3-31-2011

Transformation of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by Permanganate

Chanat Chokejaroenrat
University of Nebraska-Lincoln

Steven Comfort
University of Nebraska - Lincoln, scomfort1@unl.edu

Clifford E. Harris
Albion College

Daniel D. Snow
University of Nebraska-Lincoln, dsnow1@unl.edu

David A. Cassada
University of Nebraska-Lincoln, dcassada1@unl.edu

See next page for additional authors

Follow this and additional works at: http://digitalcommons.unl.edu/watercenterpubs

Part of the Water Resource Management Commons

Chokejaroenrat, Chanat; Comfort, Steven; Harris, Clifford E.; Snow, Daniel D.; Cassada, David A.; Sakulthaew, Chainarong; and Satapanajaru, Tunlawit, "Transformation of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by Permanganate" (2011). Faculty Publications from The Water Center. Paper 22.
http://digitalcommons.unl.edu/watercenterpubs/22

This Article is brought to you for free and open access by the Water Center, The at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Faculty Publications from The Water Center by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.
Authors
Chanat Chokejaroenrat, Steven Comfort, Clifford E. Harris, Daniel D. Snow, David A. Cassada, Chainarong Sakulthaew, and Tunlawit Satapanajaru

This article is available at DigitalCommons@University of Nebraska - Lincoln: http://digitalcommons.unl.edu/watercenterpubs/22
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is a common groundwater contaminant at numerous military sites where munitions were either formulated, manufactured, or used in military exercises. Permanganate (MnO$_4^-$) is an oxidant commonly used with in situ chemical oxidation (ISCO) and has been widely accepted for treating chlorinated ethenes. Past research has shown that MnO$_4^-$ preferentially attacks compounds with carbon−carbon double bonds, aldehyde groups, or hydroxyl groups and is attracted to the electron-rich region of chlorinated alkenes.(1) Although RDX possesses none of these characteristics, laboratory studies performed by Adam et al.(2) showed that MnO$_4^-$ could effectively transform and mineralize RDX (i.e., ~87% recovered as $^{14}$CO$_2$). Moreover, a pilot-scale demonstration at the Nebraska Ordnance Plant further supported MnO$_4^-$ as a possible in situ treatment for RDX-contaminated groundwater.(3) Despite demonstrating efficacy in removing RDX from tainted waters, the reaction rates and mechanisms by which MnO$_4^-$ transforms RDX (and other explosives) have not been thoroughly studied.(4) While a carbon mass balance of the RDX−MnO$_4^-$ reaction has been observed,(2) a similar nitrogen mass balance for this reaction has not been reported.

Transformation of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by Permanganate

Chanat Chokejaroenrat,1 Steve D. Comfort,2 Clifford E. Harris,3 Daniel D. Snow,4 David Cassada,4 Chainarong Sakulthaew,2,5 and Tunlawit Satapanajaru 6

1. Department of Civil Engineering, University of Nebraska–Lincoln, Lincoln, Nebraska 68588-0531, USA
2. School of Natural Resources, University of Nebraska–Lincoln, Lincoln, Nebraska 68583-0915, USA
3. Department of Chemistry, Albion College, Albion, Michigan 49224, USA
4. Water Sciences Laboratory, University of Nebraska–Lincoln, Lincoln, Nebraska 68583-0844, USA
5. Department of Veterinary Technology, Kasetsart University, Bangkok, Thailand 10900
6. Department of Environmental Science, Kasetsart University, Bangkok, Thailand 10900

Corresponding author — S. D. Comfort, tel 402 472-1502, fax 402 472-7904, email scomfort@unl.edu

Abstract

The chemical oxidant permanganate (MnO$_4^-$) has been shown to effectively transform hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) at both the laboratory and field scales. We treated RDX with MnO$_4^-$ with the objective of quantifying the effects of pH and temperature on destruction kinetics and determining reaction rates. A nitrogen mass balance and the distribution of reaction products were used to provide insight into reaction mechanisms. Kinetic experiments (at pH ~7, 25 °C) verified that RDX−MnO$_4^-$ reaction was first-order with respect to MnO$_4^-$ and initial RDX concentration (second-order rate: 4.2 × 10$^{-5}$ M$^{-1}$ s$^{-1}$). Batch experiments showed that choice of quenching agents (MnSO$_4$, MnCO$_3$, and H$_2$O$_2$) influenced sample pH and product distribution. When MnCO$_3$ was used as a quenching agent, the pH of the RDX−MnO$_4^-$ solution was relatively unchanged and N$_2$O and NO$_3^-$ constituted 94% of the N-containing products after 80% of the RDX was transformed. On the basis of the preponderance of N$_2$O produced under neutral pH (molar ratio N$_2$O/NO$_3^-$~5:1), no strong pH effect on RDX−MnO$_4^-$ reaction rates, a lower activation energy than the hydrolysis pathway, and previous literature on MnO$_4^-$ oxidation of amines, we propose that RDX−MnO$_4^-$ reaction involves direct oxidation of the methylene group (hydride abstraction), followed by hydrolysis of the resulting imides, and decarboxylation of the resulting carboxylic acids to form N$_2$O, CO$_2$, and H$_2$O.

Introduction

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is a common groundwater contaminant at numerous military sites where munitions were either formulated, manufactured, or used in military exercises. Permanganate (MnO$_4^-$) is an oxidant commonly used with in situ chemical oxidation (ISCO) and has been widely accepted for treating chlorinated ethenes. Past research has shown that MnO$_4^-$ preferentially attacks compounds with carbon−carbon double bonds, aldehyde groups, or hydroxyl groups and is attracted to the electron-rich region of chlorinated alkenes.(1) Although RDX possesses none of these characteristics, laboratory studies performed by Adam et al.(2) showed that MnO$_4^-$ could effectively transform and mineralize RDX (i.e., ~87% recovered as $^{14}$CO$_2$). Moreover, a pilot-scale demonstration at the Nebraska Ordnance Plant further supported MnO$_4^-$ as a possible in situ treatment for RDX-contaminated groundwater.(3) Despite demonstrating efficacy in removing RDX from tainted waters, the reaction rates and mechanisms by which MnO$_4^-$ transforms RDX (and other explosives) have not been thoroughly studied.(4) While a carbon mass balance of the RDX−MnO$_4^-$ reaction has been observed,(2) a similar nitrogen mass balance for this reaction has not been reported.

One analytical challenge to identifying degradation products in a MnO$_4^-$ matrix is that the solution is highly colored (i.e., purple), so colorimetric and UV detection techniques are not possible unless samples are quenched to remove MnO$_4^-$ before analysis. However, the choice of quenching agent may influence pH or product distribution and further complicates understanding the RDX−MnO$_4^-$ reaction mechanism.

The transformation of RDX by various treatments has revealed several possible reaction pathways. These include direct ring cleavage, nitro-group reduction, concerted decomposition, and N-denitration.(5-12) While intermediates produced by some of these pathways are fleeting and difficult to mea-
sure, the end products produced are often similar (N₂O, NO₃⁻, NO₂⁻, NH₄⁺) but produced in different ratios depending on the reaction mechanisms. In this paper, we report results from laboratory investigations designed to describe the kinetics of the RDX–MnO₄⁻ interaction, quantify the effect of temperature on RDX destruction kinetics, and provide a nitrogen mass balance of the RDX–MnO₄⁻ reaction. On the basis of experimental results, possible mechanisms by which RDX is degraded by MnO₄⁻ are proposed.

**Experimental Section**

Details of the chemical standards, analytical instruments (e.g., HPLC, IC, GC/ECD, and UV spectrophotometer), analysis of N-containing gases, RDX purification procedures used for mass balance experiments, and experimental controls are provided in Supporting Information (SI-1, SI-2, SI-3).

