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Radical-Based Destruction of Nitramines in Water: Kinetics and Efficiencies of Hydroxyl Radical and Hydrated Electron Reactions

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Abstract

In support of the potential use of advanced oxidation and reduction process technologies for the removal of carcinogenic nitro-containing compounds in water reaction rate constants for the hydroxyl radical and hydrated electron with a series of low molecular weight nitramines ($R^1R^2\text{-NNO}_2$) have been determined using a combination of electron pulse radiolysis and transient absorption spectroscopy. The hydroxyl radical reaction rate constant was fast, ranging from $0.54\text{--}4.35 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, and seen to increase with increasing complexity of the nitramine alkyl substituents suggesting that oxidation primarily occurs by hydrogen atom abstraction from the alkyl chains. In contrast, the rate constant for hydrated electron reaction was effectively independent of compound structure, ($k_{av} = (1.87 \pm 0.25) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) indicating that the reduction predominately occurred at the common nitramine moiety. Concomitant steady-state irradiation and product measurements under aerated conditions also showed a radical reaction efficiency dependence on compound structure, with the overall radical-based degradation becoming constant for nitramines containing more than four methylene groups. The quantitative evaluation of these efficiency data suggest that some (~40%) hydrated electron reduction also results in quantitative nitramine destruction, in contrast to previously reported electron paramagnetic measurements on these compounds that proposed that this reduction only produced a transient anion adduct that would transfer its excess electron to regenerate the parent molecule.

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INTRODUCTION

The fate of emerging contaminants in the environment (air, soil, and water) continues to be an intense area of research throughout the world.¹ One important class of compounds that has attracted considerable attention are molecules containing a nitrogen–nitrogen single bond. This class of compounds includes the hydrazines, nitrosamines, and nitramines (Figure 1). These three classes of compounds can exist in multiple states related through oxidation and reduction.

Nitrosamines have been the most extensively studied group of these chemicals and have been shown to be carcinogenic, teratogenic, and mutagenic.² Nitrosamines can be produced by the oxidation of hydrazines by typical oxidative chemicals that are added to water to remove microbial pathogens.³ Further, increased formation of nitrosamines through the production of dichloramine (NHCl_2) has also been shown to occur when utilities deliberately increase the chlorine to ammonia molar ratio to control nitrification during chloramination.⁴

Nitramines have also been identified as possible human carcinogens having similar characteristics to their corresponding nitrosamines.⁵ In the presence of sunlight, *N*-nitrosodimethylamine (NDMA) has been shown to exist in a redox equilibrium with its oxidized form *N*-nitrodimethylamine.⁶ In water, the formation of *N*-nitrodimethylamine has previously been postulated,⁷ and subsequently demonstrated, to form upon the addition of hypochlorite to solutions containing dimethylamine and sodium nitrite at pH 6.9.⁸

In addition to these low molecular weight mononitramines being environmental contaminants, another group of nitramines, those containing multiple sites of nitration, have become of concern in both soils⁹ and waters.^{10,11} Highly energetic nitro compounds such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and CL-20 are commonly used in propellants and munitions. RDX has been used as an explosive since the beginning of the 20th century and has been classified by the EPA as a possible human carcinogen.^{12–15}

Previous investigations have examined the degradation of these high energetic explosives under thermal,^{16,17} reductive,^{18–20} hydrolytic,^{21–24} biological,^{25,26} and radical-based reaction conditions.^{27–30} For fast, active, removal of chemically contaminated waters, the radical-based advanced oxidation/reduction (AO/RP) approach may prove to be most beneficial.³¹ The strongly oxidizing hydroxyl radical ($\cdot\text{OH}$) is produced in situ by most AO/RPs, including $\text{O}_3/\text{H}_2\text{O}_2$, $\text{O}_3/\text{UV-C}$, $\text{H}_2\text{O}_2/\text{UV-C}$, UV irradiation of titanium dioxide, sonolysis, or the irradiation of water via electron beams or γ rays. The use of sonolysis or irradiation will also produce strongly reducing hydrated electrons (e_{aq}^-) and/or hydrogen atoms ($\text{H}\cdot$).

