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Fenton oxidation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)

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Abstract

Oxidation of the high explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) using Fenton's reagent proceeds rapidly between 20°C and 50°C at pH 3. At an $H_2O_2 : Fe^{2+}$: RDX molar ratio of 5178 : 48 : 1, RDX and HMX were completely removed in 1 to 2 h. All the experimental data could be fit to a pseudo first-order rate equation. The reaction rate was also strongly dependent on Fenton's reagent concentrations. NO_3^- and N_2 were identified as nitrogen byproducts from RDX and HMX oxidation. The experiment with radiolabeled RDX showed that approximately 37% of organic carbon in RDX was mineralized to CO_2. We observed formaldehyde and formic acid as a short-lived intermediate. No other volatile or nonvolatile byproducts were found from GC/MS analysis. The results show that RDX and HMX can be effectively mineralized with Fenton's reagents.

Keywords: Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); Octahydro-1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane (HMX); Fenton oxidation; Nitrate; Mineralization; Formaldehyde; Formic acid

1. Introduction

Wastewaters generated at former munitions production facilities contain high explosives. Among these, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are important explosives used by the US and European munitions industry [1]. Both RDX and HMX are more energetic and stable than TNT, and have been used in both conventional and nuclear weapons. These explosives are known to be toxic to aquatic and terrestrial organisms [2–4]. The US EPA classifies RDX as a possible human carcinogen (Class C) [5]. HMX is typically found together with RDX as an environmental contaminant, and has been classified as Class D carcinogen [6]. Therefore, the US EPA has set a lifetime health advisory for exposure to RDX and HMX in drinking water of 0.002 and 0.04 mg/L, respectively [7].

Past methods for disposing of munitions wastes included disposal in lagoons and open burning or open detonation (OB/OD). These practices may cause serious harm to ecosystems, and have resulted in numerous acres of contaminated soils and groundwater near many munitions facilities [8]. Economic and efficient methods for wastewater treatment and cleanup of soils or groundwater laden with RDX and HMX are needed.

Incineration is currently the most common method for treating munitions-contaminated soils and groundwater, but is costly, produces unusable ash, and has poor public acceptance due to safety concerns regarding air emissions such as cyanide, and NO_x. The high cost and associated disadvantages of incineration have

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motivated researchers to seek more cost-effective and environmentally benign alternatives.

Bioremediation [9–13], although possible, may require excessive time to oxidize RDX and HMX. Furthermore, unresolved issues exist with respect to mineralization and end products. Strong oxidants may be a useful treatment technique. Products resulting from chemical oxidation might be more amenable to biological treatment than the parent compound.

Advanced oxidation processes (AOP) are commonly used for remediating wastewaters contaminated with recalcitrant organic pollutants [14–16]. These methods are attractive because of the possibility of the mineralizing the target compounds. Among those, Fenton reagent [17] is one of the oldest and powerful oxidation treatments available.

The objective of this study is to determine the potential to use the Fenton reaction to destroy RDX and HMX in aqueous solution. We investigated the degradation kinetics of Fenton oxidation of RDX and HMX under acidic conditions. Various factors that are important to maximize the oxidation were studied, including H_2O_2 concentration, Fe^{2+} concentration, and temperature. Furthermore, the identification and quantification of principal reaction byproducts were also examined using various techniques, and finally the reaction mechanisms are suggested.

2. Materials and methods

2.1. Reagents

Technical grade RDX and HMX were obtained from Lawrence Livermore National Laboratory (Livermore, CA). Reagent grade 30% H_2O_2 and $FeSO_4 \cdot 7H_2O$ (Fisher Scientific, Pittsburgh, PA) were used as purchased. Uniformly labeled [U-^{14}C] RDX (specific activity of 17.9 mCi/mmol of RDX; Chemsyn Laboratories, Lenexa, KS) was also generously obtained from Lawrence Livermore National Laboratory.

2.2. Experimental section

The experiments were conducted in the dark in 500-mL flasks at constant temperature in a water bath at between 20°C and 50°C. The reaction was initiated by adding $FeSO_4 \cdot 7H_2O$ and the calculated amounts from 30% H_2O_2 stock solution to a known solution of RDX (10 mg/L) or HMX (4.5 mg/L). Molar ratios of 5178 : 48 : 1 of Fe^{2+} : H_2O_2 : RDX (or HMX) were maintained during the reactions except for the experiments with changing Fenton reagent concentration. The initial pH of the solution was reduced to 3 using 1 N H_2SO_4 to maximize reaction rates [14,15]. Samples were taken at predefined times using microsyringes, and were filtered into cooled (0°C) HPLC vials; they were immediately analyzed (<30 s) using HPLC. Another aliquot was collected for TOC analysis. The TOC analysis was performed with *Standard Methods* [18] using a Beckman Model 915B TOC analyzer.

2.3. Analysis of RDX and HMX

Analysis of RDX and HMX were performed with a Hewlett Packard 1500 Series HPLC instrument (Avondale, PA). The HPLC was equipped with a variable wavelength detector and autosampler. Liquid samples were first filtered through sterile Acrodisc-13 0.2-μm syringe-microfilters (Gelman Sciences; Ann Arbor, MI) before the analysis by HPLC. An Adsorbosphere C-18 10-μm reversed-phase column (Alltech Associates Inc., Deerfield, IL) with prefilter element and guard column (C-18, 5-μm, Alltech) was used with an isocratic mobile phase consisting of 30% methanol, 30% acetonitrile, and 40% water (volume%) at a flow rate of 1. 0 mL/min. A UV detector set to 236 nm was used, and RDX and HMX peaks at retention times of 3.6 and 4.1 min were observed.

