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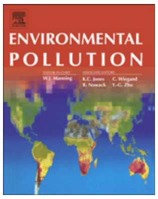

One-electron standard reduction potentials of nitroaromatic and cyclic nitramine explosives

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Reduction of explosives becomes less thermodynamically favorable as the one-electron standard reduction potential decreases from di- and tri-nitroaromatic, nitramine, to nitroimino compounds.

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ABSTRACT

Extensive studies have been conducted in the past decades to predict the environmental abiotic and biotic redox fate of nitroaromatic and nitramine explosives. However, surprisingly little information is available on one-electron standard reduction potentials ($E^{o}(R\text{-}NO_2/R\text{-}NO_2^{-})$). The $E^{o}(R\text{-}NO_2/R\text{-}NO_2^{-})$ is an essential thermodynamic parameter for predicting the rate and extent of reductive transformation for energetic residues. In this study, experimental (linear free energy relationships) and theoretical (*ab initio* calculation) approaches were employed to determine $E^{o}(R\text{-}NO_2/R\text{-}NO_2^{-})$ for nitroaromatic, (caged) cyclic nitramine, and nitroimino explosives that are found in military installations or are emerging contaminants. The results indicate a close agreement between experimental and theoretical $E^{o}(R\text{-}NO_2/R\text{-}NO_2^{-})$ and suggest a key trend: $E^{o}(R\text{-}NO_2/R\text{-}NO_2^{-})$ value decreases from di- and tri-nitroaromatic (e.g., 2,4-dinitroanisole) to nitramine (e.g., RDX) to nitroimino compound (e.g., nitroguanidine). The observed trend in $E^{o}(R\text{-}NO_2/R\text{-}NO_2^{-})$ agrees with reported rate trends for reductive degradation, suggesting a thermodynamic control on the reduction rate under anoxic/suboxic conditions.

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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 encountered as energetic residues in live-fire military training ranges (Jenkins et al., 2006). Detailed information on the fate of current and emerging energetic compounds is necessary for an accurate assessment of potential site risks and remediation strategies. In particular, redox transformation can lead to natural remediation or increased toxicity of the contaminant. Reduction is the key chemical transformation pathway of highly oxidized energetic compounds under anoxic and suboxic conditions. Extensive studies have been conducted on the reduction of nitroaromatic compounds (NACs) by Fe(II) sorbed on iron (hydr)oxides and other minerals (Klausen et al., 1995), dissolved Fe(II) alone and in the presence of dissolved organic matter (DOM) (Hakala et al., 2007) or catecholate ligand (Naka et al., 2006), juglone in the presence of hydrogen sulfide (Hartenbach et al., 2006), and structural iron within clay minerals (Hofstetter et al., 2006). NACs are expected to engage in stepwise electron transfer reactions with experimentally observable (Colon et al., 2006b) nitrosobenzene and *N*-hydroxylaniline intermediates to form the final stable product aniline (Fig. 1a). However, NACs and reduction products can engage in irreversible side-reactions such as polymerization (Thorn and Kennedy, 2002; Thorn et al., 2004), making an accurate prediction of their environmental fate a challenge.

Depending on reaction conditions and reductant characteristics, cyclic nitramines such as RDX, HMX, and 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) undergo complex biotic (see Crocker et al., 2006 for a review and Kwon and Finneran, 2008 for more recent studies) and abiotic (Balakrishnan et al., 2004; Gregory et al., 2004; Alessi and Grundl, 2008; Larese-Casanova and Scherer, 2008; Oh et al., 2008; Boparai et al., 2010) reductive degradation pathways. In addition, insensitive munitions compounds (IMs) that are structurally distinct from NACs and cyclic nitramines, such as 5,5′-hydrazinebistetrazole, 1,2-ditetrazolylhydrazine (HBT) and 1,1-diamino-2,2-dinitroethylene (FOX-7) (Klapötke and Miró Sabaté, 2008)

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14. ABSTRACT

Extensive studies have been conducted in the past decades to predict the environmental abiotic and biotic redox fate of nitroaromatic and nitramine explosives. However, surprisingly little information is available on one-electron standard reduction potentials (Eo(R-NO2/R-NO2)). The Eo(R-NO2/R-NO2) is an essential thermodynamic parameter for predicting the rate and extent of reductive transformation for energetic residues. In this study, experimental (linear free energy relationships) and theoretical (ab initio calculation) approaches were employed to determine Eo(R-NO2/R-NO2) for nitroaromatic, (caged) cyclic nitramine, and nitroimino explosives that are found in military installations or are emerging contaminants. The results indicate a close agreement between experimental and theoretical Eo(R-NO2/R-NO2) and suggest a key trend: Eo(R-NO2/R-NO2) value decreases from di- and tri-nitroaromatic (e.g., 2,4-dinitroanisole) to nitramine (e.g., RDX) to nitroimino compound (e.g., nitroguanidine). The observed trend in Eo(R-NO2/R-NO2) agrees with reported rate trends for reductive degradation, suggesting a thermodynamic control on the reduction rate under anoxic/suboxic conditions.