**Aliquot Sample Preparation.** To accurately quantify RDX and degradation product concentrations during oxidation by MnO₄⁻, samples were quenched to prevent further RDX transformation. To avoid interference during RDX and degrade analyses, three different quenching agents were tested (MnSO₄, MnCO₃, and H₂O₂). The choice of quenching agent was found to influence pH and product distribution (see Supporting Information, SI-4). The two quenching agents we used most frequently included MnCO₃ (0.10 g per mL of sample unless otherwise stated) and MnSO₄·H₂O [0.10 mL of a MnSO₄ solution (0.10 g/mL) per mL of sample]. The typical quenching procedure involved removing 1-mL aliquots from the RDX–MnO₄⁻ batch reactors, placing the aliquots in a 1.5-mL centrifuge tube, adding the quenching agent, and centrifuging at 14,000 rpm for 10 min. When MnCO₃ was used, an addition 5 min of shaking on a vortex was performed before centrifuging. The supernatant was then transferred to an HPLC or an IC vial and stored at 4 °C until analysis.

**RDX Kinetic Experiments.** Kinetic experiments were performed under batch conditions by placing 150 mL of RDX solution in 250-mL Erlenmeyer flasks and agitating on an orbital shaker. Solution samples were taken every 2−3 d, quenched with MnSO₄, and analyzed for RDX by HPLC. We initially prepared RDX solutions by spiking 150 mL of H₂O with 1.04 mL of RDX stock solutions prepared in acetone, but held constant for 2−3 h prior to the start of the experiment. Reaction rates were determined by the initial rate method. The rate law describing a second-order reaction between RDX and MnO₄⁻ was 0.98 ± 0.06 ([MnO₄⁻]₀). By plotting log[kₚri] versus log [MnO₄⁻]₀ (Figure 1A), the calculated slope (b) of this regression was 0.98 ± 0.06 (r² = 0.99) and indicates that reaction was first-order with respect to MnO₄⁻. Likewise, kinetic experiments estimated the reaction order with respect to RDX (a). Upon treatment of varying RDX concentrations with 33.61 mM MnO₄⁻, the initial reaction rates (rₚri) based on Equation S8 were approximated from the tangent of the concentration–time curves (Figure S12). The log of the initial reaction rate (log[rₚri]) was plotted against initial RDX concentration to es-

**4-NDAB Experiments.** To determine the stability of 4-NDAB in the presence of MnO₄⁻, we conducted batch experiments with 4-NDAB as the starting substrate. Batch experiments were performed in a 250-mL Erlenmeyer flask containing 100 mL of 4-NDAB (0.04 mM) covered with parafilm and agitated with an orbital shaker at ambient temperature (24 °C). 4-NDAB was treated with 4.20, 8.40, 16.81, and 33.61 mM of MnO₄⁻. Samples were collected every 30 min and quenched with MnCO₃ as previously described. 4-NDAB was immediately analyzed by HPLC.

**RDX Nitrogen Mass Balance Experiment.** Aqueous RDX (0.10 mM) prepared from purified RDX was placed into a 10-mL serum vial (Wheaton, Millville, NJ). The vial was closed with a silicone septum with zero headspace and crimped with an aluminum cap. So that we could precisely calculate the nitrogen mass balance, each vial was weighed before and after introducing any chemicals. Once the vial was sealed, a 21G (i.e., needle gauge no. 21) needle and a 3-mL syringe were inserted through the septum. Helium gas was then added to the 21G needle to push out 2.5 mL of solution into the 3-mL syringe. The 21G needle was removed and another syringe was inserted into the He headspace where MnO₂⁻ stock solution was introduced to produce an initial concentration of 33.61 mM. Because the added MnO₂⁻ stock replaced a portion of the He headspace gas back into the 3-mL syringe, experimental treatments began at ambient pressure (t = 0 d). Vials were again weighed to determine the precise volume of solution and headspace in each replicate. To avoid possible gas losses through the needle-end-of-septa, the septa were sealed with thermoplastic adhesive. Each vial was then covered with aluminum foil to prevent MnO₄⁻ photodegradation (14, 15) before shaking on a reciprocal shaker until analysis.

Saccharification sampling occurred at 0, 1, 2, 3, 6, 9, 15, 19, 23, and 28 d. Each replicate (n = 4) was used to analyze three different types of analytes. For N₂O gas production, 0.5 mL of headspace gas was removed and injected directly into GC/ECD. For changes in solution concentrations of RDX and NO₃⁻/NO₂⁻, 2.0 mL of sample were quenched with MnCO₃. One aliquot (1.0 mL) was analyzed by HPLC while the other was used to quantify NO₃⁻/NO₂⁻ by IC. Each replicate solution was also analyzed for MnO₂⁻ with a UV spectrophotometer to ensure uniformity in MnO₂⁻ concentrations among replicates.

**Results and Discussion**

**RDX Kinetics Experiments.** Treating aqueous RDX with varied MnO₂⁻ concentrations resulted in a wide range of RDX destruction rates (i.e., pseudo-first-order rate, k = 0.02−0.37 d⁻¹, Figure S11A). By plotting log(kₚri) versus log [MnO₂⁻]₀ (Figure 1A), the calculated slope (b) of this regression was 0.98 ± 0.06 (r² = 0.99) and indicates that reaction was first-order with respect to MnO₂⁻. Likewise, kinetic experiments estimated the reaction order with respect to RDX (a). Upon treatment of varying RDX concentrations with 33.61 mM MnO₂⁻, the initial reaction rates (rₚri) based on Equation S8 were approximated from the tangent of the concentration–time curves (Figure S12). The log of the initial reaction rate (log[rₚri]) was plotted against initial RDX concentration to es-
Transformation of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by Permanganate

3645

estimated reaction order for RDX (α). Results indicated α values very close to 1, also verifying the reaction is first-order with respect to RDX (Figure 1B).

Both sets of kinetic experiments (Figure 1) demonstrate that the initial reaction between RDX and MnO$_4^-$ is second-order (i.e., α = β = 1) with a rate constant ($k''$) of 4.16 × 10$^{-5}$ M$^{-1}$ s$^{-1}$ (±0.22 × 10$^{-5}$) (Equation S6). A compilation of destruction rates of various contaminants by MnO$_4^-$ revealed that a number of contaminants may react with MnO$_4^-$ as fast as or faster than the chlorinated ethenes, the groundwater contaminants most commonly treated by MnO$_4^-$. One of those contaminants reported to have a second-order rate constant similar to that of the chlorinated ethenes was TNT. Given that TNT and RDX are often cocontaminants in the field, a parallel set of kinetic experiments were performed with TNT (see Supporting Information, Figures S11B and S13). These experiments concluded that the TNT-MnO$_4^-$ reaction is first-order with respect to TNT and MnO$_4^-$ or second-order overall (Figure S14) with a $k''$ of 1.18 × 10$^{-3}$ M$^{-1}$ s$^{-1}$ (±0.02 × 10$^{-3}$). While the second-order rate constant observed for RDX in this study is similar to those reported, our $k''$ for TNT is lower than that reported by Waldemer and Tratnyek (0.03 M$^{-1}$ s$^{-1}$) but still 28-fold higher than what we observed for RDX, indicating a large difference in reactivity between these two explosives. This observation is perhaps not surprising and undoubtedly related to differences in chemical classes (nitramine vs nitroaromatic).

Effect of Temperature on RDX-MnO$_4^-$ Reaction. Albano et al.(3) previously reported that RDX transformation rates were slowed 3-fold under temperatures indicative of aquifer conditions (11.5 vs 23 °C). We treated aqueous RDX with MnO$_4^-$ at four temperatures to further elucidate the temperature dependency of the reaction at elevated temperatures. Results showed the RDX destruction rates were significantly increased with increasing temperature with pseudo-first-order rates ranging from 0.01 to 0.89 d$^{-1}$ (Figure 2A). At 20 °C, RDX concentration was only reduced by 30% after 30 d ($k = 0.01$ d$^{-1}$) while complete RDX transformation (100%) was achieved within 6 d at 65 °C ($k = 0.89$ d$^{-1}$). A comparison of
controls (temperature only) showed that RDX was relatively stable at temperatures ≤50 °C but decreases in RDX concentrations were observed at 65 °C, albeit at a slower rate than when MnO$_4^-$ was also present (Figure 2B). A comparison of previously reported destruction rates shows that, in order to get the destruction rate we observed at 65 °C with 4.20 mM MnO$_4^-$, Adam et al. (2) needed 168 mM MnO$_4^-$ at room temperature (a 40-fold higher concentration).