2.4. Ion chromatography

A Dionex Ion Chromatograph (Basic chromatography module CMB-2, gradient pump GPM-1; Dionex, Sunnyvale, CA) with suppressed conductivity detection (conductivity detector CDM-1) was used for analyzing the ions from Fenton reaction. An Ion Pac AS9-SC analytical column (4 mm I. D.; Dionex) was used as an analytical column. The mobile phase consisted of 0.75-mM $NaHCO_3$ and 2-mM Na_2CO_3 in deionized water. The eluent flow rate was 1.5 mL/min, and the peaks were detected at 4.9 min retention times for NO_3^-. All samples were filtered through 0.2-μm microfilters before injection.

2.5. Formyl intermediates analysis

The 2,4-dinitrophenylhydrazine (DNPH) technique [19,20] for aldehyde and ketone analysis was modified to identify Fenton oxidation byproducts. The DNPH reagent solution was prepared by dissolving 0.5 g of DNPH in 500 mL of 2 N hydrochloric acid and was purified by shaking with 5 mL of chloroform. Formyl intermediates in the sample, if present, were first allowed to react with DNPH reagent solution in order to form 2,4-dinitrophenylhydrazone, and solid phase extraction (SPE) was used to exchange solvents from acidic water to acetonitrile. This final solution was analyzed by HPLC with the same column used for RDX/HMX determination. The HPLC solvent system was an isocratic mobile phase consisting of 50% acetonitrile and 50% water (volume%) at a flow rate of 1.5 mL/min.

A UV detector set to 254 nm was used to detect the 2,4-dinitrophenylhydrazone peak.

2.6. GC/MS analysis following liquid–liquid-extraction or purge and trap

Prior to GC/MS analysis, the samples were extracted and concentrated with dichloromethane (Optima-grade, Fisher Scientific; Pittsburgh, PA). A total of 500 mL of the sample was first contacted with 100 mL of dichloromethane in a Pyrex accelerated one-step extractor (Pyrex, Corning, NY). The concentrator tube was kept in a water bath at 80°C. Recondensation of the recirculating dichloromethane was achieved with a condenser on top of the extractor body, which operated at 2–4°C. The extraction was completed after 6 h, and the dichloromethane solvent was then concentrated to 1–5 mL by gradual heating. The sample volume was further reduced by evaporation to 500 μL with 99.999% helium gas. This concentrated sample was transferred into the vial using a gas-tight syringe with attached luer-tip needle. This vial was closed and sealed with a Teflon-lined cap, and stored for GC/MS analysis. Using this method, the sample was concentrated 2000 times.

After the extraction, the concentrated samples were analyzed using a Finnigan gas chromatograph Model 9610 equipped with a Grob-type splitless injector and a Finnigan quarupole mass spectrometer Model 4000, with an INCOS Model 2300 data system. The GC/MS was operated with electron energy of 70 eV, a source temperature of 240°C, and a scan speed of 1 s scan-1 from 50 to 550 amu. A 30-m DB5-MS fused silica column (0.25 mm ID., 25-μm film thickness; J&W Scientific, Folsom, CA) was held for 4 min at 30°C and then programmed at 6°C/min to 300°C.

Volatile byproducts from Fenton oxidation were analyzed using an HP 7695 purge and trap with an HP 6890 GC and HP5973 MSD. The trap was a VOCARB 3000 (Agilent Technologies, Santa Clarita, CA) and the chromatography column was a DB 624 column (30 m, 0.25 mm ID; J&W Scientific, Folsom, CA) with temperature programming of 35°C for 2 min, 8°C/min to 125°C, hold 2 min, using helium carrier gas. The MSD was operated in EI mode, scanning 25–260 amu at 5.87 scans/sec.

2.7. Gas byproducts analysis

In order to identify and quantify the gas byproducts from RDX and HMX oxidation, 5-mg/L of RDX (or HMX) was placed into a gas-tight glass reactor with total reactor volume of 200 mL. The system was then sealed and purged with 99.999% helium gas for 10–15 min in order to remove all the air inside the reactor. Syringes, in the closed position, were attached to the reactor in order to measure gas volume produced after the reaction. The solution was kept at a constant temperature ($T = 25°C$) and continuously stirred. The reaction was started by adding the calculated amounts of $FeSO_4 \cdot 7H_2O$ and 30% H_2O_2 into the sealed system using syringes with needles. Gas samples were taken during the reaction (about 6 h). The total liberated gas volume was measured by allowing the attached syringes to expand. The gases were transferred to a gas chromatograph with 1-mL glass Pressure-Lok series A-2 syringes equipped with a Teflon plunger and push-button valve (Precision Scientific; Winchester, VA). For the gas analysis, a Varian 3400 series gas chromatograph was used with a thermal conductivity detector and a 2 m × 2 mM Pyrex column packed with 80/100 mesh Porapak QG (Alltech). The carrier gas was helium (99.9995% purity at 80 mL/min), and the temperatures were 100°C (injector), 60°C (column), and 110°C (detector), respectively.

2.8. ^{14}C Experiment

Radiolabeled RDX was used to investigate the mineralization from Fenton oxidation of RDX. Erlenmeyer flasks (125-mL) containing 100-mL of solution containing were spiked 5-mg/L of RDX and 0.5 μCi of [U-^{14}C] RDX. This flask was then covered with a glue cap and sealed tightly with parafilm; the nitrogen gas was continuously purged during the reaction. CO_2 produced from the reaction was trapped in a series of three bottles containing 12-mL of scintillation cocktail. The cocktail consisted of 1-mL of β-phenylethylamine (Sigma, St. Louis, MO) for capturing CO_2, 1-mL of methanol, and 10 mL of Ecolite(+)™ (ICN Pharmaceuticals Inc., Costa Mesa, CA). After the reaction, the ^{14}C in the series of bottles, and in the final solution was measured using a Beckman LS 3801 scintillation counter (Beckman Instruments Inc., Fullerton, CA).