For a thorough understanding of the AO/RP radical chemistry involved in nitramine decontamination of water, critical to the development of quantitative engineering schemes, the characterization of the reactivity and fate of all redox forms of nitramines under treatment conditions is necessary. This chemistry involves elucidating the kinetic parameters of the reactions and the mechanisms of the organic contaminant destruction that define these

processes. These data then can be formulated into kinetic models that describe the process completely.³² In this study, we have determined the kinetics and dominant redox mechanisms for the reactions of the highly oxidizing $\bullet\text{OH}$ radical and reducing e_{aq}^- species for a library of low molecular weight nitramines in water. In addition, we have also established radical degradation efficiencies for these redox reactions. This work augments the paucity of kinetic data available in the literature for these reactions, consisting of our preliminary study on the three lowest molecular weight nitramines³³ (see Table 1) and a recent measurement of the reactivity of both of these radicals with cyclotrimethylenetrinitramine, where $k_{\text{OH}}^{\bullet} = (7.5 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_e^- = (1.4 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ was reported.³⁴ The rate constants for these four compounds demonstrate that the reduction of nitramines is considerably faster than for its oxidation.

EXPERIMENTAL SECTION

As no commercial source of nitramines was found, these compounds were synthesized in this study³³ from their corresponding *N*-dialkyl nitrosamines using peroxytrifluoroacetic acid, generated in situ by the reaction of trifluoroacetic anhydride with 50% hydrogen peroxide.

The seven new synthesized nitramines (see Table 1) were typically obtained in high purity (>98%), as determined by ^1H NMR. All other chemicals were obtained from the Sigma-Aldrich company or Fisher-Scientific and used at the highest purity available.

Nitramine solutions were made using Millipore Milli-Q charcoal filtered water that was constantly illuminated by a UV lamp to keep organic contaminant concentrations below $13 \mu\text{g L}^{-1}$. All nitramine solutions were made by dissolving the pure compound in water that had been presaturated with high purity N_2O (for $\bullet\text{OH}$ isolation) or N_2 (e_{aq}^- isolation). During the kinetic measurements, the solution vessels were again bubbled with only the minimum amount of gas necessary to prevent air ingress.

The electron linear accelerator (LINAC) pulse radiolysis system at the Radiation Laboratory, University of Notre Dame, was used for all kinetic measurements. This irradiation and accompanying transient absorption detection system has been described in detail previously.³⁵ In the pH range 3–10, the radiolysis of water using ionizing radiation produces a mixture of radical and molecular species according to the stoichiometry³⁶

The numbers in brackets represent the final homogeneous absolute yields³⁷ (G-values) of each species produced in units of $\mu\text{M J}^{-1}$.

Absolute radical concentrations were determined using thiocyanate dosimetry,³⁸ using N_2O -saturated $1.00 \times 10^{-2} \text{ M}$ KSCN solutions and monitoring the maximum absorbance of the formed $(\text{SCN})_2^{\bullet-}$ transient. Typically, kinetic data in this study were collected using doses of

3–5 Gy per 2–3 ns pulse. Throughout this article, G is defined in $\mu\text{mol J}^{-1}$, and ϵ is in units of $\text{M}^{-1} \text{cm}^{-1}$.³⁷

The hydroxyl radical reaction with these nitramines was studied using SCN^- competition kinetics,³⁶ monitoring the change of absorption intensity of the produced $(\text{SCN})_2^{\bullet-}$ transient at 475 nm. The hydrated electron rate constant was determined by directly following its absorption at 700 nm.³⁹ All kinetic experiments were performed at ambient temperature ($20 \pm 1^\circ\text{C}$) and in neutral pH solution. The reported total errors for the kinetic data are the sum of experimental precision and compound purity.