Computed pseudo-first-order constants (k$_{obs}$ Figure 2A) were converted to second-order rate constants at β = 1 based on Equation S6 (see Supporting Information, SI-6, SI-7, and Table S2). The temperature dependency was further calculated by using an Arrhenius plot (Figure 3). The activation energy for the reaction between RDX and MnO$_4^-$ in the temperature range 20–65 °C was 77.48 ± 5.13 kJ/mol (Figure 3) with an Arrhenius parameter (i.e., In A) of 25.77 ± 1.96 L/mol min. For comparison, the temperature dependency of RDX hydrolysis from previously published work is also plotted (Figure 4) versus days for RDX (Figure S6A). 4-NDAB is likely oxidized faster than RDX because oxidation of the formamide group to a carbamic acid and the subsequent decarboxylation are known to be very fast reactions. (22-24) While 4-NDAB was found to be a dead-end product of RDX via photodestruction, (8) aerobic biodegradation, (5) and alkaline hydrolysis, (6) we showed that it was not stable in MnO$_4^-$ (Figure 4).

Treatment of 4-NDAB with MnO$_4^-$ also produced N$_2$O. A separate N-mass balance attempt showed that >50% of the N in 4-NDAB was converted to N$_2$O. In contrast to what was observed with RDX (see below), NO$_3^-$ was not formed in the 4-NDAB–MnO$_4^-$ reaction.

4-NDAB Experiments. Past research has shown that 4-NDAB is an RDX degradation product after ring cleavage for both abiotic and biological treatments. (8, 9, 16) such as aerobic biodegradation (16-19) and alkaline hydrolysis. (6) In aerobic degradation, 1 mol of RDX yields 1 mol of 4-NDAB and 2 mols of NO$_3^-$. (20) Adam et al. (2, 21) also separately reported observing 4-NDAB during treatment with MnO$_4^-$ or ozone. While Adam et al. (2) also used peroxide to quench MnO$_4^-$, which would explain the detection of 4-NDAB (Figure S6B), their experiments with ozone required no quenching agent. (21) A question surrounding 4-NDAB detection during RDX degradation is whether it is formed during the RDX–MnO$_4^-$ reaction or if it is just a product of the quenching process (see Supporting Information, SI-4).

Because only a trace of 4-NDAB (Figure S6) was observed in the RDX–MnO$_4^-$ reaction when MnCO$_3$ was used as a quenching agent, additional explanations for its lack of detection were pursued. In testing the stability of 4-NDAB under the different pH values, we found that 4-NDAB was relatively stable for the first 10 d (>90% remaining) (Figure S8). Therefore, the stability of NDAB was not influenced by the pH of our treatments.

We also used 4-NDAB as the starting substrate by treating it with varying concentrations of MnO$_4^-$: Results showed that 4-NDAB is much more quickly transformed by MnO$_4^-$ than RDX, with transformation occurring within hours (Figure 4) versus days for RDX (Figure S6A). 4-NDAB is likely oxidized faster than RDX because oxidation of the formamide group to a carbamic acid and the subsequent decarboxylation are known to be very fast reactions. (22-24) While 4-NDAB was found to be a dead-end product of RDX via photodestruction, (8) aerobic biodegradation, (5) and alkaline hydrolysis, (6) we showed that it was not stable in MnO$_4^-$ (Figure 4).

Nitrogen Mass Balance Experiment. Using purified RDX, we prepared an aqueous solution and treated it with MnO$_4^-$: Initial experiments screened for a variety of N-containing products (NO$_2^-$, NO$_3^-$, N$_2$O, NH$_4^+$, 4-NDAB, and MEDINA), but only NO$_3^-$ and N$_2$O were found to be formed in significant quantities. Temporal tracking of RDX, N$_2$O, and NO$_3^-$ revealed that, after approximately 25% of the RDX had been transformed, a 99% N balance was obtained (day 2, Figure 5). By day 9, roughly 80% of the RDX had been transformed and RDX, N$_2$O, and NO$_3^-$ still constituted 95.6% of the N balance. During the time when most of the RDX was transformed (i.e., 0–9 d), roughly 5 times as much N$_2$O was produced than NO$_3^-$ (molar basis). The production of N$_2$O declined after 9 d, and concentrations reached a plateau by day 15; NO$_3^-$ production continued with a slow steady increase until 28 d, the time when RDX was no longer detectable (Figure 5). The nitrous oxide production was calculated by summing the direct headspace measurement plus the calculated dissolved liquid phase concentration in equilibrium with the measured gas phase concentration (25). Possible reasons why N$_2$O production did not continue to mirror RDX loss after 15 d include the inability of our microcosms to retain the headspace gases, the relationship between dissolved (i.e., calculated) and headspace N$_2$O concentrations changing as headspace pressure (i.e., N$_2$O production) increased, or other nitrogen gases or dissolved species being produced.

The possibility of other N-containing gases (NO, NO$_2$, N$_2$) forming from the RDX–MnO$_4^-$ reaction was investigated using $^{15}$N-RDX but could not be confirmed (see Supporting In-
Transformation of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by Permanganate

Oxidation of methylene by hydride abstraction, cation hydrolysis

Oxidation of N,N-dinitroaminol to N,N-dinitroimide by permanganate

Imide hydrolysis and decarboxylation

Overall reaction mechanism

Generation of NO$_3^-$ and trace of 4-NDAB: Possible examples

Figure 6. Proposed RDX degradation pathway of RDX-MnO$_4^-$ reaction under neutral pH.

RDX Degradation Mechanism. RDX is known to be degraded within days (~15 d) by base hydrolysis (pH 10) at ambient temperature(6) and within hours to minutes at elevated temperatures.(28, 29) We show that RDX was degraded by MnO$_4^-$ at neutral pH over several days at room temperature (Figure S6A) and that increasing temperature increased destruction rates (Figures 2 and 3). On the basis of results obtained from the various experiments (quenching agents, pH, temperatures, and activation energies), and the lack of readily identifiable carbon-containing intermediates (other than a trace of 4-NDAB), the initial step in the RDX−MnO$_4^-$ reaction is likely rate-limiting. On the basis of the various experimental treatments imposed, we believe this initial step can be described in one of two ways. When solution pH was alkaline, either as an artifact of the quenching agent (Figure S6B) or purposely increased (Figure S6C), then it is probable that the first step in the RDX−MnO$_4^-$ reaction is similar to the previously reported hydrolysis pathway (N-denitration;(6) see Supporting Information, SI-9, Figure S18). This mechanism would produce 4-NDAB, which was observed. And although 4-NDAB is a relatively stable intermediate during alkaline hydrolysis,(28) we show that 4-NDAB reacts with MnO$_4^-$ at a much faster rate than RDX (Figures 2, 4, and S6A). Under alkaline pH then, 4-NDAB was apparently produced by hydrolysis faster than it is oxidized by MnO$_4^-$ (Figures S6B and S6C), which allowed it to be detected.
Under neutral pH, which is more indicative of treating aqueous RDX with MnO$_4^-$ (pH 7.2 observed), we believe the initial step is an oxidation mechanism that begins with abstraction of a hydride from the methylene carbon by MnO$_4^-$, causing a carbocation to form (Figure 6). This proposed step is supported by past research on MnO$_4^-$-amine reactions. Permanganate oxidation of amines has been shown to proceed in one of two ways, namely single electron transfer (SET) from the amine nitrogen and hydride, or hydrogen atom abstraction from the carbon. A detailed consideration of both possible first steps (SET vs hydride loss) for RDX oxidation is presented in Supporting Information (SI-8, Figure S17). In brief, theoretical explanations and experimental observations indicate that SET will dominate the reactivities of tertiary amines with MnO$_4^-$, but hydrogen abstraction becomes more prominent in secondary and primary amines. Second-order rate constants have also been shown to significantly decrease when the mechanism shifts from SET to hydrogen atom loss. Moreover, when the initial intermediate can be stabilized with resonance as previously shown for benzylamine, the rate determining step proceeds by loss of hydride (or hydrogen atom) rather than SET. Given that the initial carbocation intermediate proposed for RDX (Figure 6) would be more stable than the intermediate formed by SET (Figure S17), we believe the hydride loss mechanism would be operative.