3. Results and discussion

3.1. Mechanisms and kinetics

Fenton's reagent is receiving renewed interest because of its potential ability to oxidize many organic compounds [16,21,22]. Fenton's reagent is a mixture of ferrous iron (Fe^{2+}) and hydrogen peroxide (H_2O_2) that generates reactive radicals, primarily hydroxyl radical ($^{\bullet}OH$). In an acidic environment, Walling [23] proposed that hydrogen peroxide in the presence of excess ferrous ions reacts in the following way:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad k_1 = 76\ M^{-1}\ s^{-1}. \tag{1}$$

The products of the reaction are the ferric ion (Fe^{3+}), the hydroxyl radical ($^{\bullet}OH$), and the hydroxide ion

(OH^-). The hydroxyl radical produced in Eq. (1) is capable of reacting with a variety of organic compounds.

A reasonable pathway for the decomposition of a target compound, RH, with the hydroxyl radical in Fenton reaction and regeneration of Fe^{2+} catalysis is shown in Eqs. (2)–(8) (Walling, 1976) [24].

$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet}, \quad (2)$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^{+} + Fe^{2+}, \quad (3)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} + R' + HO_2^{\bullet}, \quad (4)$$

$$R^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + R'' + \text{products}, \quad (5)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+}, \quad (6)$$

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O, \quad (7)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+}. \quad (8)$$

Hydroxyl radicals are nonspecific oxidants that react with most organic contaminants at rates close to diffusion rates in water [$\sim 10^{10}\,M^{-1}\,s^{-1}$] [25].

The following reaction can represent the chemical oxidation of the Fenton process reaction kinetics. A second-order rate equation can be applied to fit the data

$$\frac{dC_{HE}}{dt} = -k_{HE} C_{HE} C_{OH^{\bullet}}, \quad (9)$$

where C_{HE} is the concentration of high explosive compound (RDX or HMX), $C_{OH^{\bullet}}$ is the hydroxyl radical concentration, and k_{HE} is the second-order rate constant. In case of constant OH radical concentration, and in excess concentration compared to substrate (explosives), Eq. (9) can be reduced to a pseudo first-order rate equation

$$\frac{dC_{HE}}{dt} = -k'_{HE} C_{HE}, \quad (10)$$

where k'_{HE} is the pseudo first-order rate constant. When $t = 0$, C_{HE} is equal to $C_{HE,t=0}$ and the solution of the Eq. (10) becomes

$$\ln \frac{C_{HE}}{C_{HE,t=0}} = -k'_{HE} t. \quad (11)$$

Pseudo first-order rate constants can be obtained through a linear least square fit of the sample data to Eq. (11).

3.2. Temperature dependence of RDX and HMX oxidation

A series of batch experiments was conducted to determine the temperature dependence of RDX and HMX oxidation with Fenton's reagents. Since the maximum solubility at 25°C is only 60 mg-RDX/L and 5 mg-HMX/L [26], initial conditions were fixed to 0.045 mmol/L (10 mg/L) for RDX and 0.015 mmol/L for HMX (4.5 mg/L). $[H_2O_2]_o$ and $[Fe^{2+}]$ concentrations were 233. 0, 2.16 mmol/L for RDX, and 77.6, 0.72 mmol/L for HMX, respectively. The pH was fixed at 3.0 and experiments were performed at temperatures 20°C, 25°C, 30°C, 40°C, and 50°C.

Fig. 1 shows the results of RDX Fenton oxidation at different temperatures. At 25°C and pH 3, oxidation of RDX is very fast, and after 70 min, only 10% of RDX remains. At higher temperatures, the rate is still greater. Similar results were obtained for HMX oxidation, but the rate of HMX oxidation is only about 1/3 the rate of the RDX reaction. Fig. 2 and Table 1 show the rates of oxidation of RDX and HMX. These show excellent agreement between pseudo first-order reaction mechanism and observations over the temperature range (20–50°C); R^2 ranges from 0.994 to 0.999.

The temperature dependence of the observed rate constants can be represented by the Arrhenius equation, as follows:

$$k = A \exp(E_a/RT), \quad (12)$$

where A is the frequency factor, E_a is the activation energy, T the temperature, R the gas constant. Fig. 3 shows the Arrhenius plot of the reaction rate constant for RDX and HMX oxidation. As shown in this figure, the E_a/R value is 6286 for RDX, and 5826 for HMX, and therefore activation energy of Fenton oxidation for RDX and HMX is 0.76 and 0.70 kJ/mol, respectively. Few studies have dealt with the effect of temperature in Fenton oxidation. These low activation energies values are well matched with other results [27,28], and are

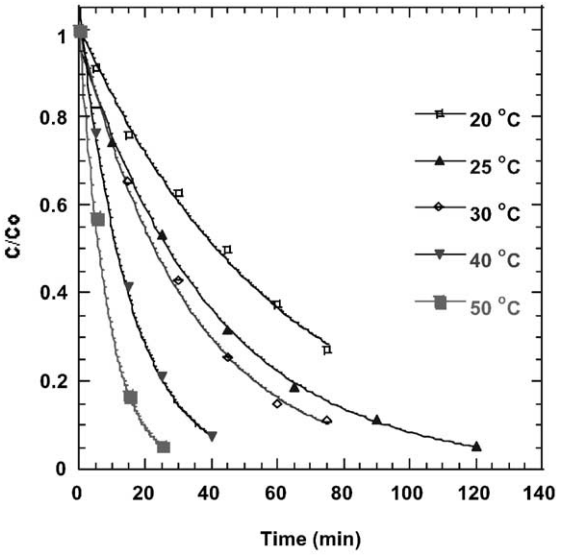

Fig. 1. Fenton oxidation of RDX at different temperatures. ([RDX] = 0.045 mmol/L, $[Fe^{2+}]$ = 2.16 mmol/L, $[H_2O_2]$ = 233.0 mmol/L, pH = 3).

