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Kinetics and Mechanisms of the Reactions of Hydroxyl Radicals and Hydrated Electrons with Nitrosamines and Nitramines in Water

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Absolute rate constants for hydroxyl radical, $^{\bullet}OH$, and hydrated electron, e_{aq}^-, reactions with low-molecular-weight nitrosamines and nitramines in water at room temperature were measured using the techniques of electron pulse radiolysis and transient absorption spectroscopy. The bimolecular rate constants obtained, k (M^{-1} s^{-1}), for e_{aq}^- and $^{\bullet}OH$ reactions, respectively, were as follows: methylethylnitrosamine, $(1.67 \pm 0.06) \times 10^{10}$ and $(4.95 \pm 0.21) \times 10^{8}$; diethylnitrosamine, $(1.61 \pm 0.06) \times 10^{10}$ and $(6.99 \pm 0.28) \times 10^{8}$; dimethylnitramine, $(1.91 \pm 0.07) \times 10^{10}$ and $(5.44 \pm 0.20) \times 10^{8}$; methylethylnitramine, $(1.83 \pm 0.15) \times 10^{10}$ and $(7.60 \pm 0.43) \times 10^{8}$; and diethylnitramine, $(1.76 \pm 0.07) \times 10^{10}$ and $(8.67 \pm 0.48) \times 10^{8}$, respectively. MNP/DMPO spin-trapping experiments demonstrated that hydroxyl radical reaction with these compounds occurs by hydrogen atom abstraction from an alkyl group, while the reaction of the hydrated electron was to form a transient radical anion. The latter adduct formation implies that the excess electron could subsequently be transferred to regenerate the parent chemical, which would significantly reduce the effectiveness of any free-radical-based remediation effort on nitrosamine/nitramine-contaminated waters.

Introduction

Nitrosamines are present within a number of environments; in particular, the presence of *N*-nitrosodimethylamine (NDMA) has been detected in rubber, leather, metal, chemical, and mining industries,[1] around factories producing secondary amines or the rocket fuel 1,1-dimethylhydrazine[2] (UDMH), and near industrial plants that use amines such as dimethylamine in organic synthesis.[3,4] They have also been found in many food and beverage products,[5−8] especially after fermentation or cooking,[9] in cigarette smoke,[10] and recently in highly purified wastewater[11] and drinking waters.[12−14] Nitrosamines are of concern, as they belong to a class of chemicals that have been shown to be carcinogenic, mutagenic, and teratogenic.[15,16]

The formation of gaseous nitrosamines has been established to occur via at least two major pathways. In the dark, NDMA formation has been shown to occur by the reaction of dimethylamine with nitrous acid (HNO_2) or nitrogen oxides (NO_x),[17] or alternatively by oxidation of UDMH, especially with ozone.[18−20] In the presence of sunlight, NDMA exists in a redox equilibrium with the oxidized species the corresponding dimethylnitramine $(CH_3)_2N{-}NO_2$, (DMNM)[21]

$$(CH_3)_2N{-}NO \xrightleftharpoons{\text{redox}} (CH_3)_2N{-}NO_2 \qquad (1)$$

Low-molecular-weight nitramines have also been demonstrated to be carcinogenic.[22] While both gaseous NDMA and DMNM have been shown to be degraded by reaction with the hydroxyl radical, ozone, or by photolysis,[19] these loss reactions can be relatively slow, which means that these airborne nitrosamines or nitramines can enter aqueous systems.

Recently, studies have also shown that NDMA can be formed in situ under water disinfection conditions, from the reaction of monochloramine with dissolved dimethylamine[12,13] and UDMH.[13] NDMA was also a common contaminant of UDMH, and prior waste management and general processing procedures introduced both NDMA and UDMH into the groundwater supply.[23,24] Nitramines can also be introduced to water from the anaerobic sludge biodegradation of explosives such as RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine).[25]

The California Department of Health Services has set an action level of 10 ng L^{-1} for NDMA in drinking water.[11] No limits are currently established for the higher-molecular-weight nitrosamines, nor for any nitramines. To achieve such low chemical concentrations in water, various water treatment technologies have been suggested. It has been demonstrated that UV irradiation can reduce NDMA levels in water,[26,27] producing methyl- and dimethylamine.[28] However, if the water is turbid, colored, or contains chemicals that can interfere with the short-wavelength (<270 nm) light used (e.g., nitrate, TOC), the effectiveness of this technique can be substantially reduced. There is also a possibility of NDMA reformation,[29] especially if chloramination of UV-treated effluent is performed.

To overcome these potential difficulties, the use of free radicals generated in situ by advanced oxidation technologies (AOTs) to destroy carcinogenic chemicals from water is being investigated. These technologies include ozone, UV/ozone, and UV/H_2O_2, which proceed via oxidation with the hydroxyl radical ($^{\bullet}OH$), or heterogeneous catalysis by TiO_2, sonolysis, or the electron beam process, which produce a mixture of oxidizing $^{\bullet}OH$ radicals with reducing hydrated electrons (e_{aq}^-) and hy-

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drogen atoms (•H). One recent study utilizing low- and medium-pressure Hg lamps for photodegradation of NDMA in simulated drinking water[30] has also shown that this methodology is feasible under certain conditions. It has been demonstrated that the pulsed UV/H_2O_2 process was far more efficient than pulsed UV alone in inhibiting NDMA reformation,[29] suggesting that the generated hydroxyl radicals degraded the nitrosamine differently from direct photolysis. There has been only one study[31] using steady-state ^{60}Co-ionizing radiation to determine breakdown rates for NDMA in various solvents (ethanol, dichloromethane, and water). The reported data showed that reduction of NDMA was the dominant process in the overall degradation, and there was no reformation of NDMA unless nitrite was present.