Following through with the proposed mechanism (Figure 6), the carbocation intermediate would react with water by hydrolysis to form a C-O bond (alcohol) and the resulting N,N-dinitroaminol with MnO$_4^-$ itself to form an imide. It is well established that MnO$_4^-$ oxidizes alcohols to carbonyl compounds, but the mechanisms have been shown to change completely as pH, reagent, and structure are varied. To our knowledge an oxidation mechanism for the proposed N,N-dinitroaminol has not been studied, so no specific mechanism for this conversion (aminol to imide) is presented. Once formed, however, water would attack the imide carbon (hydrolysis) to open the ring and lead to a carboxylic acid/amide anion. The carboxylic acid/amide ion would then undergo decarboxylation and liberation of CO$_2$. The accelerated rate of N,N-dinitroimide hydrolysis and decarboxylation has been previously observed in N-nitrourea chemistry. This same three-step cycle of oxidation, hydrolysis, and decarboxylation would continue leading to the production of CO$_2$ and H$_2$NNO$_2$ (nitramide), which would rapidly be converted to N$_2$O(6) and water (Figure 6).

While the proposed mechanisms are presented separately (Figures 6 and S18) and in a stepwise fashion, it is possible that several of these steps occur simultaneously. The dominant mechanism, however, can be inferred by the distribution of nitrogen-containing degradation products observed. RDX hydrolysis is reported to produce N$_2$O, NO$_3^-$, NH$_3$, and N$_2$ in the proportions 3.2:4.7:2:6.1, respectively. The hydride removal mechanism predicts that if RDX is exclusively degraded by oxidation, only N$_2$O would be produced; any nitrate observed would have to result from hydrolysis of postoxidation intermediates (Figure 6). Restated, if the solution chemistry is dominated by oxidation, we should observe ratios of N$_2$O/NO$_3^-$ which strongly favor N$_2$O. If the process is mainly hydrolysis followed by oxidation, the same ratio would strongly favor NO$_3^-$.

Supporting Information, providing details of experimental procedures and further explanation of results, is presented following the References.

Acknowledgment — Funding was provided in part by the EPA Region 7 and the Environmental Security Technology Certification Program (ESTCP), Project ER-0635. Partial support was also provided by the University of Nebraska School of Natural Resources and Water Center. This paper is a contribution of Agricultural Research Division Projects NEB-38-071. The authors also gratefully acknowledge Ms. Melissa S. Love and Dr. Daniel M. Steffenson (Chemistry Department, Albion College, Albion, MI), for their suggestions and contribution to this study.

References


Supporting information follows.
Supporting Information for:

Transformation of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by Permanganate

CHANAT CHOKEJAROENRAT †, STEVE D. COMFORT ‡*, CLIFFORD HARRIS §, DANIEL D. SNOW ‡, DAVID CASSADA ‡, CHAINARONG SAKULTHAEW ‡, AND TUNLAWIT SATAPANAJARU ⊥

* Corresponding author phone: 402-472-1502; fax: 402-472-7904; e-mail: scomfort@unl.edu.
† Department of Civil Engineering, University of Nebraska-Lincoln
‡ School of Natural Resources, University of Nebraska-Lincoln
§ Department of Chemistry, Albion College, MI
‖ Water Science Laboratory, University of Nebraska-Lincoln
⊥ Department of Environmental Science, Kasetsart University, Bangkok, Thailand
Contents

SI-1. Additional Experimental Section
    Figs. S1; S2

SI-2. RDX Purification

SI-3 Experimental Controls
    Fig. S3; Table S1; Figs. S4; S5

SI-4. Effect of quenching agents on RDX degradation products
    Figs. S6; S7; S8

SI-5. RDX Batch Experiments (Autocatalysis of permanganate)
    Figs. S9; S10

SI-6. Kinetic Models
    Figs. S11; S12; S13; S14

SI-7. Temperature dependency
    Table S2

SI-8 Single electron transfer versus hydride (or hydrogen) atom removal
    Fig. S15; S16; S17

SI-9. Proposed RDX degradation via proton abstraction
    Fig. S18

SI-10. References
SI-1. Additional Experimental Section

Chemical Standards. Commercial-grade RDX (~90% purity) was obtained from the Fort Detrick U.S. Biomedical Research and Development Laboratory (Frederick, MD). 4-nitro-2,4-diazabutanal, (4-NDAB, >99% purity) was custom synthesized by SRI International (Menlo Park, CA). Sodium permanganate (NaMnO₄, 40% by weight) and potassium permanganate (KMnO₄) were obtained from Fisher Scientific (Pittsburgh, PA). Reagent grade hydrogen peroxide (H₂O₂, 30% v/v), methanol, manganous sulfate (MnSO₄•H₂O) (J.T.Baker,Phillipsburgh, NJ), and manganous carbonate (MnCO₃, 99.9%, metals basis) (Alfa Aesar, Ward Hill, MA) were used as purchased. All solvents used in this research were HPLC grade (Fisher Scientific, Springfield, NJ). An analytical RDX standard (100 µg/mL) in a 50:50 acetonitrile-methanol matrix was purchased from AccuStandard (New Haven, CT). Nitrate (NO₃⁻), Ammonium (NH₄⁺) (1000 mg/L, GFS Chemicals, Columbus, OH) and nitrite (NO₂⁻) (1000 mg/L, Absolute Standards Inc., Hamden, CT) standards were used as purchased. Nitrous oxide (N₂O) standards were prepared from the 2% stock gases (mole basis) obtained from Scott Specialty Gases (Plumsteadville, PA).

High-Performance Liquid Chromatography (HPLC). Temporal changes in RDX and degradate concentrations were quantified at a 220 nm by HPLC equipped with a photodiode array detector (Shimadzu Scientific Instruments, Columbia, MD). Peak separations were performed by injecting 20 µL of sample into a Supelcosil LC-8, 250 x 4.6 mm, (Supelco, Sigma-Aldrich Corporation, PA) or a Fluophase PFP perfluorinated column, 250 x 4.6 mm, coupled with a guard column (Thermo Scientific, MA). A variety of mobile phases and flow rates (0.50-1.50 mL/min) were tested to separate peaks but the typical mobile phase was an isocratic mixture of methanol and H₂O (30:70), or acetonitrile and H₂O (50:50) at a flow rate of 0.75 mL/min.
**Ion Chromatography (IC).** Analysis of NO$_2^-$/NO$_3^-$ and NH$_4^+$ were performed with a Dionex DX-120 Ion Chromatograph (Sunnyvale, CA) with suppressed conductivity detection (conductivity detector, CDM-3). For anion analysis, separation was performed with an AS-15 IonPac column, 250 x 4.0 mm, using an eluent of 38 mM NaOH at a flow rate of 1 mL/min. For cation analysis, separation was performed with a CS12A IonPac column, 250 x 4.0 mm, using an isocratic eluent of 5.5 mM H$_2$SO$_4$ at a flow rate of 1.2 mL/min. The injection volume for both analyses was 25 µL. To effectively analyze samples by IC, RDX samples treated with MnO$_4^-$ were quenched with MnCO$_3$.

