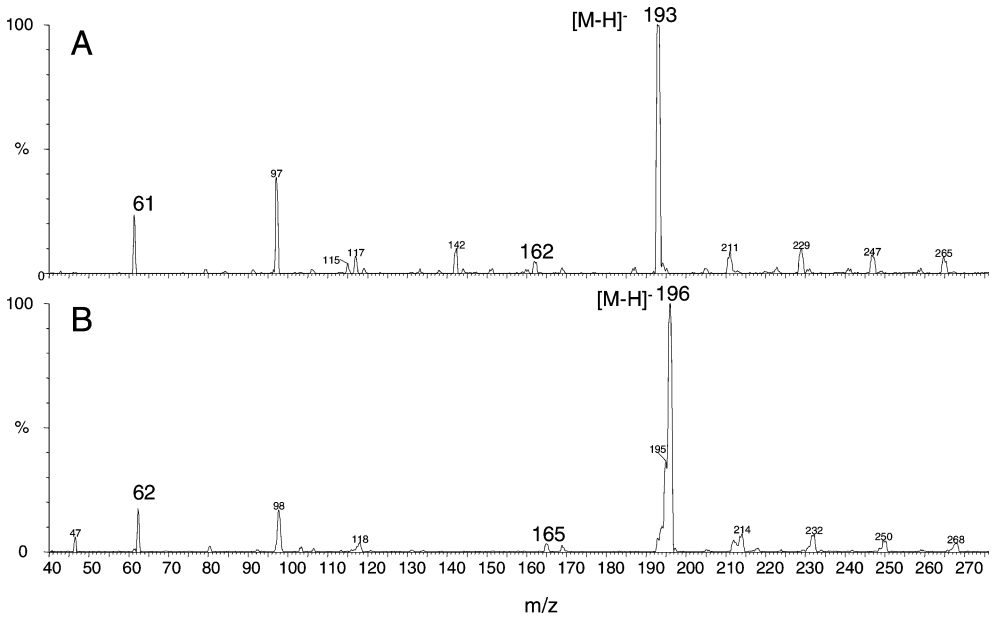

FIGURE 3. LC/MS (ES−) spectra of intermediate VI observed during transformation of HMX with ZVI from (A) nonlabeled HMX and (B) ring labeled [^{15}N]−HMX.

TABLE 2. Normalized Molar Yields of the Final Products Obtained upon Reduction of HMX (1.02 μmol) with ZVI (10 g L^{-1})[a]

product	HCHO	NH_4^+	N_2O	NH_2NH_2	Σ products
		Preequilibrated			
norm. molar yields	3.24 ± 0.03	2.15 ± 0.07	0.59 ± 0.07	0.26 ± 0.02	
% of total C	79.4				79.4
% of total N		26.3	14.5	6.4	47.2
		Nonequilibrated			
norm. molar yields	3.66 ± 0.01	1.88 ± 0.09	0.27 ± 0.06	0.34 ± 0.02	
% of total C	91.5				91.5
% of total N		23.5	6.8	8.5	38.8

[a] Values were calculated after complete disappearance of intermediates **I**−**VI** (24 h reaction time) based on the moles of product observed for each mole of HMX consumed; Values of triplicate measurements expressed as the mean ± standard deviation.

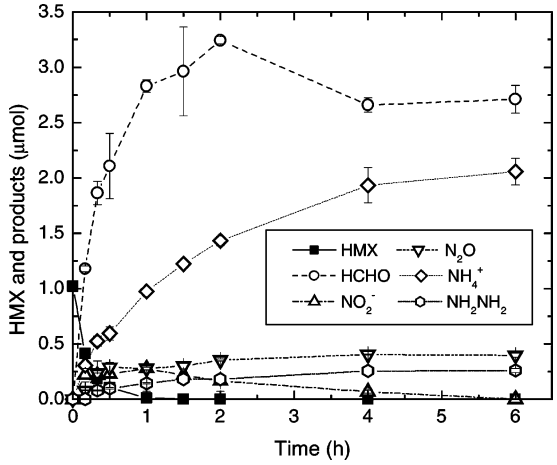

FIGURE 4. Time course for the transformation of HMX (1.02 μmol) with preequilibrated ZVI (10 g L^{-1}) showing formation of formaldehyde (HCHO), ammonium (NH_4^+), nitrous oxide (N_2O), hydrazine (NH_2NH_2), and nitrite (NO_2^-). Data points are the mean of duplicate experiments and error bars are the standard error.

occurrence of initial denitration (cleavage of the N−NO_2 bond) of HMX or its nitroso derivatives (Figure 4). Nitrite ion is unstable in the presence of iron and can be reduced to nitrous oxide (*17*) and ammonium (*13*, *17*, *34*, *35*). Using [^{15}N]HMX and GC/MS analysis, we detected both $^{14}N^{14}NO$ (44 Da) and $^{14}N^{15}NO$ (45 Da), indicating that nitrous oxide originated from both N-NO_2 and NO_2 groups of HMX.