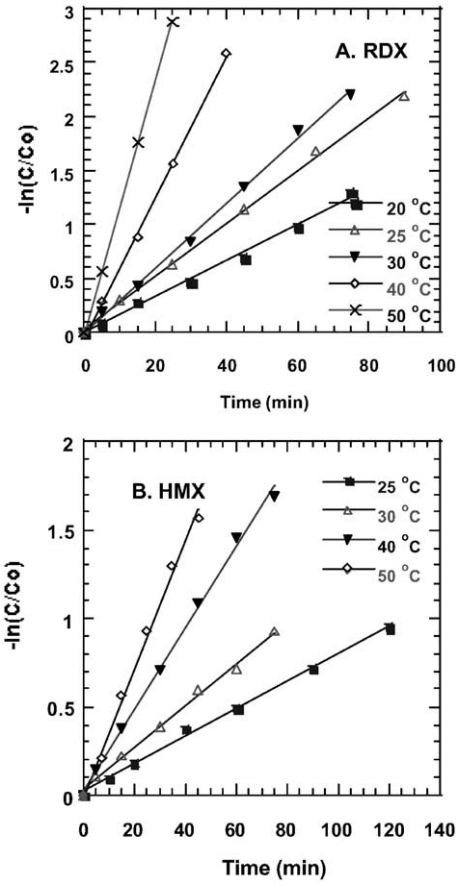

Fig. 2. Temperature dependence of Fenton oxidation rate constant at pH = 3 ([RDX] = 0.045 mmol/L, $[Fe^{2+}]$ = 2.16 mmol/L, $[H_2O_2]$ = 233.0 mmol/L; [HMX] = 0.015 mmol/L, $[Fe^{2+}]$ = 0.72 mmol/L, $[H_2O_2]$ = 77.6 mmol/L).

Table 1
Pseudo first-order rate constants (min^{-1}) of Fenton oxidation of RDX and HMX at different temperatures

T (°C)	RDX	R^2	HMX	R^2
20	0.0167	0.994		
25	0.0241	0.998	0.0080	0.994
30	0.0294	0.997	0.0119	0.995
40	0.0647	0.998	0.0239	0.999
50	0.1159	0.999	0.0358	0.996

possibly caused by the initial step (Eq. (1)) of Fenton Oxidation to generate hydroxyl radical, which is the rate determining limiting step.

3.3. Changing Fenton's reagent concentration

Since the primary factor contributing to the chemical costs of Fenton's reagent is the cost of H_2O_2, it is important to minimize the H_2O_2 required, especially for treating large volumes, such as RDX and HMX contaminated soils. Also, using too high concentration of Fenton reagent may result in excessive iron sludge. For these reasons, the impacts of changing Fe^{2+} or H_2O_2 concentration on Fenton oxidation of RDX and HMX were investigated.

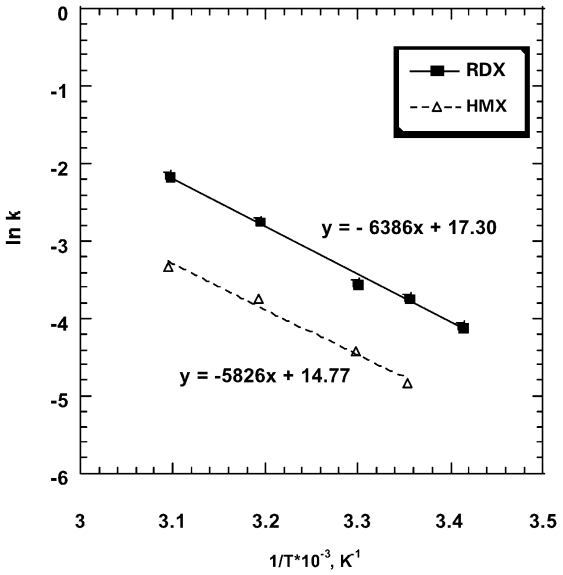

Fig. 3. Arrhenius plot of Fenton oxidation rate constants.

In the first series of experiments using HMX, H_2O_2 concentration was increased from 7.76 to 77.6 mmol/L while maintaining Fe^{2+} concentration at 0.72 mmol/L. The second series of experiments was performed with increasing Fe^{2+} concentration from 0.36 to 2.16 mmol/L, while keeping H_2O_2 concentration at 77.6 mmol/L. Initial HMX concentration was 4.5 mg/L, and the temperature was 30°C in both series. The results showed that the reaction rate was not significantly improved with these concentration changes (Table 2).

A third series of experiments was performed with RDX and HMX by proportionally increasing both Fe^{+2} and H_2O_2 concentrations. The H_2O_2/Fe^{2+} molar ratio was maintained 108, and the temperature was 25°C. Tables 3 and 4 show the results. As both concentrations increased, the rate constant increased from 0.024 to 0.061 min^{-1} for RDX oxidation, and from 0.008 up to 0.03 min^{-1} for HMX oxidation.

