THERMODYNAMIC CONTROL ON THE REDOX FATE OF NITROAROMATIC AND CYLIC NITRAMINE EXPLOSIVES

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ABSTRACT

Nitroaromatic and cyclic nitramine compounds are frequently encountered as energetic residues in live-fire military training ranges. Careful assessment on the redox fate of current and emerging explosives will allow accurate assessment of potential site risks and remediation strategies to protect the warfighter. This study employed the naturally-occurring reductant ferrous iron to investigate the factors controlling the rate and extent of electron transfer processes between the energetic residues and the environmental media. Reliable experimental and theoretical techniques were first established to accurately determine the one-electron reduction potentials of explosives, a thermodynamic measure indicative of the “reducibility” of a given explosive. Experimental studies employing ferrous iron and various iron-coordinating ligands suggested that kinetic factors such as the coordination environment of the metal ion reductant and surface catalysis must be considered, in addition to the thermodynamic parameter, to accurately predict the fate of energetic residues.

1. INTRODUCTION

Nitroaromatic and cyclic nitramine compounds such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are frequently encountered as energetic residues in live-fire military training ranges (Jenkins et al., 2006). Detailed information on the fate and transport of current and emerging energetic compounds is necessary for an accurate assessment of potential site risks and remediation strategies. Under anoxic and suboxic conditions, reduction is the key chemical transformation pathway of energetic compounds in aqueous environments. Careful assessment on the redox fate of current and emerging explosives is essential, as the reductive transformation leads either to natural remediation or increased toxicity of the target contaminant. The unique reduction potential (E) corresponding to the half reaction for a given explosive (R-NO$_2$) and its one-electron reduction product (R-NO$_2\cdot^-$) predicts the geochemical conditions that will favor reductive transformation of the explosive. Consider an electron transfer process with iron, the most abundant redox-active metallic element on the earth’s surface:

$$Fe(OH)_3(s, \text{amorphous}) + 3H^+ + e^- = Fe^{2+}(aq) + 3H_2O \quad E = 0.059 \text{ volts}$$

(pH 7, excess $Fe(OH)_3$(s, amorphous), 125 μM Fe^{2+}(aq))

Under the conditions used for calculating the E value, an energetic compound having E > 0.059 volts is thermodynamically capable of oxidizing Fe(II) to Fe(III). To predict the biogeochemical fate of current and emerging explosives (e.g., insensitive munitions compounds), a reliable technique for determining the E(R-NO$_2$/ R-NO$_2\cdot^-$) values is necessary. The present study employs complementary experimental and theoretical approaches to determine the E(R-NO$_2$/R-NO$_2\cdot^-$) values of nitroaromatic and cyclic nitramine explosives. Experimental approach employed the linear free energy relationships (LFER). Theoretical approach employed *ab initio* calculation of solvation free energies (ΔGs^0) and the determination of $E_h^{1'}$ (in volts) using the following equation:

$$-E_h^{1'} = EA(M) + \Delta G_{evr,gas}(M\bullet^- \rightarrow M + e^-) + \Delta G_s^0(M\bullet^-) - \Delta G_s^0(M) + 4.44eV$$

where EA(M) is the electron affinity of form M that includes thermal and entropic contributions, $\Delta G_{evr,gas}(M\bullet^- \rightarrow M + e^-)$ is the difference in thermal contributions to the solute free energy derived from changes in the electronic, vibrational and rotational partition functions upon ionization, $-\Delta G_s^0(M)$ and $\Delta G_s^0(M\bullet^-)$ are the solvation free energies of the neutral and reduced forms of the solute, respectively, and 4.44eV is the free energy change associated with the standard hydrogen electrode half-reaction. A plot of theoretical versus experimental (literature) $E_h^{1'}$(R-NO$_2$/R-NO$_2\cdot^-$) values for a series of nitroaromatic compounds produced a strong linear correlation ($y = 1.08(\pm 0.13) + 0.02 (\pm 0.05)$; $R^2 = 0.88$), indicating the accuracy of the theoretical approach (Fig. 1).

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **DEC 2008**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **Thermodynamic Control On The Redox Fate Of Nitroaromatic And Cylic Nitramine Explosives**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **US Army Engineer Research and Development Center, Environmental Laboratory, 3909 Halls Ferry Road Vicksburg, Mississippi, 39180**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES

See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**UU**	**4**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

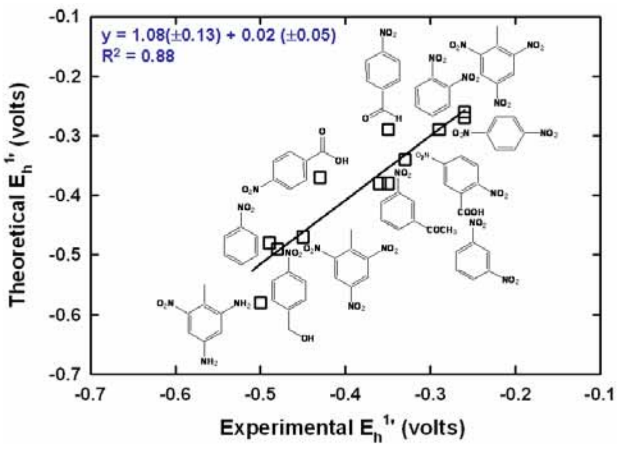

Fig. 1, The comparison of theoretically determined E_h^{1}'(R-NO_2/R-$NO_2^{\cdot -}$) with literature (experimental) values for selected nitroaromatic compounds.