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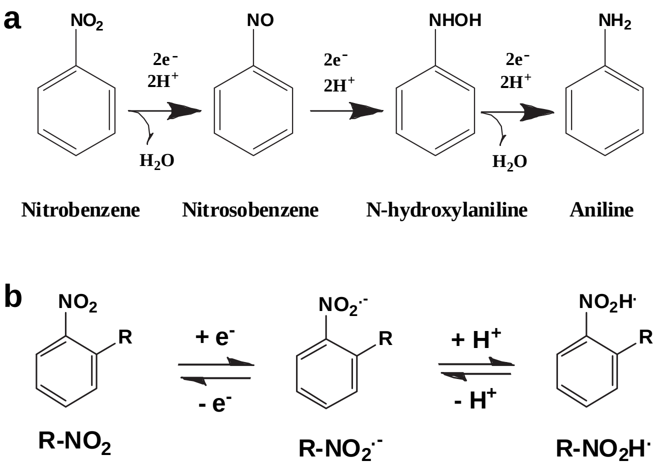

Fig. 1. Two (a) and one-electron (b) transfer reactions of nitro-based explosives.

are emerging for potential use. Preferred use of IMs arises from low sensitivity to shock and friction and lower toxicity of degradation products. However, fate of these emerging IMs in aqueous environments is largely unknown. The unique reduction potential (E) corresponding to the half reaction for a given explosive ($R\text{-}NO_2$) and its one-electron reduction product ($R\text{-}NO_2-$) predicts the geochemical conditions that will favor the reductive transformation.

Under anoxic and suboxic conditions, nitro-based explosives such as NACs and cyclic nitramines ($R\text{-}NO_2$) can accept one electron to form nitro(aryl) radicals ($R\text{-}NO_2^{-}$) where R denotes substituent (Fig. 1b). A balanced single electron transfer reaction with a corresponding Nernst Equation for calculating E^o is provided below:

$$R\text{-}NO_2 + e^- = R\text{-}NO_2^{-} \tag{1}$$

$$E = E^o + \frac{RT}{F}\ln\left(\frac{\{R\text{-}NO_2\}}{\left\{R\text{-}NO_2^{\bullet-}\right\}}\right) \tag{2}$$

where E^o is the standard one-electron reduction potential for Equation (1), R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature, and F is the Faraday constant (9.6485×10^4 C mol^{-1}). Both E and E^o are directly tied to the partial molar Gibbs Free Energy values ($\mu^o{}_i$) (Stumm and Morgan, 1996) and the activities of the species in Equation (2). If $R\text{-}NO_2$ is neutral (no ionizable side-groups), the activity coefficient (γ) only arises from the radical anion:

$$E = E^o + \frac{RT}{F}\ln\left(\frac{1}{\gamma_-}\right) + \frac{RT}{F}\ln\left(\frac{[R\text{-}NO_2]}{\left[R\text{-}NO_2^{\bullet-}\right]}\right) \tag{3}$$

Many reports of standard reduction potentials for organic species fail to provide sufficient information about the medium composition, especially the ionic strength, that allows activity coefficients to be calculated (Clark, 1960). When this situation is encountered, the first two terms in Equation (3) must be lumped together:

$$E_o = E^o + \frac{RT}{F}\ln\left(\frac{1}{\gamma_-}\right) \tag{4}$$

Equation (3) can then be rewritten as the following:

$$E = E_o + \frac{RT}{F}\ln\left(\frac{[R\text{-}NO_2]}{\left[R\text{-}NO_2^{\bullet-}\right]}\right) \tag{5}$$

Therefore, E^o denotes standard reduction potentials for which reliable activity corrections can be made and E_o denotes standard reduction potentials that can vary depending on the medium composition (Clark, 1960). For the reaction presented in Equation (1), the discrepancy between E^o and E_o is 0.001 volts at an ionic strength of 1.0×10^{-3} M, 0.008 volts at 0.25 M (experimental condition employed in this study), and 0.010 volts at 0.50 M. Hence, reduction potentials calculated using E_o are not far off from values achievable if E^o values were available.