3.4. Byproducts of Fenton oxidation

Previous researchers often reported only the disappearance of explosives, and neglected to determine byproducts. Byproducts must be determined since unmineralized byproducts can be benign or in some

Table 2
Reactions rates of HMX at varying Fenton reagent concentration at pH = 3 (Temperature = 30°C)

H_2O_2 concentration (mmol/L)	Fe^{+2} concentration (mmol/L)	$[H_2O_2]/[Fe^{+2}]$ ratio	Reaction rate (min^{-1})
7.76	0.72	10.8	0.0154
38.8	0.72	53.9	0.0136
77.6	0.72	108	0.0120
77.6	0.36	216	0.0154
77.6	2.16	35.9	0.0195

Table 3
Reaction rates of RDX when changing both Fe^{2+} and H_2O_2 concentration at pH = 3 (Temperature = 25°C)

H_2O_2 concentration (mmol/L)	Fe^{+2} concentration (mmol/L)	$[H_2O_2]/[Fe^{+2}]$ ratio	Reaction rate (min^{-1})
233	2.16	108	0.0241
582.5	5.40	108	0.0229
1165	10.80	108	0.0613

Table 4
Reaction rates of HMX when changing both Fe^{2+} and H_2O_2 concentration at pH = 3 (Temperature = 25°C)

H_2O_2 concentration (mmol/L)	Fe^{+2} concentration (mmol/L)	$[H_2O_2]/[Fe^{+2}]$ ratio	Reaction rate (min^{-1})
77.6	0.72	108	0.0080
194	1.80	108	0.0159
776	7.20	108	0.0292

cases more problematic than the parent compound. Several series of experiments was performed to determine byproducts.

Nitrate (NO_3^-) was easily identified as a byproduct in both RDX and HMX oxidation using ion chromatography. Fig. 4 shows the kinetics of RDX and HMX degradation and NO_3^- formation by Fenton oxidation. The molar yields are approximately 1.5 M NO_3^- formed/M RDX oxidized and 1.75 M NO_3^- formed/M HMX oxidized. The timing of NO_3^- appearance and RDX or HMX disappearance suggests that is a direct reaction product formed during the first reaction step. It is likely that NO_2^- is the actual byproduct, but is then quickly oxidized to NO_3^-. No nitrite was observed in any or byproduct experiments with RDX or HMX. Therefore, nitrate can be chosen as a surrogate parameter to indicate reaction rate during Fenton oxidation.

Nitrate production accounted for only 25% and 22% of the nitrogen in RDX and HMX, respectively. Visible gas evolution from the reaction vessels suggested gaseous byproducts. Therefore, we analyzed the evolved gas during the oxidation using a GC with thermal conductivity detector. From the analysis, gas composition in the syringes from RDX oxidation was 0.41% N_2 and 0.07% CO_2, and the rest was mainly oxygen. Gas composition from HMX oxidation was 0.34% N_2 and 0.08% CO_2, and the rest was also mainly oxygen. The CO_2 data were abandoned because the concentrations were below the quantification limits of the chromatograph. The results indicated that N_2 is produced when the $-N=N-$ bond in RDX and HMX is cleaved from Fenton oxidation. In fact, N_2 gas evolution has been observed in the hydrolysis of azo-dyes containing $-N=N-$ bond [29].

Nitrogen molar yields were calculated from the nitrate results and the nitrogen contained in the evolving gas. The ideal-gas law was used to calculate the mass of nitrogen contained in the evolved gas. Table 5 shows the total nitrogen balance, and is close to 100% for RDX but only 70% for HMX. The result of producing nitrate and nitrogen gas from each oxidation implicates that RDX and HMX oxidation occur through the same mechanism. The difference of the nitrogen recovery in RDX and HMX may be due to experimental precision; the lower solubility of HMX makes the experiments more difficult to perform, since the evolved gas is less.

Another series of experiments was performed while measuring the total organic carbon (TOC) from Fenton oxidation of RDX. Fig. 5 shows TOC removal vs time during oxidation at pH 3.0 containing 20 mg/L (0.090 mmmol/L) of RDX. Approximately 85% of TOC was removed after 8 h of oxidation. This experiment was repeated and the same results were obtained. It was not possible to perform TOC measurement

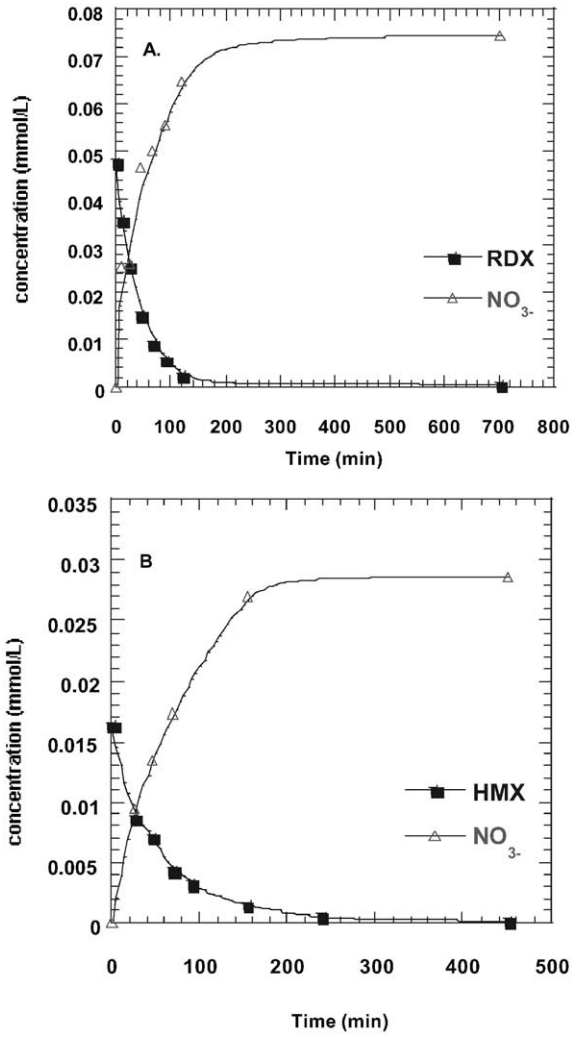

Fig. 4. The kinetics of RDX and HMX degradation and NO_3^- formation by Fenton oxidation ([RDX] = 0.045 mmol/L, $[Fe^{2+}]$ = 2.16 mmol/L, $[H_2O_2]$ = 233.0 mmol/L; [HMX] = 0.015 mmol/L, $[Fe^{2+}]$ = 0.72 mmol/L, $[H_2O_2]$ = 77.6 mmol/L).

during HMX oxidation due to the lower initial HMX concentration because of its reduced solubility. This is indirect evidence of RDX mineralization.