**Gas Chromatography/Electron Capture Detector (GC/ECD).** Nitrous oxide (N$_2$O) emitted from the RDX-MnO$_4^-$ reaction was measured by direct injection into a Hewlett-Packard (Palo Alto, CA) 6890 GC operated with a HP-Plot column (Molecular sieve 5A) 30 m/0.53 mm (50 µm film thickness) and electron capture detector (ECD). A P-5 gas (a mixture gas of 95% Argon and 5% CH$_4$) was used as a carrier gas for the GC system. The GC oven was equilibrated at least two hours at 225°C before analysis.

**UV-Spectrophotometer.** Changes in MnO$_4^-$ concentrations were monitored by diluting solution with Ultra Pure water in 20-mL vials and quantifying concentrations with a HACH Spectrophotometer DR2800 (HACH Company, Loveland, CO) at a wavelength of 525 nm. A test of whether colloidal MnO$_2$ interfered with quantification of MnO$_4^-$ is presented in SI-3.

**Analysis of N-containing gases.**

**Nitrogen Gas (N$_2$)** To determine if N$_2$ gas was a product of the RDX-MnO$_4^-$ reaction, experiments were conducted under vacuum in a Rittenburg tube, a two-legged Y-shaped tube (Fig. S1), containing crystalline RDX (both $^{14}$N-RDX and $^{15}$N-RDX) in one side and concentrated MnO$_4^-$ solution in the other. Uniformly labeled, [U-$^{15}$N]RDX, ($^{15}$N abundance of 97 atom%) was purchased from PerkinElmer (Waltham, MA). Prior to starting the reaction (i.e., mixing), all gases were evacuated through a vacuum line.
while the MnO$_4^-$ solution was simultaneously frozen. Once the frozen solution melted, we mixed it with the crystalline RDX in the other side. The tube was then immersed in water (~20°C) to confirm no leakage and avoid atmospheric gas contamination. We also mirrored this experiment without vacuuming so as to monitor the RDX concentration by HPLC. When RDX was completely degraded, gas emission was drawn by a vacuum system passing through a cold trap to freeze all gases but N$_2$ gas (Fig. S2; (1)). Gas samples were then collected in sample bulb and cryogenically transferred to an Optima Dual Inlet mass spectrometer (VG Isotech, Colchester, VT).

Results indicated that no increase in gas pressure was observed during the sample transfer and full scan measurement showed that, very little, if any N$_2$ gas ($m/z = 28, 29, 30$) formed during treatment. The primary reaction gas formed, N$_2$O, was trapped in the preparation line but was not analyzed on the instrument.
Figure S1: (Left) The Rittenburg tube containing MnO$_4^-$ solution was frozen in liquid nitrogen while all gases were being vacuumed. (Right) thawed RDX- MnO$_4^-$ solution after mixing.
Figure S2: Experimental system for trapping of N$_2$ gas. When RDX was completely degraded, all gases were evacuated from the Rittenburg tube (Lower Circle) and trapped in the vacuum system except N$_2$ gas which was forced to the gas-tight sampling tube (Upper Circle).

$\textit{NO}_x$ gases (i.e., NO$_2$ and NO) Besides the N$_2$ and N$_2$O gases, we also investigated the production of $\textit{NO}_x$ gases (i.e., NO$_2$ (nitrogen dioxide) and NO (nitric oxide)) to determine if they were released during the RDX-MnO$_4^-$ reaction. NO$_2$ is known to produce from the reaction of concentrated nitric acid and copper and is a toxic brownish gas with a pungent acid odor. However, in the diluted solution of nitric acid and copper, water molecules cause the reaction to produce NO instead. Although we did not observe a distinct brownish color of NO$_2$ during the RDX- MnO$_4^-$ reaction, we attempted to identify NO$_2$ and other possible transformation products by treating 5 mL of
saturated RDX (12.1 mg $^{15}$N-labeled and 0.4 mg non-labeled RDX) with 168.067 mM of MnO$_4^-$ in a 12-mL vial with a gastight septum. Each vial was degassed for 5 min and purged with Helium for 5 min by the acid injector (3.2 psi, Gilson, Middleton, WI) at a flow rate of 20.5 mL min$^{-1}$. NaMnO$_4$ (0.2 mL of 40% by weight) was injected into a vial by a gastight syringe. The temperature was controlled in a Precision 180 Series water bath at 60°C (Precision Scientific Co., Baltimore, MD) to increase RDX destruction rate. At 11 d, a 10 µL gas sample was removed from the vial and injected directly into a Hewlett-Packard 5890 GC (Palo Alto, CA) an Agilent 5972 quadrupole mass spectrometer. The N gases were separated on a 30 m/0.32 mm PLOT Moleseive column (J&W Scientific, Folsom, CA). The instrument was calibrated using Helium reference gas.

Results indicated that NO$_2$ and NO were not detectable during the RDX-MnO$_4^-$ reaction. A complicating factor, however, is that if NO$_x$ gasses (i.e., NO or NO$_2$) are liberated during the treatment of RDX with MnO$_4^-$, it will be difficult to quantify because MnO$_4^-$ provides an excellent means of removing NO by oxidizing it to NO$_2^-$ and NO$_3^-$, depending on pH (2-4). Alkaline or acidic MnO$_4^-$ has also been shown to be capable of trapping NO$_x$ gas emission from soils (5-8).
SI-2. RDX Purification

The commercial grade RDX contains ~90% RDX and ~10% HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine). To remove interferences and degradation artifacts associated with HMX, we removed the HMX by preparing a concentrated RDX solution (in acetonitrile) and purified to ≥99% RDX by using a Waters 2695 HPLC (Waters Corp., Milford, MA) with a temperature-controlled (30°C) Kromasil C18 column, 250 x 4.6 mm, (Thermo Scientific, MA) and Photodiode Array Detector (Waters 2996, Waters Corp., Milford, MA). The flow rate for this purification procedure was 1.5 mL/min with a repeated injection volume of 25 µL. A mobile phase of methanol (in H₂O) was used with the following gradient: 60:40 for 9 min followed by 90:10 for 3.5 min and 60:40 for the remainder of the run (~7.5 min). A Spectrum CF-2 fraction collector was used to isolate the RDX peak eluting from the column. The RDX fractions were combined and concentrated by the RapidVap evaporation system (Labconco, Kansas city, MO) in which a cylindrical receptacle was swirled and blown by N₂ gas at 50°C until dry.
SI-3. Experimental Controls

A series of experiments were performed under batch conditions to verify that RDX destruction rates by MnO$_4^-$ were similar when the initial pH was controlled or allowed to drift as the reaction proceeded (Fig. S3), the use of MnCO$_3$ as a quenching agent did not significantly influence sample pH or temperature (Table S1), RDX concentrations after quenching with MnCO$_3$ were stable and not subject to hydrolysis (Fig. S4), and that quantification of MnO$_4^-$ concentrations were not influenced by colloidal MnO$_2$ (Fig. S5).

**Figure S3.** Changes in RDX concentration and pH by various concentrations of MnO$_4^-$ under controlled and unbuffered pH.

Supporting Information for Chokejaroenrat et al./ ENVIRONMENTAL SCIENCE & TECHNOLOGY SUBMISSION
Table S1. Changes in pH and temperature of RDX-MnO₄⁻ solution following quenching with various mass of MnCO₃.

<table>
<thead>
<tr>
<th>MnCO₃ (g per mL of sample)</th>
<th>pH before quenching</th>
<th>pH after quenching</th>
<th>Temp before quenching (°C)</th>
<th>Temp after quenching (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 g</td>
<td>5.88</td>
<td></td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>0.03 g</td>
<td>5.82</td>
<td>6.15</td>
<td>25</td>
<td>24</td>
</tr>
<tr>
<td>0.04 g</td>
<td>5.81</td>
<td>6.02</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>0.05 g</td>
<td>5.85</td>
<td>6.02</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>0.06 g</td>
<td>5.80</td>
<td>5.93</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>0.07 g</td>
<td>5.74</td>
<td>5.86</td>
<td>25</td>
<td>22.5</td>
</tr>
</tbody>
</table>
Figure S4. Temporal changes in RDX concentrations following treatment with varying MnO$_4^-$ concentrations. Solid symbols signify concentrations of samples analyzed immediately, open symbols are the same samples analyzed 9 d later.
Figure S5. Changes in RDX and MnO$_4^-$ concentrations following treatment with varying MnO$_4^-$ concentrations. Solid symbols indicate MnO$_4^-$ concentrations determined without filtration, open symbols with filtration (0.45 µm glasswool filter).
SI-4. Effect of quenching agents on RDX degradation products

To determine the effect of quenching agents on RDX degradation products, aqueous solutions of RDX (0.07 mM) were treated with 33.61 mM of MnO$_4^-$.