In order to account for the protonation and deprotonation of $R\text{-}NO_2^{-}$, we write a mass balance equation for the radical anion:

$$R_T = \left[R\text{-}NO_2^{\bullet-}\right] + [R\text{-}NO_2H^\bullet] \tag{6}$$

Since ${}^cK_{a1} = [R\text{-}NO_2^{\bullet-}][H^+]\Big]_{[R\text{-}NO_2H^\bullet]}$, Equation (6) becomes the following

$$R_T = \left[R\text{-}NO_2^{\bullet-}\right] + \frac{\left[R\text{-}NO_2^{\bullet-}\right]\left[H^+\right]}{{}^cK_{a1}} \tag{7}$$

Rearrangement of Equation (7) yields Equation (8):

$$\left[R\text{-}NO_2^{\bullet-}\right] = \frac{R_T}{\left(1 + \frac{[H^+]}{{}^cK_{a1}}\right)} \tag{8}$$

Substitution of Equation (8) into Equation (5) yields Equation (9).

$$E = E_o + \frac{RT}{F}\ln\frac{O_T}{R_T} + \frac{RT}{F}\ln\left(1 + \frac{\left[H^+\right]}{{}^cK_{a1}}\right) \tag{9}$$

where $O_T = [R\text{-}NO_2]$.

When $R_T = O_T$, a mid-point potential (E_m) (Wardman, 1989) can be defined as the following:

$$E_m = E_o + \frac{RT}{F}\ln\left(1 + \frac{\left[H^+\right]}{{}^cK_{a1}}\right) \tag{10}$$

Majority of reported one-electron reduction potentials for NACs are the E_m values obtained at pH 7.0 and are often denoted $E_h^{1\prime}$ (where h denotes standard hydrogen electrode, 1 denotes single electron transfer, and ′ denotes neutral pH) (Wardman, 1989). Most of nitroaryl radicals are short-lived and do not exhibit reversible one-electron transfer required for the use of electrochemical methods such as cyclic voltammetry. As a result, E_m values are determined kinetically using rapid spectrophotometric techniques such as pulse radiolysis and flash photolysis (Wardman, 1989). Equilibrium concentrations of radical and ground state species are determined spectrophotometrically in order to calculate the E_m values (Wardman, 1989). Reported E_m values of NACs are summarized (Table A1, Appendix A). As shown in Equation (10), the discrepancy between E_m and E_o arises from the pK_{a1} value of the nitroaryl radical anion. The discrepancy between E_m and E_o increases with pK_a and is 3×10^{-5} volts for $pK_a = 4.0$ and 0.02 volts for $pK_a = 7.0$. Since pK_a values of most nitroaryl radical anions are below 4.0 (2.2 for 1,2-dinitrobenzene; 3.9 for 1-ethoxy-2-nitrobenzene) (Wardman, 1985), E_m values reported in the literature (Table A1) are not far off from E_o values.

A number of studies demonstrated linear free energy relationships (LFER) between literature E_m values (Table A1) and experimentally observed rate constants for reduction of a series of monosubstituted nitrobenzenes. Examples of reductants include Fe (II) sorbed on goethite (Colon et al., 2006a) or magnetite (Klausen et al., 1995), soluble Fe(II) in the presence of iron-coordinating ligand tiron (Naka et al., 2006), hydrogen sulfide or cysteine in the

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presence of electron shuttles juglone, lawsone, and naphthoquinone (Schwarzenbach et al., 1990), structural Fe(II) in clay minerals (Neumann et al., 2008), and flavins (Li and Fu, 2008). Resulting LFER has often been used to determine the E_m of target explosives for which literature E_m values are not available (Hofstetter et al., 1999; Li and Fu, 2008). In addition, the slope of LFER (log(rate constant) versus E_m (0.059 volts)$^{-1}$) has been used to elucidate the rate determining step. For homogeneous reduction of NACs by hydrogen sulfide in the presence of juglone (Schwarzenbach et al., 1990) and Fe(II) in the presence of a catecholate ligand tiron (Naka et al., 2006), the slopes of LFER were close to 1.0, suggesting that outer-sphere initial one-electron reduction of NACs (to form nitroaryl radicals, Equation (1)) is the rate-determining-step. On the other hand, the slopes were significantly lower than 1.0 for Fe(II) sorbed on goethite and magnetite (Klausen et al., 1995), and was nearly zero for microbial reduction in column reactors (Hofstetter et al., 1999). This suggests alternative rate determining steps such as the sorption to, and regeneration of, reactive surface sites for NACs reduction.