All experiments were conducted in batch reactors under inert (N_2) atmosphere and constant stirring at room temperature. The LFER approach employed ferrous complexes possessing sufficiently low reduction potentials to reduce a wide range of nitroaromatic and cyclic nitramine explosives at a fixed E(Fe(III)/(II). Pseudo first order rate constants (k_{obs} in seconds^{-1}) were first determined for compounds with known E_h^{1}'(R-NO_2/R-$NO_2^{\cdot -}$) values (Fig. 2).

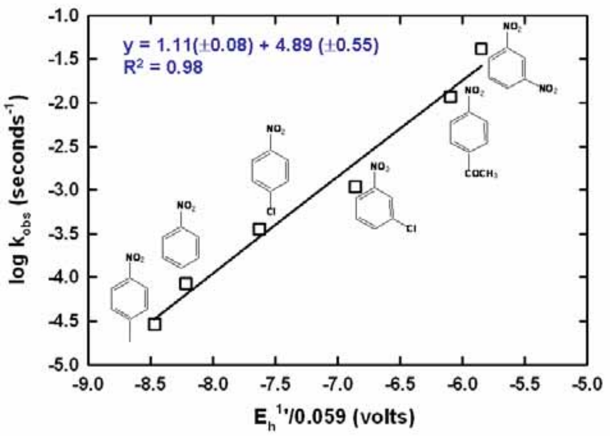

Fig. 2, Experimentally determined LFER between pseudo first order rate constants (k_{obs} in seconds^{-1}) and one-electron reduction potentials E_h^{1}'(R-NO_2/R-$NO_2^{\cdot -}$) for nitroaromatic compounds. Initial Conditions: 25 μM explosive, 500 μM $FeCl_2$, 10 mM Tiron, 0.25 M I (NaCl), pH 5.75 (50mM MES buffer), 25 °C.

Resulting LFER was used to determine the E_h^{1}'(R-NO_2/R-$NO_2^{\cdot -}$) values of target explosives. Our results suggest that cyclic nitramine explosives RDX and HMX are weaker oxidants compared to tri- and dinitrobenzenes, as well as the majority of mononitrobenzenes. Caged cyclic nitramine CL-20, on the other hand, is a significantly stronger oxidant than RDX and HMX (Fig. 3).

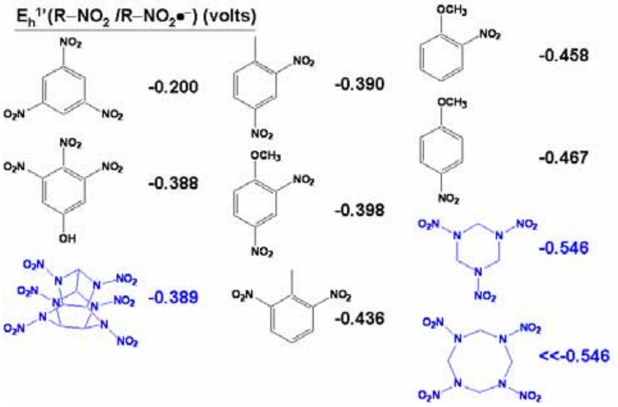

Fig. 3, Experimentally determined one-electron reduction potentials (E_h^{1}'(R-NO_2/R-$NO_2^{\cdot -}$) in volts) for nitroaromatic and cyclic nitramine explosives.

The trend observed in Fig. 3 suggests that for a series of nitroaromatic compounds, nitro substituent strongly withdraws electrons both inductively and by resonance, thereby stabilizing the negatively charged nitroaryl radical anions. Inductive, resonance, field, and steric effects of additional substituents impact the final one-electron reduction potential of each nitroaromatic compound (Fig. 3).

As illustrated below, results from this study facilitate understandings in the underlying factors controlling the rate and extent of energetic contaminant degradation in soils and sediments. As shown in Table 1, the decrease in (more negative) one-electron reduction potentials of nitroaromatic and cyclic nitramine explosives (TNT, RDX, HMX, and CL-20) correlated with increasing half-lives in dithionite-reduced sediments reported in the literature.

Table 1, Reduction of nitroaromatic and cyclic nitramine explosives in dithionite-reduced sediments (reaction half-lives obtained from Boparai et al., 2008; Szecsody et al., 2004).