Finally, in order to document the presence of nonvolatile organic byproducts from Fenton oxidation, the reaction endproducts of RDX and HMX were extracted using liquid–liquid extraction (LLE), and were analyzed by GC/MS. The organic intermediates or end products, if extractable by dichloromethane, can be detected with this method. First, a comprehensive set of blank samples was extracted with LLE and analyzed with GC/MS. The blank included LLE system blanks (100-mL of dichloromethane with no sample), deionized water (500 mL of deionized water), and reagent system

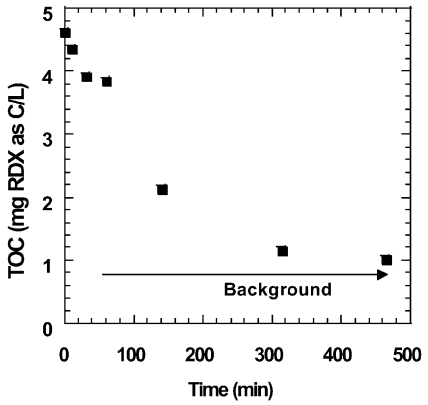

Fig. 5. TOC change during oxidation of RDX using Fenton's reagent. ([RDX] = 0.090 mmol/L, $[Fe^{2+}]$ = 4.32 mmol/L, $[H_2O_2]$ = 466 mmol/L).

blanks containing the same concentration of Fenton reagent except no RDX or HMX. These blank samples were extracted for 6 h, and analyzed with GC/MS. Also, GC/MS system blanks (GC/MS injection of pure Optima-grade dichloromethane, Fisher Scientific) were analyzed at various stages in the experiment to detect any system changes or contamination. Fig. 6 compares Fenton reagent system blank (most complicated blank chromatogram) and the reaction products from RDX and HMX oxidation. Compared with these blank chromatograms, only the internal standards and documented laboratory contaminants (cyclotetra-siloxane) were observed in RDX and HMX reaction endproducts; no byproducts were present.

Samples were next analyzed using a purge and trap GC/MSD to detect volatile carbon byproducts. Again, only known laboratory contaminants were observable. It should be noted that this instrument does not detect formaldehyde or formic acid.

3.5. Radiolabeled RDX experiment

Radiolabeled RDX was used to further investigate mineralization. $^{14}CO_2$ was captured from oxidation of radiolabeled RDX using three series of scintillation cocktails containing β-phenylethylamine. The reaction solution was purged with nitrogen gas during the reaction. After the reaction was finished, ^{14}C was measured in the scintillation cocktails and the reaction bottle. Table 6 shows that about 37% of the ^{14}C was mineralized to CO_2 while 38% remained in the final liquid, to produce a total recovery of 75%. These results suggested two phenomena: a significant amount of the carbon in the RDX was indeed being mineralized to CO_2, and the presence of a reaction byproduct that is purgeable in the TOC analysis, but not purgeable during the $^{14}CO_2$ recovery.

Table 5
Normalized molar yields for products of Fenton oxidation of RDX and HMX (Results from liquid and gas analysis)

Byproducts	1 M RDX (6 nitrogen)	1 M HMX (8 nitrogen)
NO_3^-	1.50 M	1.75 M
N_2	2.36 M (4.72 M for nitrogen atom)	1.94 M (3.88 M for nitrogen atom)
Total nitrogen recovery (%)	107%	70.4%