In the past decades, computational techniques emerged as a powerful alternative for the experimental determination of reduction potentials. The fully computational technique is based on recent advances in *ab initio* quantum chemistry. Computational techniques are particularly useful when experimental measurements are difficult or independent verification of experimental data is needed, and for designing molecules with unique redox properties. The computational technique also facilitates understandings in complex factors controlling the changes in reduction potentials. The computational approach affords reduction potentials that are within the accuracy of reference experimental values. For example, a close agreement between theoretical and experimental values was reported for one-electron oxidation potentials of anilines (Winget et al., 2000) and reduction potentials of substituted flavins (Li and Fu, 2008) and quinine derivatives (Namazian and Coote, 2007; Pakiari et al., 2008). Recently, we reported a refined computational protocol to predict one-electron standard reduction potentials of nitro-compounds (Zubatyuk et al., 2010) based on Faraday's law:

$$E^o = -\frac{\Delta G^{\mathrm{red}}}{nF} + E_H \tag{11}$$

where ΔG^{red} is the Gibbs free energy of reduction, n is the number of electrons transferred, F is the Faraday constant, and E_H is the absolute potential of the reference electrode. Free energy of reduction in solution is calculated using the following equation (see Materials and Methods for detailed computational approach for calculating ΔG^{red}).

$$\Delta G^{\mathrm{red}}_{\mathrm{sol}}(O) = \Delta G^{\mathrm{EA}}_{\mathrm{gas}} + \Delta G^{\mathrm{solv}}\left(R^{-\cdot}\right) - \Delta G^{\mathrm{solv}}(O) \tag{12}$$

The present study employed experimental and theoretical approaches for a systematic determination of the standard one-electron reduction potentials for the key current and emerging nitroaromatic and cyclic nitramine explosives. Determined reduction potentials (in volts) will allow quantitative comparison of energetics of half-reaction between an explosive and a reductant relevant to geochemical conditions. The comparison of reduction potentials will allow us to document substituent effects and structure-reactivity relationships (Bailey et al., 1983; Bailey and Ritchie, 1985).

2. Materials and methods

2.1. Chemicals and glassware

Unless otherwise stated, all solution handling operations were performed inside a controlled-atmosphere glove bag (95% N_2, 5% H_2, Pd catalyst; Coy Laboratory Products, Grass Lake, MI). All chemical reagents were of the highest purity available. Distilled, deionized water (DDW) with a resistivity of 18 MΩ cm (Millipore, Milford, MA) was boiled and nitrogen-sparged (2 h L^{-1}) prior to the preparation of solutions. Glassware and plasticware was rinsed with acetone and distilled water prior to soaking overnight in a 5.0 M nitric acid bath. Upon removal from the acid bath, glassware and plasticware was rinsed with DDW and air dried prior to use. Glassware and plasticware that had prior contact with metal ions was soaked in a 5.0 mM oxalic acid bath overnight before following the above procedure.

4′-Nitroacetophenone, 1,3-dinitrobenzene, 4-nitrotoluene, 1-chloro-3-nitrobenzene, 1-chloro-4-nitrobenzene, nitrobenzene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX), nitroguanidine, and 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt (tiron) were purchased from Sigma-Aldrich (Milwaukee, WI). HMX and RDX were received as 1 mg mL^{-1} acetonitrile solutions. 2,4-Dinitroanisole, 4-nitroanisole, and 2-nitroanisole were purchased from Alfa Aesar (Ward Hill, MA). CL-20 was obtained from Naval Air Warfare Center (China Lake, CA). For explosives received in solid phase, aqueous stock solutions were prepared daily and were stored in the dark. Explosives having low aqueous solubility were first dissolved in methanol (J.T. Baker, Phillipsburg, NJ). The volume fraction of methanol in reaction solutions was kept below 1%. Control experiments demonstrated negligible effects of methanol on reaction rate at the volume fraction below 5%. All organic stock solutions were filtered (0.22 μm Millipore Millex-GS; Millipore, Billerica, MA) prior to use. In order to minimize Fe(III) contamination, Fe(II) stock solutions were prepared by acidifying filtered (Anatop 25-Plus inorganic 0.02 μm membrane filter; Whatman Scientific, Maidstone, England) neutral $FeCl_2$ solution with HCl for the final concentration of 1.0 M $FeCl_2 \cdot 4H_2O$ (Aldrich) in 1.0 mM HCl.