Radical degradation efficiency measurements were made as described previously for nitrosamines,^{40,41} using 20.0 mL samples of 1.0 mM nitramine *aerated* solutions in a continuous, low-intensity ($\sim 100 \text{ Gy/min}$), ^{60}Co -irradiation source, again at the Radiation Laboratory. Ionizing gamma irradiation produces the same mix of oxidizing and reducing radicals as given for the LINAC irradiation in eq 1. For these steady-state irradiations, the total radical production rate was about $40 \mu\text{M/min}$. Vials of each separate nitramine at 1.00 mM initial concentration were irradiated for different doses up to 6.0 kGy, which ensured almost complete loss of the parent compound (final concentration values were typically $<100 \mu\text{M}$, significantly higher than the detection limit of $\sim 1\text{--}2 \mu\text{M}$). The capped irradiated solutions were then sealed and were kept at 4°C to prevent significant hydrolysis or further reaction of parent or products until analysis. All samples were analyzed within several weeks of irradiation.

The extraction procedure used 5.00 mL of the irradiated nitramine sample to which $100 \mu\text{g}$ of *N*-nitrosodiethylamine had been added as a surrogate standard to measure extraction efficiency. Samples were then extracted using three separate 3–4 mL aliquots of CH_2Cl_2 . The combined organic layers were dried using anhydrous sodium sulfate and then quantitatively transferred into a 10.00 or 25.00 mL volumetric flask. A 1.00 mL aliquot of this latter sample was then transferred to an autosample vial, and had $20 \mu\text{g}$ of 1,3-dimethyl-2-nitrobenzene added as an internal standard. Standard calibration curves were also built on an internal basis for the surrogate standards. Extractions performed on the same solutions several weeks later gave the same results within experimental error ($\pm 5\%$).

These irradiated samples and calibration standards were analyzed by an Agilent 6890N Gas Chromatography (GC) system in tandem with an Agilent 5973 mass selective detector (MSD). An Agilent 7683B autosampler was used to deliver sample injections to a JW Scientific DB-5 ms column. GC parameters were as follows: injection temp, 225°C , with pulsed splitless injection; pulse pressure, 30 psi; He as the carrier gas with a constant flow rate of 1.5 mL/min . Initial oven temperature was 45°C for 5 min, ramped at 15°C/min to 125°C , 5°C/min to 150°C , then 15°C/min to 250°C , and finally held for 5 min. MSD transfer line temperature was 225°C ; MSD quad, 150°C ; MSD source, 230°C . Electron ionization detection was used, with an ionizing energy of 70 eV. MSD Chemstation software version D.01.02.16 was used for data analysis.

RESULTS AND DISCUSSION

Hydroxyl Radical Kinetic Reactions

Presaturating the nitramine solutions with N₂O gas allows the fast, quantitative conversion of the radiation-generated hydrated electrons, e_{aq}⁻, and some hydrogen atoms to the hydroxyl radical³⁶

which isolates this radical's reaction with added solute. However, the reaction of hydroxyl radicals with all of the nitramines of this study did not produce any significant transient absorbance change over the UV-visible region (250–800 nm). Therefore, these rate constants were determined using SCN⁻ competition kinetics. This approach was based upon the following competing reactions:³⁶

and monitoring the decrease in the (SCN)₂^{•-} absorption with added nitramine concentration (see Figure 2a). This hydroxyl radical competition can be solved analytically to give the following equation:

$$\frac{\text{Abs}^{\circ}(\text{SCN})_2\bullet^{-}}{\text{Abs}(\text{SCN})_2\bullet^{-}} = 1 + \frac{k_4[R^1R^2N - NO_2]}{k_5[SCN^{-}]} \quad (6)$$

where Abs[°](SCN)₂^{•-} is the maximum absorbance of (SCN)₂^{•-} measured at 475 nm for only the blank SCN⁻ solution, and Abs(SCN)₂^{•-} is the reduced absorbance of this transient when the nitramine was present. Therefore, a plot of Abs[°](SCN)₂^{•-}/Abs(SCN)₂^{•-} against the ratio [R¹R²N-NO₂]/[SCN⁻] gives a straight line of slope k₄/k₅ (see Figure 2b). Knowing that k₅ = 1.1 × 10¹⁰ M⁻¹ s⁻¹,³⁶ the k₄ rate constant can then be readily calculated.