Reduction of 10 μM TNT, RDX, and HMX in dithionite-reduced sediments

Explosive	Half-life (minutes)	$E_h^{1\prime}$ (volts)
TNT	14 (≥ pH 8; K_2CO_3)	-0.300
RDX	21 (≥ pH 8; K_2CO_3)	-0.546
HMX	96 (≥ pH 8; K_2CO_3)	<<-0.546

Source: Boparai et al. (Chemosphere, 2008)
Szecsody et al. (SERDP ER-1376)

Explosive	Half-life (minutes)	$E_h^{1\prime}$ (volts)
CL-20	3 (pH 7)	-0.389

Source: Szecsody et al. (Chemosphere, 2004)

Further experimental studies suggested that in addition to the thermodynamic parameter (E_h^{1}'(R-NO_2/R-$NO_2^{\cdot-}$)), kinetic factors strongly impact the reductive fate of explosives. Surface catalysis and the coordination environment of metal ion reductants are the key kinetic factors controlling the environmental fate of explosives. Thermodynamically, the addition of iron-coordinating ligands (Fig. 4 for citrate, EDTA, oxalate, tiron) lowers the reduction potential of iron (E(Fe(III)/(II), relative to the "no ligand" case) in the pH range where the experiments were conducted ($3.5 < pH < 6.8$). Therefore, the addition of ligands results in increased thermodynamic driving force for the reduction of explosives by Fe(II) (Uchimiya and Stone, 2006). For nitroaromatic compounds having sufficiently high E_h^{1}'(R-NO_2/R-$NO_2^{\cdot-}$) (e.g., 2,4-dinitroanisole) (Fig. 3,) the iron-coordinating ligands presented in Fig. 4 increased the rate of reduction by Fe(II). In addition, the rate of reaction increased as a function of pH for a given explosive and iron-coordinating ligand. However, no rate enhancement was observed when EDTA was added to the eaction solution. Similar inhibitory effects of EDTA was observed for the oxidation of Fe(II) by a variety of oxidants (O_2, Cr(VI), and carbamate pesticides), suggesting that EDTA can decrease the reactivity of Fe(II) by prohibiting the oxidant access to the inner-coordination shell of Fe(II) (Strathmann and Stone, 2002).

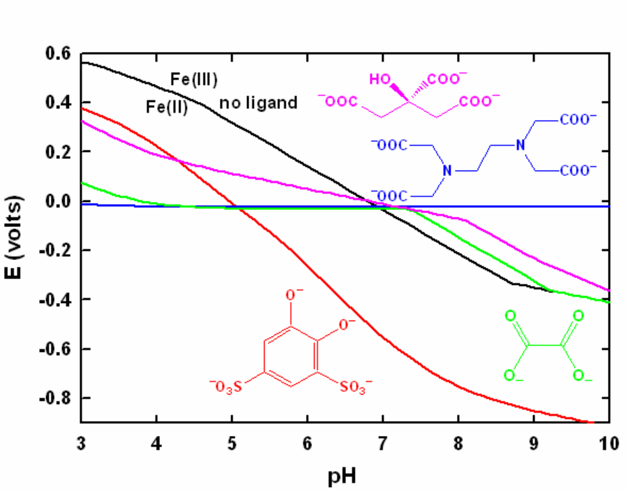

Fig. 4, E_h-pH diagram for Fe(III)/(II) redox couple in the presence of iron-coordinating ligands citrate (pink), EDTA (blue), oxalate (green) and tiron (red). Calculation conditions: 499 μM Fe(II), 1 μM Fe(III), 10 mM ligand $Fe(OH)_3$(s,amorphous) as solubility-limiting phase.

For the reduction of a series of benzoquinones, naphthoquinones, and anthraquinones by Fe(II), in contrast, the addition of all iron-coordinating ligands in Fig. 3, including EDTA, enhanced the reaction rate (Uchimiya, 2005). These observations suggest that the kinetic factors (inner- versus outer-sphere electron transfer mechanisms) must be taken into account in addition to the thermodynamic considerations, in order to accurately predict the redox fate of specific military contaminants in aqueous environments.

CONCLUSIONS

Our present study suggested that complementary experimental and theoretical approaches allow accurate determination of thermodynamic parameters (E_h^{1}'(R-NO_2/R-$NO_2^{\cdot-}$)) necessary for predicting the fate of energetic contaminant in military training ranges. Our results demonstrated that in addition to thermodynamic parameters, kinetic factors such as the coordination environment of metal ion reductant must be taken into account to accurately predict the environmental fate of energetic materials. The DoD and the Army in particular continue to lead in the development of environmentally benign remediation technologies for the long-term sustainability of live-fire training ranges. Of particular interest is *in situ* natural remediation of energetic residues using naturally-occurring electron donors such as Fe(II), and the enhancement of natural remediation using additional electron donors such as zero valent iron and catalysts such as quinones and humic substances. The success of future remediation strategies will depend upon the outcomes of this research providing fundamental information on the reactivity of nitroaromatic and cyclic nitramine explosives under a wide range of environmental conditions.

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