2.2. Experimental setup

Ionic strength of all reaction solutions were set to 0.25 M using 3.0 M NaCl (Sigma-Aldrich). To set pH, a 50 mM solution of 2-(N-Morpholino)ethanesulfonic acid monohydrate (MES; pK_a 6.15, $5.5 \leq pH < 6.5$) buffer (Sigma-Aldrich) was used. Within the glove bag, electrolyte, buffer, Fe(II), and tiron were added to capped glass bottles and preequilibrated for 24 h under constant stirring. The reaction was initiated by adding an explosive. At successive time intervals, aliquots were pipetted into amber glass HPLC autosampler vials containing known volumes of (1) 0.26 M Na_2EDTA (Sigma-Aldrich) for the final concentration of 50 mM Na_2EDTA or (2) 50 mM HCl for the final concentration of 1–10 mM HCl to quench the reaction. The vials were capped inside the glove bag, shaken, and transferred to the HPLC autosampler outside of the glove bag, and immediately injected. A semi-micro glass electrode pH probe (Orion, Waltham, MA) was used to measure the pH of each collected aliquot. An isocratic HPLC system with a diode array detector (Agilent Technologies, Inc., Santa Clara, CA) and a μBondapak™ C_{18} column (3.9 × 300 mm column) was used. Depending upon the analytes under investigation, different ratios of (i) methanol or acetonitrile (J.T. Baker) and (ii) DDW for a total flow of 1.0 mL min^{-1} were required. All reactions were monitored for two half-lives or longer.

2.3. Ab initio quantum mechanical calculation of one-electron standard reduction potentials (E^o)

The computational protocol was described in a previous report (Zubatyuk et al., 2010). Briefly, free energies of electron attachment were calculated as the energy difference between neutral and anion-radical forms after full geometry optimization, including vibrational corrections to Gibbs free energy calculated using rigid rotor approximation. Spin-unrestricted Kohn-Sham orbitals were used for the computation of anion-radical species. Because the most accurate results were obtained using the newly developed meta-GGA functionals, the 6-311++G(d,p) basis set and M05 GGA density functional (Zhao and Truhlar, 2006) were used for all calculations. Solvation free energies were evaluated using PCM model by single-point energy calculation on molecular geometry optimized at the same level of theory.

3. Results and discussion

3.1. Establishment of LFER

The experimental approach employed LFER using ferrous complexes possessing sufficiently low reduction potentials (Fig. A5, Appendix A) to reduce a wide range of nitroaromatic and cyclic nitramine explosives. Specifically, Fe(II) complexed with catecholate ligand tiron was selected for obtaining LFER for the following reasons: (1) Fe(II) is a single electron donor (Equation (1)), (2) the presence of excess tiron prevents the formation of iron (hydr)oxides, allowing the reactions to proceed in homogeneous phases at stable pH and ionic strength, and (3) the system has been studied previously for the reduction of NACs (Naka et al., 2006),

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RDX, and HMX (Kim and Strathmann, 2007). Pseudo-first-order rate constants (k_{obs}) were first determined for compounds with known E_m(R-NO$_2$/R-NO$_2$−) values. Resulting LFER was used to determine the $E_m(R\text{-}NO_2/R\text{-}NO_2-)$ and $E^o(R\text{-}NO_2/R\text{-}NO_2^-)$ values of target explosives.

When 25 μM 4-chloronitrobenzene is reacted with 500 μM $FeCl_2$ in the presence of 10 mM tiron (pH 5.8, I = 0.25), first-order decay in 4-chloronitrobenzene coincided the buildup of the N-hydroxylaniline intermediate and aniline product (Fig. A2, Appendix A). In HPLC analyses, nitrobenzenes elute after the corresponding anilines, which elute after the corresponding N-hydroxylanilines, i.e., 4.7 min for 4-chloro-N-hydroxylaniline, 5.3 min for 4-chloroaniline, and 12.8 min for 4-chloronitrobenzene (Fig. A1, Appendix A). Similar first-order decay behaviors were observed for additional reference compounds (Table 1) and k_{obs} values were obtained as the slope of ln(nitrobenzene concentration in M) versus time (in seconds) (Fig. A3, Appendix A). The LFER could then be obtained from a plot of log k_{obs} (in s^{-1}) versus $E_m \cdot (0.059\ \text{volts})^{-1}$ for a series of reference NACs as $\log k_{obs} = 1.11(\pm 0.08) \cdot E_m \cdot (0.059\ \text{volts})^{-1} + 4.89(\pm 0.55)$ ($R^2 = 1.0$; Fig. A4, Appendix A). This LFER was then used to determine E_m values of target explosives from experimentally determined k_{obs}. The slope of LFER suggests that initial one-electron transfer is the rate-determining-step in the reaction between explosives and Fe(II) species (Schwarzenbach et al., 1990; Naka et al., 2006). From duplicate experiments, determined errors in E_m values (mean ± standard deviation) were -0.3982 ± 0.0002 volts for 2,4-dinitroanisole, -0.40 ± 0.01 volts for 2,4-dinitrotoluene, and -0.5748 ± 0.0008 volts for 4-nitroanisole.