Table 1 summarizes the hydroxyl radical rate constant values for all the nitramines measured in this study, along with the rate constants for the three compounds determined previously.³³ The reaction rate constant is seen to be faster with increasing complexity of the alkyl substituents. This is demonstrated in Figure 3a, where a plot of the natural logarithm of hydroxyl radical rate constant against the number of methylene (CH₂) groups in each nitramine gives a very good linear correlation.⁴⁰ These data are consistent with the thermodynamic expectation that the hydroxyl radical is abstracting a hydrogen atom to create a carbon-centered radical on the alkyl ligand. This behavior was postulated previously based upon steady-state radiolysis spin-trap electron paramagnetic resonance (EPR) measurements³³ for the three simplest aliphatic nitramines, where the measured EPR spectra

did not exhibit any large nitrogen coupling from the parent radical. This suggested that the formation of nitrogen-centered radical species was not a major reaction pathway. Similarly, the production of an oxygen-centered radical was eliminated.⁴¹

Hydrated Electron Kinetic Reactions

To isolate the reaction of only the reducing hydrated electron, nitramine solutions were presaturated with nitrogen gas (to remove dissolved oxygen) and then an excess (0.10–0.50 M) of alcohol (tert-butanol) was added. Under these conditions, the formed hydroxyl radicals and hydrogen atoms preferentially reacted with the excess alcohol:³⁶

allowing the hydrated electron to react with the nitramine present:

The formed alcohol radicals have a relatively low reactivity, and do not interfere in the reductive hydrated electron measurements.³⁶

The hydrated electron has a very strong UV–visible absorption spectrum peaking at ~720 nm ($\epsilon \approx 19\,000 \text{ M}^{-1} \text{ cm}^{-1}$).³⁹ Reduction kinetics were therefore performed by directly measuring the change in absorption decay as a function of added nitramine concentration near this wavelength (see Figure 4a). Pseudofirst-order kinetics were maintained by keeping the solute concentrations at least a factor of 20 greater than the initial hydrated electron concentrations. By plotting the calculated pseudofirst-order rate constants against the nitramine concentration, a straight line is obtained with the slope corresponding to the true second-order rate constant value. For *N*-nitropiperidine, a value of $k_9 = (2.17 \pm 0.04) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ is obtained (see Figure 4b). A summary of all the hydrated electron rate constants determined in this study are also given in Table 1. No significant difference in rate constant with ligand structure was apparent in these data (see Figure 3b), which suggests that the hydrated electron reaction with nitramines species occurs predominantly at the nitramine (>N-NO₂) group, at an average rate constant of $k_{\text{av}} = (1.87 \pm 0.25) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This behavior is consistent with previous spin-trap EPR measurements⁴¹ where, based upon the stable radicals produced, it was inferred that the initial reduction was only to form a transient anion adduct,⁴² which subsequently transferred its excess electron to the DMPO to give the reduced DMPO-H observed.

Hydroxyl Radical Reaction Efficiency Measurements

Although the hydroxyl radical oxidation of the nitramines is fast, it has been previously demonstrated that rate constants alone do not provide a complete accounting of the effectiveness of the hydroxyl radical in organic contaminant removal.⁴³ The reaction

efficiency, which is defined as the percentage of contaminant molecules destroyed per 100 hydroxyl radical reactions, has to be multiplied by the pure water measured rate constant to give an effective contaminant removal rate constant. The effective value is the correct number required for any kinetic modeling studies.³²

Low reaction efficiency values have been reported for $\bullet\text{OH}$ reaction with sulfonamides (~55%)⁴⁴ BPA (~76%)⁴³ and even for nitrosamines.⁴¹ For the latter, *N*-dimethylnitrosamine was shown to only have a reaction efficiency of 80%, *N*-methylethyland *N*-diethylnitrosamine were slightly higher, but 100% efficiency was only achieved for the more complex aliphatic nitrosamines (see Figure 5).