We initially prepared RDX solutions by spiking 150 mL H$_2$O with 1.04 mL of RDX stock solutions prepared in acetone but the acetone-MnO$_4^-$ reaction resulted in autocatalysis of MnO$_4^-$ at alkaline pH and prevented further degradation of RDX >10 d (see Supporting Information; SI-5). Consequently, all aqueous RDX solutions were prepared by dissolving purified crystalline RDX in water over several days. Once MnO$_4^-$ was added to RDX solutions to initiate the reaction, samples were periodically collected and quenched with MnCO$_3$ or H$_2$O$_2$. Quenching with MnCO$_3$ (pH = 6.7) was performed as described in the main manuscript. When quenched with 30% H$_2$O$_2$ (0.04 mL per mL of sample), samples were required to mix continuously to control H$_2$O$_2$ consumption. The pH of samples quenched with H$_2$O$_2$ were found to increase significantly (pH = 11.5). To elucidate this pH effect, one set of batch samples were quenched with MnCO$_3$, and we increased the pH to that observed with the H$_2$O$_2$ by adding NaOH. Temporal changes in RDX, 4-nitro-2,4-diazabutanal (4-NDAB), NO$_3^-$, and NO$_2^-$ concentration were monitored by using HPLC and IC.

Results indicated that an RDX solution treated with MnO$_4^-$ led to complete RDX transformation within 15 d (Fig. S6A). To quantify temporal changes in RDX concentrations, samples were removed from the batch reactors every 2 to 3 d and chemically quenched to remove MnO$_4^-$ and prevent further RDX oxidation. While MnSO$_4$ is commonly used as a quenching agent (9-13) and does not interfere in HPLC analysis of RDX (12-13), the sulfate liberated interferes with NO$_2^-$ and NO$_3^-$ analyses by ion chromatography (IC). By using MnCO$_3$, we avoided this interference during IC analysis. However, the disadvantage of using MnCO$_3$ is that, at the concentrations of
quenching agents used, MnCO$_3$ takes longer than MnSO$_4$ to quench the MnO$_4^-$. Given the typical time course of the batch experiments (15 d), we compared RDX destruction rates from the same batch experiment and observed similar RDX destruction rates (Fig. S7).

Another consideration is that the quenching agent can alter the pH of the sample and possibly influence product formation or stability. When samples were quenched with MnSO$_4$, solution pH decreased from ~7.2 (before quenching) to pH 2.6 after quenching as predicted by the following reaction (Eq. S1).

$$2\text{NaMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + \text{3SO}_4^{2-} + 4\text{H}^+ + 5\text{MnO}_2 \quad \text{[Eq. S1]}$$

When RDX-MnO$_4^-$ solutions were quenched with MnCO$_3$ (Eq. S2), sample pH (after quenching) remained near 6.7, which is closer to the pH of the unquenched RDX-MnO$_4^-$ solution.

$$2\text{NaMnO}_4 + 3\text{MnCO}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 3\text{HCO}_3^- + 5\text{MnO}_2 + \text{H}^+ \quad \text{[Eq. S2]}$$

Product analysis during the RDX-MnO$_4^-$ reaction showed that when MnCO$_3$ was used as a quenching agent, we observed NO$_3^-$ production in the reaction but no NO$_2^-$ and only a trace of 4-NDAB (~0.004 mM) (Fig. S6A).

Peroxide was also used as a quenching agent. Here, peroxide reacts with MnO$_4^-$ by the following reaction (Eq. S3):

$$2\text{NaMnO}_4 + 4\text{H}_2\text{O}_2 \rightarrow 2\text{Na}^+ + 2\text{OH}^- + \text{Mn}_2\text{O}_3 + 3\text{H}_2\text{O} + 4\text{O}_2 \quad \text{[Eq. S3]}$$

Because OH$^-$ is liberated, the pH of samples quenched with H$_2$O$_2$ increased (pH
and we observed NO$_2^-$, NO$_3^-$, and 4-NDAB (Fig. S6B). Although the magnitude of NO$_3^-$ generated was similar to what we observed when MnCO$_3$ was used as a quenching agent (Fig. S6A, S6B), RDX destruction kinetics were much faster ($k = 1.83$ d$^{-1}$). Because we suspected excess peroxide may have contributed to RDX destruction, we conducted an experiment where RDX solution was treated with H$_2$O$_2$ in the same ratio as used in quenching process (0.04 mL of 30% H$_2$O$_2$ to 1 mL RDX or 1.2% (v/v) H$_2$O$_2$; no MnO$_4^-$). Results showed that RDX concentration was not significantly affected, pH remained constant, and RDX degradation products (NO$_2^-$ NO$_3^-$, and 4-NDAB) were not observed.

The peroxide concentration used in this control experiment (RDX + H$_2$O$_2$ only) was higher than what the quenched RDX-MnO$_4^-$ samples would have experienced because most, if not all, of the H$_2$O$_2$ would have reacted with the MnO$_4$. Therefore, the increased RDX destruction kinetics observed (Fig. S6B) does not appear to be directly related to the presence of excess peroxide. Rather, catalytic decomposition of H$_2$O$_2$ into various radicals (i.e., superoxide anion (O$_2^-$), hydroperoxide radical (HO$_2^*$), and hydroxyl radical (•OH)) may have played a role in the enhanced degradation of RDX (Fig. S6B). Although MnO$_2$ surfaces can enhance oxidation reactions (14), this precipitate, which forms during RDX-MnO$_4^-$ reaction (12), is also a catalyst for decomposition of H$_2$O$_2$ and both O$_2^-$ and HO$_2^*$ are favored at high pH (15-16). O$_2^-$ itself is known to be capable of degrading RDX (17). Furthermore, during the quenching process, Mn$_2$O$_3$ is liberated (Eq. S3) and can simultaneously act as a catalyst for degradation of organic compounds in the presence of H$_2$O$_2$ (15, 18). Another possibility is that the alkaline pH created during the quenching process (Eq. S3) facilitated H$_2$O$_2$ decomposition into •OH which contributed to RDX degradation. Moreover, Gates-Anderson et al. (19) observed that in strongly basic solutions (pH > 9) •OH can also be generated from MnO$_4^-$ and directly oxidize organic contaminants. These explanations support a seven-fold increase of
RDX destruction kinetics (Figs. S6A, S6B).

Finally, an elevated temperature may also have been responsible for greater RDX destruction in the H$_2$O$_2$ quenched samples. Heilmann et al. (20) showed that alkaline hydrolysis rates of RDX in aqueous solution dramatically increased at high temperature (50°C). We observed that using H$_2$O$_2$ as a quenching agent caused a rapid 9°C increase in sample temperatures. Because H$_2$O$_2$-MnO$_4^-$ reaction is exothermic, it is reasonable that the combination of alkaline pH and heat may have contributed to RDX degradation (See also Effect of Temperature on RDX-MnO$_4^-$ Reaction in the main manuscript).