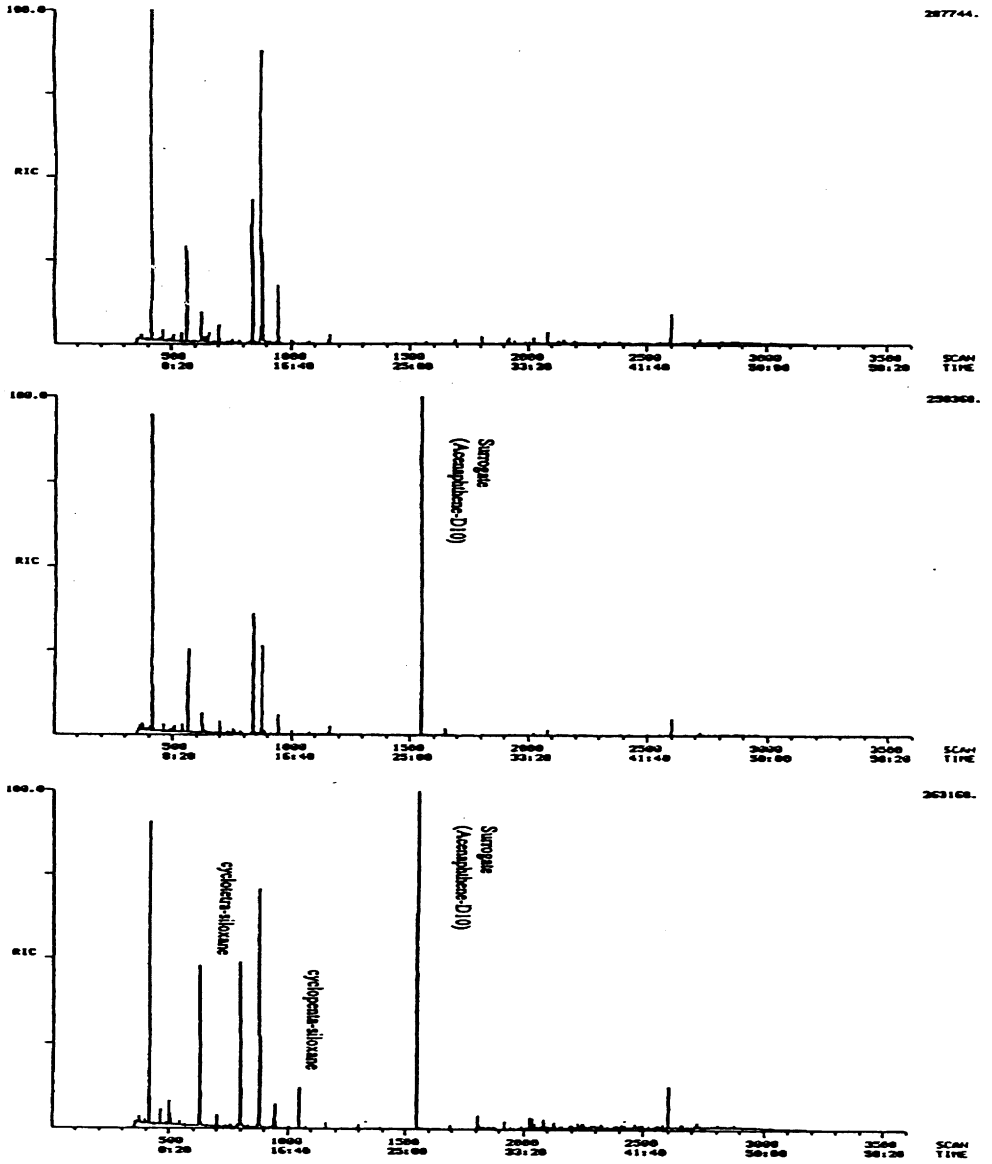

Fig. 6. GC/MS chromatogram for Fenton oxidation of RDX and HMX. [(A) System blank (Fenton reagents in deionized water without explosives). (B) HMX reaction products. (C) RDX reaction products.]

Table 6
Mineralization study using ^{14}C-RDX

Source	CPM (^{14}C)
Initial solution	306259
Sum of CO_2 in three series of CO_2 capture bottle	114627
Final solution	113716
	%
^{14}C percent as CO_2	37%
^{14}C percent in final solution	38%
Total ^{14}C recovery	75%
^{14}C lost	25%

The mineralization result can be compared with [30,31] studies which found no mineralization using various AOP technologies (UV, UV/H_2O_2, O_3, O_3/H_2O_2, and UV/ozone). They observed no carbon mineralization but did determine that approximately 50% of the nitrogen was converted to nitrate.

3.6. Formyl intermediates identification

A final series of experiments was performed to determine the liquid phase intermediate observed in the $^{14}CO_2$ recovery experiments. Likely candidates are formic acid or formaldehyde because RDX contains three carbons in the ring, and each carbon exists with nitrogen alternatively. Formaldehyde is also a byproduct from alkaline hydrolysis of RDX [32]. We analyzed formaldehyde using the modification of aldehyde and ketone group identification method of Patnaik [19] and Zoh et al. [20]. 2,4-dinitrophenylhydrazone is produced by the reaction with aldehyde and ketones and can be detected by HPLC.

We observed an HPLC peak corresponding to 2,4-dinitrophenylhydrazone during the reaction. However, this peak existed for a very short time, always disappearing with time, and was not quantifiable. This suggests that Fenton oxidation of RDX can produce either formaldehyde or other aldehydes as an intermediate. Previous researchers have shown that formaldehyde can be converted to formic acid, and finally to CO_2 by Fenton's reagent [33]. This result may also explain the difference between TOC reduction (85%) and CO_2 evolution (37%) from ^{14}C experiment. TOC analysis is performed at pH 1 to strip inorganic carbon, and $^{14}CO_2$ recovery experiment is performed at pH 3. Since the pKa of formic acid is 3.75, formic acid would be essentially 100% unionized at pH 1, and therefore more purgeable than at pH 3.

To determine the presence of formic acid, a series of Fenton oxidations were performed at higher RDX concentration. The concentration of RDX was increased to 20 mg/L to increase the byproduct concentration to increase the likelihood of finding it. The same ratio of Fenton reagent to RDX was maintained in this experiment. From the ion chromatograph, a peak corresponding to formic acid was observed during the reaction. Formic acid was added to reaction samples to verify retention times; only one peak at the same retention time was observed after adding formic acid. The concentration of formic acid increased during the reaction and then decreased; a small residual formic acid peak remained after 600 min. After performing these experiments, we learned of work of Bier et al. [34], who observed formic acid production when treating RDX-containing soils with Fenton's reagent.

3.7. Proposed mechanism

Based on these findings, we suggest a general pathway for mineralization of RDX to CO_2 at pH 3.0 with Fenton's reagent. The suggested pathway is shown in Fig. 7. In the Fenton oxidation, the main oxidizing species is known to be $^{\bullet}OH$, although some reactions with $HO_2^{\bullet}$ could also be present. The mineralization process can be initiated by hydrogen abstraction of carbon from RDX by hydroxyl radical. The resulting carbon radical can undergo the destruction of N = N bond, and can produce $^{\bullet}NO_2$ radical. This $^{\bullet}NO_2$ radical can further react with $^{\bullet}OH$ to release of NO_3^-, which we observed by ion chromatography.