The radical reaction efficiencies for all 10 nitramines were also determined in this study using the same methodology as previously established for nitrosamines.⁴⁰ These data are also listed in Table 1 and shown in comparison to the nitrosamine values in Figure 5. It is important to note that these nitramine efficiency values in *aerated* solution were calculated based on only the fundamental yield of the $\bullet\text{OH}$ radical in water, $0.28 \mu\text{M J}^{-1}$,³⁷ as done previously for the nitrosamines. However, as these nitramine efficiencies were all 100%, clearly some additional nitramine degradation chemistry had to be occurring under these conditions.

Although no rate constant measurement has been reported for hydrogen atom reaction with nitrosamines or nitramines by analogy to data for other nitrogen-containing compounds,³⁶ it would be expected to be 1–2 orders of magnitude slower than the hydroxyl radical. Therefore, under aerated conditions, the dissolved oxygen concentration ($2.5 \times 10^{-4} \text{ M}$) would quantitatively scavenge all formed hydrogen atoms:³⁶

The $\text{HO}_2\bullet/\text{O}_2^{\bullet-}$ product radicals are relatively inert and would not be expected to degrade nitramines in water. Some hydrated electron scavenging by the oxygen would also be expected to occur³⁶

but the fast reaction of electrons with all nitramines ($k_{\text{av}} = 1.85 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) means that nitramine reduction still occurs. A simple competition kinetics analysis shows that 80% of the hydrated electron reactivity would be with the nitramine under our solution conditions. To explain the limiting reaction efficiency seen in Figure 5 (~130% as based on only the $\bullet\text{OH}$ radical yield), a hydrated electron reaction efficiency of 40% is required (which normalizes the nitramine total efficiency to 100% for the higher molecular weight species). This contradicts the previous assertion based on EPR spin-trap measurements that reduction did not give any compound degradation.³³

Although speculative, the hydrated electron-based reduction of nitramines in water might be favored over the nitrosamines based on the stability of the product nitrite and/or $\text{NO}_2\bullet$ over nitric oxide:

This implies that AOP treatment processes that also incorporate both the hydroxyl radical as well as the hydrated electron might be advantageous in the destruction of aqueous contaminant nitramines.

CONCLUSIONS

The kinetics of hydroxyl radical oxidation and hydrated electron reduction reactions of a library of nitramines in water were determined. The reactions of the hydroxyl radical increased with increasing complexity of the alkyl substituents on these contaminants, indicating that this oxidation was predominantly by hydrogen atom abstraction from methylene groups from the alkyl chains in these molecules. In contrast, the reaction of hydrated electron with nitramines occurs predominately at the nitramine moiety, with a rate constant of $k_{av} = (1.87 \pm 0.25) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

Concomitant steady-state irradiation radical efficiency degradation measurements for all 10 nitramines were also performed. These efficiency data show that the total radical-based removal of nitramines is greater than can be attributed to only the hydroxyl radical reactivity and that a small fraction (~40%) of hydrated electron reaction also results in compound destruction.

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Figure 1.
Structures of nitrogen–nitrogen single bond emerging contaminants.

Figure 2.