Given that the treatment of RDX with peroxide alone did not cause an increase in pH or the production of NO$_2^-$ and 4-NDAB, the alkaline pH created by the H$_2$O$_2$-MnO$_4^-$ reaction was likely responsible for the degradation products observed. To test this further, we again used MnCO$_3$ as a quenching agent and artificially raised the pH of the samples before and after quenching to pH 11.5 (similar to what was observed with H$_2$O$_2$ as a quenching agent). Results showed RDX degradation was slower than when peroxide was used to quench the MnO$_4^-$ and closer to the results obtained when MnCO$_3$ was used without pH adjustment (Fig. S6A, $k = 0.26$ d$^{-1}$; Fig. S6C, $k = 0.33$ d$^{-1}$). This observation lends credence to the possibility that peroxide radicals may have been involved during the quenching of MnO$_4^-$ with H$_2$O$_2$ (Fig. S6B). Using MnCO$_3$ + alkaline pH also produced NO$_2^-$ and 4-NDAB as reaction products (Fig. S6C). Two known RDX degradation schemes involve the removal of one nitro group (denitration) with the intermediate methylenedintramine (MEDINA) or two nitro groups and the formation of 4-NDAB (e.g. (21)). Thus, the detection of nitrite during the RDX-MnO$_4^-$ reaction (with H$_2$O$_2$ quenching agent or MnCO$_3$ + alkaline pH) is likely a result of the alkalinity stabilizing NO$_2^-$ and preventing further transformation. Numerous reports have shown
that nitrite is more persistent at alkaline pH (22-23). Balakrishnan et al. (24) also found NO$_2^-$ as an endproduct of RDX hydrolysis.

**Figure S6:** Changes in RDX concentration and production of degradation products (4-NDAB, NO$_2^-$, and NO$_3^-$) when quenched with; (A) 0.10 g MnCO$_3$ (per mL); (B) 0.04 ml 30% H$_2$O$_2$ (per mL, pH ~ 11.5); and (C) 0.10 g MnCO$_3$ (per mL) in which sample solutions pH was raised to 11.5 before and after quenching. Bars indicate sample standard deviations ($n = 3$).
**Figure S7:** Comparison of RDX degradation kinetic rates when quenched with MnSO$_4$ or MnCO$_3$. Bars indicate sample standard deviations (n = 3).

**Figure S8:** The effect of pH on 4-NDAB stability. Bars indicate sample standard deviations (n = 3).
SI-5. RDX Batch Experiments (Facilitated Decomposition of permanganate)

To evaluate the effects of initial MnO$_4^-$ concentration on RDX destruction rates, we conducted the batch experiment by treating 150 mL of aqueous $^{14}$C-RDX (0.02 mM, 30000 dpm mL$^{-1}$, uniformly ring-labeled) and varying MnO$_4^-$ concentration from 8.40 mM to 168.07 mM. Each MnO$_4^-$ concentration was replicated three times. Temporal samples were periodically collected and quenched with MnSO$_4$ as described in analytical section and monitored for the loss of RDX by HPLC and $^{14}$C-activity by Liquid Scintillation Counter (LSC).

Results indicated that treating aqueous (i.e., distilled water) RDX with 168.067 mM of MnO$_4^-$ reduced RDX concentrations to zero within 10 d ($k = 0.49$ d$^{-1}$) (Fig. S9A). Lower MnO$_4^-$ concentrations (8.40-42.02 mM) reduced RDX destruction rates and overall removal. For instance, when RDX was treated with 8.40 mM of MnO$_4^-$ destruction rates decreased ~70% ($k = 0.14$ d$^{-1}$) and only 29% of the initial RDX was removed within 10 d (25). These results are similar to those reported by Adam et al. (12) but differ in that temporal decrease in both RDX and $^{14}$C concentrations (Fig. S9B) reached a plateau after ~10 d. The reasons MnO$_4^-$ failed to continually transform and mineralize RDX beyond 10 d was investigated by monitoring temporal changes in pH and MnO$_4^-$ concentrations.

By repeating the experiment with 84.03 mM of MnO$_4^-$ and monitoring MnO$_4^-$ and pH (Fig. S10A, S10B, S10C), we observed an increase in pH from 6.5 to > 8. Using higher MnO$_4^-$ concentrations (126.05, 168.07 mM) also produced similar changes in pH. This increase in pH coincided with a significant decrease in MnO$_4^-$ concentration (Fig. S10B). By contrast, when a pH-stat (Metrohm Titrino 718S; Brinkman Instruments, Westbury) maintained the pH at 7, RDX concentrations did not plateau but continued to decrease and very little consumption of MnO$_4^-$ was observed (Fig. S10A, S10B). It is clear that in the unbuffered treatment, the rapid decrease in MnO$_4^-$ concentration
coincided with the lack of further RDX destruction beyond 7 d (i.e., plateau). We believe the loss of MnO$_4^-$ was likely caused by a facilitated decomposition of permanganate at alkaline pH. But alkaline pH alone was not solely responsible for the loss of MnO$_4^-$. Adam et al. (12) evaluated the effect of pH on RDX destruction kinetics and reported no pH effect in the range 4.1 to 11.3. A comparison of procedures used by Adam et al. (12) and our protocol revealed that a higher percentage of acetone was used in our batch reactors. This occurred by using RDX stock solutions prepared in acetone (both unlabeled and $^{14}$C-labeled) to spike the aqueous solutions with RDX. Although the volume of acetone spiked into the aqueous batch reactors was relatively low (1.04 mL acetone/150 mL H$_2$O), when this same concentration of acetone was added to 84.03 mM of MnO$_4^-$ without RDX, a similar decrease in MnO$_4^-$ was observed (Fig. S10D, S10E, S10F); similarly, when aqueous RDX solutions were prepared without acetone, the pH remained constant (Fig. S10F) and MnO$_4^-$ consumption was negligible (Fig. S10E). The plateau in RDX loss observed (Figs. S9, S10) resulted from the reaction of acetone with MnO$_4^-$ and likely included the oxidation of acetone to oxalic acid and the reaction of oxalic acid with MnO$_4^-$ to form Mn$^{2+}$, which is known to facilitate the decomposition of MnO$_4^-$. 

While the accelerated removal of MnO$_4^-$ was traced back to the use of acetone and subsequent formation of carboxylic acids in our batch reactors (Fig. S10), the implications of this observation may be more than just an experimental anomaly. Oxalic acid is a product of the TCE-MnO$_4^-$ reaction (26). Li et al. (27) also showed that oxalate was a primary oxidation product of the explosive TNT (2,4,6-trinitrotoluene) during treatment with Fe$^{2+}$ and H$_2$O$_2$ (i.e., Fenton oxidation). Thus, situations may arise where oxalate (or other carboxylic acids) are present and cause excessive MnO$_4^-$ decomposition if the pH is not monitored and prevented from becoming alkaline.
Figure S9: Loss of RDX and $^{14}\text{C}$-activity in aqueous solution treated with various concentrations of MnO$_4^-$.
Solution samples were quenched with MnSO$_4$. Bars indicate sample standard deviations ($n = 3$).
Figure S10: (A-C) Changes in RDX, MnO\(_4^-\) concentration, and pH in the presence of acetone following treatment with 84.03 mM of MnO\(_4^-\) (i.e., Unbuffered control, and control pH at 7). (D-F) Changes in RDX, MnO\(_4^-\) concentration, and pH with/without acetone. Solution samples were quenched with MnSO\(_4\). Bars indicate sample standard deviations (n = 3).
SI-6. Kinetic Models

While second-order expressions are commonly used to describe contaminant destruction rates by MnO$_4^-$ (28-32), if MnO$_4^-$ is in excess, the reaction can also be described by a pseudo first-order expression (12, 33). Like many other second-order reactions between contaminant and MnO$_4^-$, the general rate equation can be written as:

\[
\frac{dr}{dt} = k [\text{RDX}]^\alpha [\text{MnO}_4^-]^\beta
\]  
[Eq. S4]

\[
r = k_{obs} [\text{RDX}]^\alpha
\]  
[Eq. S5]

\[
k_{obs} = k [\text{MnO}_4^-]^\beta
\]  
[Eq. S6]

Where \( \alpha \) is a reaction order with respect to RDX, \( \beta \) is a reaction order with respect to MnO$_4^-$, \( r \) is a reaction rate, \( k \) is a second-order rate constant, and \( k_{obs} \) is a pseudo-order rate constant. By varying the initial concentration of MnO$_4^-$ and measuring \( k_{obs} \) by fitting the results into a pseudo first-order equation by regression analysis using computer software SigmaPlot Version 10.0 (34), the value of \( \beta \) with respect to MnO$_4^-$ can be obtained by a log-log form of Eq. S6:

\[
\log k_{obs} = \log k + \beta \log [\text{MnO}_4^-]
\]  
[Eq. S7]

Likewise, by varying the initial concentration of RDX and measuring the reaction rate, the value of \( \alpha \) with respect to RDX can be determined by a log-log form of Eq. S5. To evaluate for the reaction rates, we used the initial reaction rate \( (r_o) \) by approximating the tangent to the concentration time-curve (35); therefore, Eq. S5 can then be expressed as:

\[
\log r_o = \log k_{obs} + \alpha \log [\text{RDX}]
\]  
[Eq. S8]

Second-order rates \( (k) \) were then derived from pseudo first-order rates \( (k_{obs}) \) by the relationship in Eq. S6.
Figure S11: Loss of RDX (A) and TNT (B) when treated with various concentrations of MnO$_4^-$.