Hydrazine was detected as a salicylazine derivative and its identity was confirmed using LC/MS, by comparison with a reference standard. Both the detected intermediate and the reference hydrazine chemical gave a derivative with a chromatographic retention time of 8.0 min and a $[M - H]^-$ ion at 239 Da (Figure 5). Using ring labeled [^{15}N]HMX two mass ions were detected, a major one at 239.9 Da corresponding to labeled hydrazine ($^{14}NH_2{}^{15}NH_2$), and a minor one at 239.0 Da corresponding to hydrazine ($^{14}NH_2{}^{14}NH_2$). This finding indicates that hydrazine originates mainly from the N−NO_2 groups, and to a smaller extent, from the NO_2 groups of HMX.

Hydrazine has been previously observed as a trace product during treatment of RDX with anaerobic sludge (*11*, *36*), however, it has not been observed from HMX. The system of McCormick also gave significant amounts of the sequentially reduced nitroso products (*36*), thus suggesting that the reduced nitroso intermediates of HMX might be responsible for the formation of hydrazine. When we treated RDX (1.0 μmol) or its trinitroso derivative TNX (1.0 μmol) (reference standards are not available for the nitroso derivatives of HMX) with ZVI under the conditions applied for HMX, we observed a small amount (0.05 μmol) of hydrazine in the case of RDX and a larger yield (0.13 μmol) in the case of TNX. This result confirms our assumption that the nitroso intermediates of HMX, particularly 4NO−HMX, acted as precursors to hydrazine. In support of this conclusion, no hydrazine was ever detected in previous abiotic (*22*) and biotic (*12*, *32*) trans-

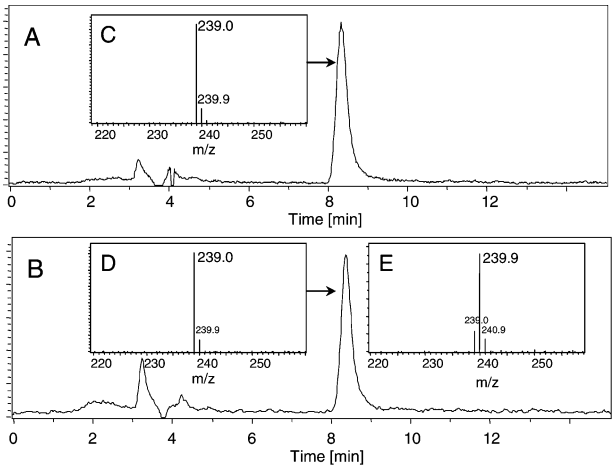

FIGURE 5. Extracted ion chromatograms (*m/z* = 239) of (A) hydrazine reference standard material and (B) a sample obtained from reaction of HMX with ZVI (*t* = 4 h) after derivatization with salicylaldehyde. Inset C represents the [M − H] of a reference standard of hydrazine. Inset D represents the [M − H] of hydrazine as a product of HMX. Inset E represents the [M − H] of hydrazine as a product of [^{15}N]-HMX.

formation of RDX and HMX that did not involve formation of appreciable amounts of di-, tri-, or tetranitroso intermediates. Hydrazine, which seemed to accumulate in the present system, is reportedly a very toxic chemical (*37*), emphasizing that the formation and the fate of the diamine product should be carefully examined in remediation technologies that involve the use of ZVI.

Environmental Significance. This study demonstrates that HMX can be rapidly degraded by ZVI to produce formaldehyde as the main carbon-containing product, and ammonium, hydrazine, and N_2O as the N-containing products. Because both formaldehyde and hydrazine are known for their toxicity, the application of iron technologies for remediation of matrices contaminated with HMX first necessitates a thorough understanding of their eventual fate.

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Supporting Information Available

Effect of hydrogen and Fe^{II} on the transformation of HMX (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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