(a) Transient absorption changes at 475 nm for 97.8 μ M KSCN in N_2O -saturated solution at natural pH containing zero ($\square$), 90.6 ($\circ$), 191 ($\triangle$), 302 (∇), and 428 ($\diamond$) μ M dipropylamine. (b) Transformed competition-kinetics plot using maximum limiting intensity values of panel a for determination of hydroxyl radical reaction with dipropylamine. Solid line corresponds to weighted linear fit, with slope of 0.2079 ± 0.0099 ($R^2 = 1.00$) corresponding to a reaction rate constant of $k = (2.25 \pm 0.11) \times 10^9$ $M^{-1} s^{-1}$ at 19.6 $^{\circ}C$.

Figure 3.

(a) Correlation plot of $\ln(k_{\text{OH}})$ vs number of methylene groups in dialkylnitramines in aqueous solution. Solid line is the weighted linear fit with intercept 20.12 ± 0.03 , and slope 0.337 ± 0.007 , $R^2 = 0.96$. (b) Correlation of $\ln(k_{\text{e}}^-)$ vs number of methylene groups in dialkylnitramines.

Figure 4.

(a) Pseudofirst-order decay kinetics measured at 700 nm for the reaction of hydrated electron with 37.0 ($\square$), 78.4 ($\circ$), 125 ($\triangle$), and 237 μ M (∇) *N*-nitropiperidine at neutral pH and 20 °C. Solid lines are fitted exponential decay kinetics, with corresponding rate constants of $(9.13 \pm 0.07) \times 10^5$, $(1.40 \pm 0.02) \times 10^6$, $(2.83 \pm 0.03) \times 10^6$, and $(5.42 \pm 0.06) \times 10^6 \text{ s}^{-1}$, respectively. (b) Second-order rate constant determination from the data of panel a. Solid line is a weighted linear fit, corresponding to reaction rate constant of $(2.17 \pm 0.04) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $R^2 = 0.990$.

Figure 5. Correlation of radical-based degradation efficiency with nitramine (□) structure in comparison to that for nitrosamines (○).⁴⁰ Both these efficiency values are based on only the fundamental $\cdot\text{OH}$ yield of $0.28 \mu\text{mol J}^{-1}$.

Table 1

Kinetic Data for the Reaction of Nitramines with Hydroxyl Radical, Hydrated Electrons, and Percentage Radical Degradation Efficiency Values; Data of This Study in Bold

compound	#CH ₂ groups	$10^{-9} k_{\bullet\text{OH}} \text{ M}^{-1} \text{ s}^{-1}$	$10^{-10} k_e \text{ M}^{-1} \text{ s}^{-1}$	radical degradation efficiency % ^a
<i>N</i> -nitrodimethylamine	0	0.544 ± 0.020	1.91 ± 0.07	100.6 ± 10.6
<i>N</i> -nitromethylethylamine	1	0.760 ± 0.043	1.83 ± 0.15	109.4 ± 10.9
<i>N</i> -nitrodiethylamine	2	0.867 ± 0.048	1.76 ± 0.07	113.8 ± 7.1
<i>N</i> -nitrodipropylamine	4	2.25 ± 0.11	1.55 ± 0.11	121.0 ± 8.7
<i>N</i> -nitrobutylethylamine	4	3.11 ± 0.17	2.15 ± 0.17	121.1 ± 3.0
<i>N</i> -nitropyrrolidine	4	1.92 ± 0.20	1.96 ± 0.14	127.2 ± 9.8
<i>N</i> -nitromorpholine	4	2.30 ± 0.19	2.18 ± 0.13	127.2 ± 1.4
<i>N</i> -nitropiperidine	5	2.80 ± 0.19	2.17 ± 0.04	129.9 ± 6.5
<i>N</i> -nitrodibutylamine	6	3.83 ± 0.11	1.64 ± 0.15	130.3 ± 4.6
<i>N</i> -nitrohexamethyleneimine	6	4.35 ± 0.27	1.54 ± 0.10	124.0 ± 1.0

^aPercentage efficiency data calculated based only on hydroxyl radical degradation occurring with $G(\bullet\text{OH}) = 0.28 \mu\text{mol Gy}^{-1}$.