Note differences in time scales. Bars indicate sample standard deviations (n = 3).
**Figure S12**: Loss of RDX (initial concentrations ranging from 0.01 to 0.09 mM) when treated with MnO₄⁻ at 33.61 mM. Bars indicate sample standard deviations (n = 3).
**Figure S13:** Loss of TNT (initial concentrations ranging from 0.01 to 0.09 mM) when treated with MnO$_4^-$ at 4.20 (A), 8.40 (B), or 33.61 mM (C). Bars indicate sample standard deviations (n = 3).
Figure S14: (A) Plot of pseudo first-order rate constants for TNT degradation vs \([\text{MnO}_4^-]\). Aqueous TNT (0.09 mM) was treated with \(\text{MnO}_4^-\) ranging from 4.20 to 84.03 mM. (B) Plot of initial rates of TNT degradation vs. \([\text{TNT}]_0\) ranging from 0.01 to 0.09 mM when treated with 4.20, 8.40, or 33.61 mM \(\text{MnO}_4^-\).
SI-7. Temperature dependency

In RDX-MnO$_4^-$ temperature experiment, the pseudo first-order rates were evaluated at four different temperatures. The activation energy, $E$, can be determined using a plot of the Arrhenius equation, as follows:

$$
\ln k(T') = \ln A - \frac{E}{RT}
$$

[Eq. S9]

Where $A$ is the empirical Arrhenius factor or pre-exponential factor; $R$ is gas constant (8.314 J/K·mol); and $T$ is the absolute temperature (K). The logarithm of the second-order rate constants ($k$) are plotted against the reciprocal temperature (1/T) to determine the Arrhenius factor $A$ and the E/R value from its linear least-squares fit (20, 36-37).
Table S2. Temperature Dependency of Kinetic Rates for Treatment of 0.02 mM RDX with 4.20 mM MnO₄⁻

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>k_{RDX1} a</th>
<th>k_{RDX2} a, b</th>
<th>k_{RDX2} a</th>
<th>Ln k_{RDX2} a</th>
<th>1/T (1/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.02</td>
<td>3.52</td>
<td>0.00</td>
<td>-6.01</td>
<td>0.0034</td>
</tr>
<tr>
<td></td>
<td>(0.00)</td>
<td>(0.13)</td>
<td>(0.00)</td>
<td>(0.04)</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>0.06</td>
<td>14.22</td>
<td>0.01</td>
<td>-4.62</td>
<td>0.0032</td>
</tr>
<tr>
<td></td>
<td>(0.00)</td>
<td>(0.21)</td>
<td>(0.00)</td>
<td>(0.01)</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.35</td>
<td>84.21</td>
<td>0.06</td>
<td>-2.84</td>
<td>0.0031</td>
</tr>
<tr>
<td></td>
<td>(0.01)</td>
<td>(2.22)</td>
<td>(0.00)</td>
<td>(0.03)</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>0.89</td>
<td>212.65</td>
<td>0.15</td>
<td>-1.91</td>
<td>0.0030</td>
</tr>
<tr>
<td></td>
<td>(0.03)</td>
<td>(7.16)</td>
<td>(0.01)</td>
<td>(0.03)</td>
<td></td>
</tr>
</tbody>
</table>

a Parenthetic values represent standard error of estimates. b k_{RDX2} = k_{RDX1}/C_{MnO4⁻}
SI-8. Single electron transfer versus hydride (or hydrogen atom) removal

Based on supporting literature (38-40), two key ideas emerge:

1) Two different mechanisms are observed in amino oxidations
   a) single-electron transfer (SET) at the amine nitrogen and
   b) hydride (or hydrogen) abstraction from the carbon;

2) The electron density on the amine nitrogen determines the operative mechanism.

Specifically, electron-poor amines or those with resonance stabilized intermediates tend to be oxidized by hydride abstraction. When these specific principles and the principles of organic oxidation chemistry are applied to RDX, the problem simplifies somewhat. For instance, there are only four distinct sites for oxidation of RDX: an oxygen atom, a nitro nitrogen atom, an amine nitrogen atom, or a carbon. This is illustrated below.

**Figure S15:** Possible sites for oxidation of RDX.

Oxidation at the oxygen atom or a nitro nitrogen atom would give extremely unstable intermediates since they place positive charge on electronegative oxygen or...
an already electron deficient nitro group nitrogen, respectively. The only two reasonable sites for oxidation of RDX remaining are the exact two options carefully studied by the cited authors (38-40). That is, oxidation at the amine nitrogen (by SET) or oxidation at the carbon (by hydride abstraction, see S16, S17 below).

Because the amino nitrogens in RDX are extremely electron-poor, the hydride loss will tend to dominate the reaction. This is probably because the intermediate resulting from an initial single-electron transfer would produce an intermediate having two positive charges on the adjacent nitrogen atoms, as shown above. Such an intermediate would be much less stable than the proposed carbocation which maximizes the distance of the two positive charges from each other, and places one of them on the more electropositive carbon atom.

**Figure S16:** Overall comparison of SET versus hydride abstraction of RDX.
Figure S17: A comparison of initial first steps via single electron transfer (A) versus hydride removal (B).

When we considered both possible first-steps in the RDX-MnO₄⁻ reaction (SET vs. Hydride loss, Fig. S15), we believe the strongly electron-withdrawing nitro groups would tend to destabilize any cation intermediate. This destabilizing effect, however, would be minimized for the carbocation intermediate formed via hydride abstraction (Fig S17B) compared to the aminium ion formed by SET (Fig. S17A) because: 1) the carbocation is further from the nitro group than the aminium ion and is therefore less destabilized by inductive effects, 2) carbon is more electropositive than nitrogen, and thus less destabilized by the cation, 3) resonance stabilization for the carbocation can occur but is completely absent for the aminium intermediate. These theoretical explanations are supported by the experimental observations that 1°, 2° and 3° alkylamines having all their electron density isolated on the nitrogen tend to be oxidized by SET (38-39), while amines with resonance distributed electron density like benzylamine clearly undergo loss of hydride (or hydrogen atom) (40). Thus, theory and experiment indicate that the carbocation intermediate will be more stable and therefore formed more quickly than the aminium cation intermediate in RDX.
SI-9. Proposed RDX degradation via proton abstraction

RDX - MnO$_4^-$ (hydrolysis and oxidation)

Figure S18: Proposed RDX degradation via proton abstraction and oxidation via MnO$_4^-$ under alkaline pH.
SI-10. References


(11) Root, D.K. In-situ chemical oxidation of chlorinated hydrocarbons in the presence of radionuclides. Presented at WM'03 Conference [Online], Tucson, AZ,


(20) Heilmann, H.M.; Wiesmann, U.; Stenstrom, M.K. Kinetics of the alkaline...


(34) SPSS. SigmaPlot for Windows Version 10.0: Chicago, IL, 2006.