Another pathway is for the carbon radical to accept another $^{\bullet}OH$, to form $^{\bullet}CHOH$. This radical can be further transformed to formaldehyde (HCHO), and further to formic acid (HCOOH), which we also identified from the experiment. This functional group finally will be transformed to CO_2 as shown in Eq. (13).

$$HCOH + {}^{\bullet}OH \rightarrow HCOOH + {}^{\bullet}OH \rightarrow CO_2. \quad (13)$$

Finally, N_2 can be produced when the C–N bond in the ring and N–O bond in nitro group are cleaved by the carbon radical.

4. Conclusions

The results show that dissolved RDX and HMX can be effectively oxidized with Fenton's reagent. The following conclusions are made;

- The degradation of RDX and HMX by the Fenton oxidation is rapid at between 20°C and 50°C. 90% of RDX was degraded in 70 min at 25°C. The rate of reaction with HMX is approximately 1/3 as rapid.
- The process can be modeled as a pseudo-first-order process when Fe^{2+} and H_2O_2 are in excess.
- The reaction rate was not particularly sensitive to the $H_2O_2 : Fe^{2+}$ ratio, but was more rapid when both $H_2O_2 : Fe^{2+}$ ratio were increased. A $H_2O_2 : Fe^{2+}$: RDX ratio of 5178 : 48 : 1 was used for most experiments.

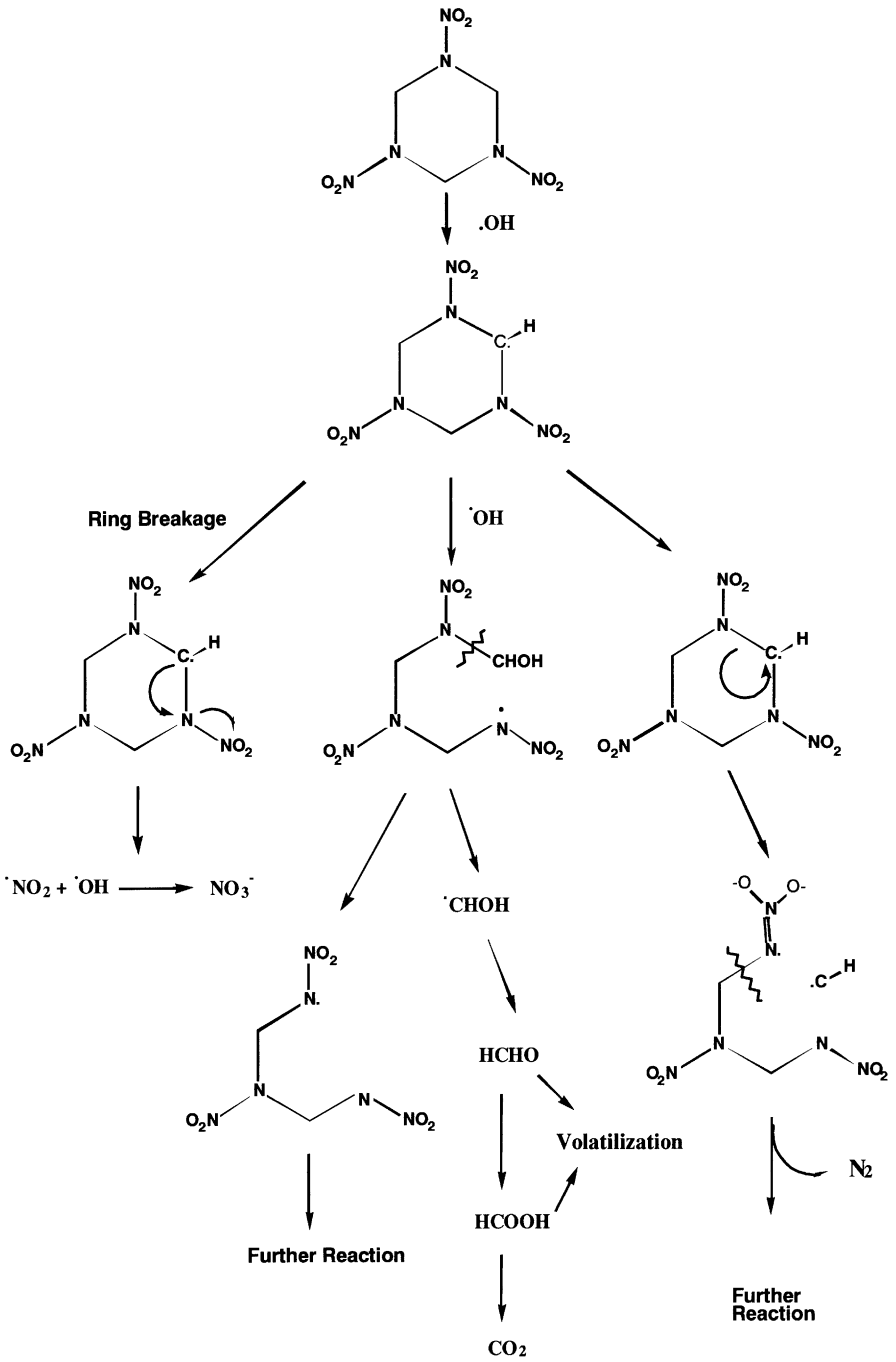

Fig. 7. Proposed mechanism of Fenton oxidation of RDX.

- The reaction rate coefficient was strongly dependent on temperature.
- Nitrate and nitrogen gas were identified as the nitrogen byproducts of RDX and HMX oxidation.
- 37% carbon mineralization was documented in ^{14}C experiments.
- A short-lived formyl group containing either formaldehyde or formic acid was qualitatively identified. Small amounts of formic acid were observed during the end of the experiment, and traces remained after the reaction was complete. No other chromatographable products were observed. Formic acid is a desirable byproduct since it is easily biodegraded.

- Fenton's reaction could be an attractive method for treating wastewater containing explosives, or contaminated groundwater and soils containing explosives.

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