3.2. Determination of E^o for target explosives

Fig. 2 presents current and emerging explosives investigated in this study. RDX, HMX, 2,4-dinitrotoluene, 2,6-dinitrotoluene, and nitroguanidine are often encountered as energetic residues at military training ranges (Jenkins et al., 2006). Picric acid (2,4,6-trinitrophenol) is a strongly acidic phenol ($pK_a = 0.38$) that has historically found an extensive military use (Tan et al., 2006). 2,4-Dinitroanisole (DNAN) is an insensitive munitions compound and is expected to replace traditionally used explosives such as TNT. 2-Nitroanisole and 4-nitroanisole were selected to gain structure-reactivity relationships for the emerging explosive DNAN. CL-20 is a caged cyclic nitramine and has received much attention in the past years as a potential alternative for RDX and HMX due to improved oxidizer-to-fuel ratio (Monteil-Rivera et al., 2009). Experimental (E^o(exp)) and theoretical (E^o(theo)) one-electron standard reduction potentials (in volts) of nitroaromatic, nitramine (cyclic and caged cyclic), and nitroimino explosives (Fig. 2) are given in Table 2 (in decreasing order of E_m(exp)). Because pK_a values of radical anions for compounds listed in Table 2 were not available, experimental E^o values were determined using Equation (4) for $I = 0.25$ M assuming $E_m = E_o$. As shown in Table 2, experimental and theoretical approaches employed in this study afforded E^o values within the accuracy of 0.01–0.10 volts (E_m(exp) − E^o(theo)) for 2,4-dinitrotoluene, 2,4-dinitroanisole, 2,6-dinitrotoluene, RDX, 4-nitroanisole, 2-nitroanisole, and HMX. Linear correlation ($R^2 = 0.79$) with slope of 0.79 was observed between E_m(exp) and E^o(theo) values. The linear relationship improved when HMX was removed from the plot ($R^2 = 0.97$). Activity correction (from E_m to E^o) of experimental values did not significantly improve the agreement between experimental and theoretical values. More positive E^o values of mono- and di-nitroaromatic compounds suggest that nitro substituent on the aromatic ring strongly withdraw electrons both inductively and by resonance to stabilize the nitroaryl radical anions (Bruice, 1998). Comparisons between 2- and 4-nitroanisole indicate that the methoxy substituent inductively withdraws electrons more strongly at para than ortho position, relative to the position of nitro substituent. Considerably more negative E^o values for 2,6-dinitrotoluene, relative to 2,4-dinitrotoluene, suggest steric effects (Carroll, 1998). In addition, comparison of E^o(theo) values for 2,4-dinitrotoluene and 2,4-dinitroanisole indicates that methoxy substituent donates electrons more strongly by resonance than methyl substituent that donates electrons inductively (Bruice, 1998).

Table 2 shows the following trends for both experimental and theoretical E^o values: di- and trinitrobenzenes possess higher (more positive) standard one-electron reduction potentials than nitramines. Greater discrepancy between E_m and E^o(theo) values of CL-20 (Table 2) likely arises from spontaneous dissociation of the C–N bond upon the one-electron transfer event, which was observed only for CL-20 in determination of E^o(theo). Because of its ionizable hydroxyl side-group with low pK_a of 0.38, picric acid exists predominantly in anionic form at near-neutral pH. Hence, Equation (1) must be rewritten to account for additional species of both oxidized and reduced forms (Appendix A). Correction of E_m to E^o resulted in a greater decrease of reduction potential compared to neutral compounds in Table 2. The lower E^o(exp) value of trinitrobenzene picric acid compared to dinitrobenzene 2,4-dinitrotoluene reflects the strongly electron donating nature of hydroxyl substituent.

One-electron standard reduction potentials obtained in this study suggest a thermodynamic control on the previously reported rates of reduction for a series of nitro-based explosives under a wide range of environmentally relevant conditions. For example, faster rate of reduction was observed for RDX than HMX by iron- and quinone-reducing bacteria, in the presence and absence of an electron shuttle anthraquinone-2,6-disulfonate (AQDS) (Kwon and Finneran, 2008). Similar rate trends were observed for abiotic reduction of RDX and HMX in dithionite-reduced sediments (Boparai et al., 2008). Faster reduction was observed for explosives having more positive one-electron reduction potentials, from HMX (E_m(exp) = −0.66 volts, Table 2), RDX (E_m(exp) = −0.55 volts, Table 2), to TNT (E_m = −0.30 volts, Table A1) (Boparai et al., 2008). In a separate study, rapid (half-life less than 3 min) abiotic reduction of CL-20 was observed in dithionite-reduced sediments, and surface complexed Fe(II) species were suggested to be the reactive reductants of CL-20 (Szecsody et al., 2004).

Nitroguanidine is a nitroimino compound that exists in two tautomeric forms (Fig. 2), and tautomer A predominates except under strongly alkaline conditions (Kaplan et al., 1982). Limited reports are available on the environmental transformation of nitroguanidine. Degradation of nitroguanidine was negligible in activated sludge under aerobic conditions and in sterile sludge under reducing conditions (Kaplan et al., 1982). However, slow but significant biodegradation of nitroguanidine and buildup of nitrosoguanidine was observed in activated sludge under anaerobic conditions (Kaplan et al., 1982). A strongly negative E^o(theo) value

Table 1

Determined k_{obs} (s^{-1}) for six reference nitroaromatic compounds. E_m values correspond to the half-reaction $R\text{-}NO_2 + e^- = R\text{-}NO_2^-$ at pH 7.0. Experimental conditions: 25 μM oxidant, 500 μM $FeCl_2$, 10 mM tiron, pH 5.8, $I = 0.25$.

Compound	E_m(volts)	Reference	k_{obs} (s^{-1})	$t_{1/2}$ (min)
1,3-dinitrobenzene	−0.345	(Wardman, 1989)	4.13×10^{-2}	0.4
4′-nitroacetophenone	−0.360	(Hofstetter et al., 1999)	1.17×10^{-2}	1.4
3-chloronitrobenzene	−0.405	(Hofstetter et al., 1999)	1.09×10^{-3}	15.3
4-chloronitrobenzene	−0.450	(Hofstetter et al., 1999)	3.54×10^{-4}	47.1
Nitrobenzene	−0.485	(Wardman, 1989)	8.48×10^{-5}	196.4
4-nitrotoluene	−0.500	(Wardman, 1989)	2.86×10^{-5}	582.8

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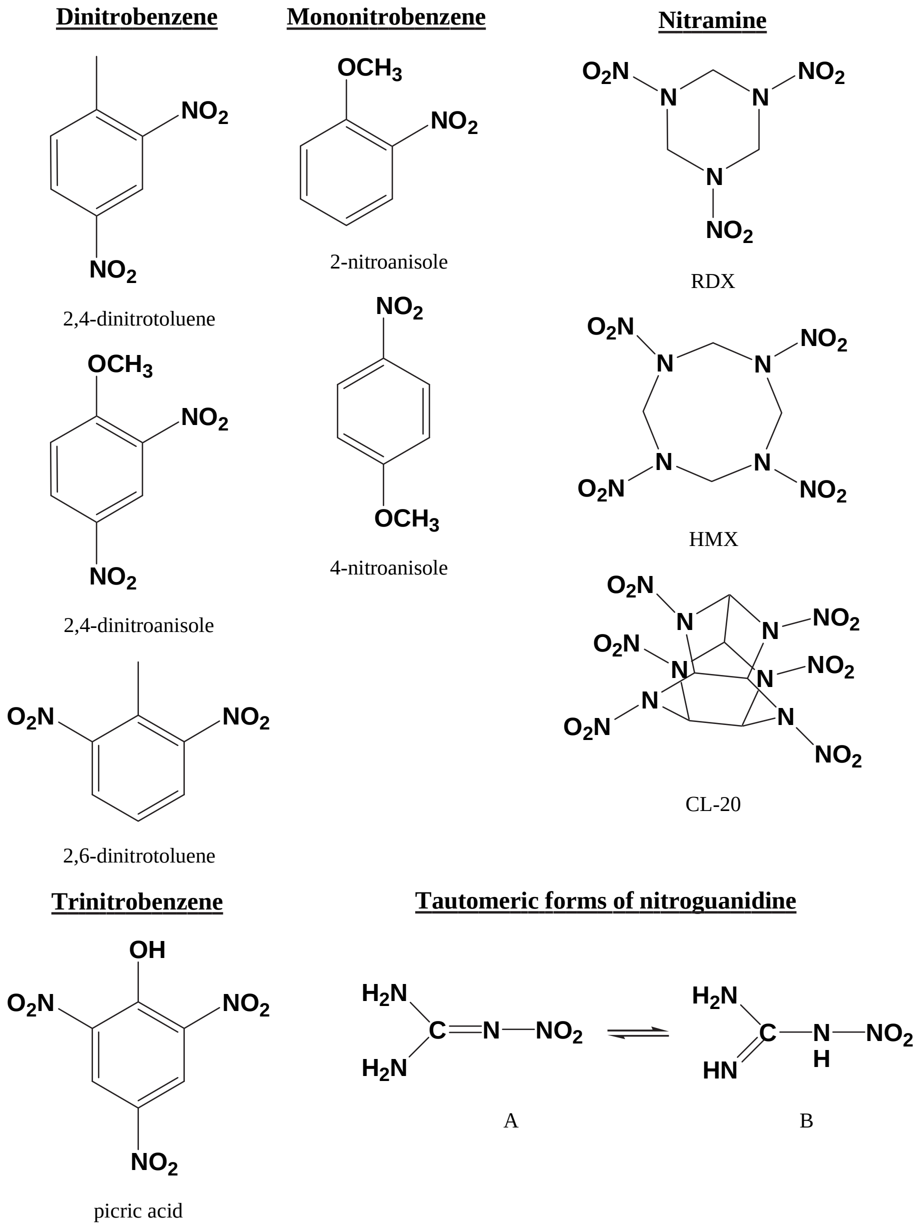

Fig. 2. Current and emerging explosives investigated in this study.

Table 2
Experimental (E(exp)) and theoretical (E(theo)) values of E^o and E_m for target explosives. All values are given in volts.

Compound	E_m(exp)	E^o(theo)	E_m(exp) − E^o(theo)	E^o(exp)[b]	E^o(exp) − E^o(theo)
Picric acid	−0.39			−0.42	
CL-20	−0.39	−0.10[c]	−0.29	−0.40	−0.30
2.4-dinitrotoluene	−0.40	−0.36	−0.04	−0.41	−0.05
2,4-dinitroanisole	−0.40	−0.39	−0.01	−0.41	−0.02
2.6-dinitrotoluene	−0.44	−0.43	−0.01	−0.45	−0.02
RDX	−0.55	−0.54	−0.01	−0.56	−0.02
4-nitroanisole	−0.58	−0.63	0.05	−0.59	0.04
2-nitroanisole	−0.60	−0.66	0.06	−0.61	0.05
HMX	−0.66	−0.56	−0.10	−0.67	−0.11
Nitroguanidine	a	−0.70			

[a] Reaction is too slow to determine E_m(exp).
[b] Determined for $I = 0.25$ M assuming $E_m = E_o$.
[c] Approximate value due to spontaneous dissociation of C—N bond upon the formation of radical anion.

of nitroguanidine correlates with negligibly slow abiotic reduction of nitroguanidine under reducing conditions in this (Table 2) and previous study (Kaplan et al., 1982).

4. Conclusion

Experimental and theoretical one-electron standard reduction potentials (E^o(R-NO$_2$/R-NO$_2^-$) in volts) determined in this study are in close agreement with one another for a wide range of nitroaromatic and nitramine explosives. These reliable approaches for determining the master variable will allow us to predict the contaminant fate under anoxic and suboxic conditions. Trends in E^o(R-NO$_2$/R-NO$_2^-$) for mono-, di-, and tri-nitroaromatic compounds followed expected inductive, resonance, and steric effects of ring substituents. Trends in determined E^o(R-NO$_2$/R-NO$_2^-$) for nitroaromatic, nitramine, and nitroimino compounds are in agreement with reported rate trends for abiotic reductive transformation of

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explosives. The results suggest that one-electron standard reduction potentials serve as the master variable for predicting the fate of energetic residues under a wide range of environmental conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2010.06.033.

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