However, to ensure that any AOT treatment process occurs efficiently and quantitatively, a full understanding of the chemistry involved under the conditions of use is necessary. Kinetic computer models give the most information and provide the best test of the model against actual engineering data, as all defined or proposed chemistry in the system is considered.[32] A critical component then for any kinetic modeling of free-radical-based technologies is a description of the kinetics and mechanisms of the reactions of all the organic compounds involved.

Recently, the kinetics and initial mechanisms for the reactions of the hydroxyl radical, hydrated electron, and hydrogen atom with NDMA in water were reported.[33] These data showed that the oxidation of the nitrosamine, with formation of the carbon-centered radical by hydrogen atom abstraction, was the only significant destruction mechanism. The reduction of NDMA by the hydrated electron was demonstrated to only form a radical anion adduct, with subsequent transfer of this electron to other species possible. In this work, we extend these free-radical degradation studies to the reactions of the hydroxyl radical and hydrated electrons with symmetrical and unsymmetrical methyl- and ethyl-substituted nitrosamines, as well as their corresponding nitramines. To the best of our knowledge, this is the first report of any kinetic data for the reaction of nitramines with hydroxyl radicals and hydrated electrons.

Experimental Section

The linear accelerator (LINAC) electron pulse radiolysis system at the Radiation Laboratory, University of Notre Dame, was used for all the hydrated electron and hydroxyl radical reaction rate constant determinations. This irradiation and transient absorption detection system has been described in detail elsewhere.[34]

The two nitrosamines used in this study, *N*-ethyl-*N*-methylnitrosamine (Pfaltz and Bauer) and *N*-nitrosodiethylamine (Sigma-Aldrich) were of the highest purity available and used as received. Solutions of these chemicals were made using water filtered by a Millipore Milli-Q system, which was constantly illuminated by a UV lamp to keep organic contaminant concentrations below 13 μg L^{-1} as measured by an on-line TOC analyzer. All solutions were continuously stirred and completely sparged with high-purity N_2O (for hydroxyl radical experiments) or N_2 (hydrated electron measurements) to remove dissolved oxygen.

No commercial source of nitramines was found. The dialkyl nitramines used in this study were synthesized from the corresponding nitrosamines by oxidation with trifluoroperacetic acid.[35] The products are obtained in high purity without contamination by the starting nitrosamine. Experimental details and compound characterization can be found in the Supporting Information.

During the rate constant measurements, the solution vessels were bubbled with only the minimum amount of gas necessary to prevent air ingress, in order to prevent loss of chemical. The solution flow rates in these experiments were adjusted so that each irradiation was performed on a fresh sample. Dosimetry[36] was performed using N_2O-saturated, 1.00×10^{-2} M SCN^- solutions at $\lambda = 475$ nm, ($G\epsilon = 5.2 \times 10^{-4}$ m^2 J^{-1}) with average doses of 3−5 Gy per 2−3 ns pulse. Throughout this paper, G is defined in μmol J^{-1}, and ϵ is in units of M^{-1} cm^{-1}.

The hydroxyl radical reaction with both nitrosamines and nitramines ($R^1R^2N{-}NO_x$) was studied using SCN^- competition kinetics, monitoring the change of absorption intensity of the produced $(SCN)_2^{\bullet-}$ transient at 475 nm. The hydrated electron rate constant was determined by directly following its absorption at 700 nm. All experiments were performed at ambient temperature (21 ± 1 °C) and in neutral pH solution.

Results and Discussion

Hydroxyl Radical Reactions. The radiolysis of water produces free radicals (for the pH range from 3 to 11) according to the stoichiometry[37,38]

$$H_2 \rightsquigarrow [0.28]{}^{\bullet}OH + [0.06]{}^{\bullet}H + [0.27]e_{aq}^- + [0.05]H_2 + [0.07]H_2O_2 + [0.27]H_3O^+ \quad (2)$$

where the numbers in brackets are the *G*-values for species production. Total radical concentrations typically generated in this study were ~2−4 μM per pulse.

The reaction of only hydroxyl radicals was achieved by presaturating the solutions with N_2O, which quantitatively converts the hydrated electrons, e_{aq}^-, and hydrogen atoms to this radical[37]

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH^- + {}^{\bullet}OH \qquad k_3 = 9.1 \times 10^9\ M^{-1}\ s^{-1} \quad (3)$$

$$ {}^{\bullet}H + N_2O \rightarrow {}^{\bullet}OH + N_2 \qquad k_4 = 2.1 \times 10^6\ M^{-1}\ s^{-1} \quad (4)$$

The hydroxyl radical reaction with all the $R^1R^2N{-}NO_x$ studied did not generate any significant intermediate-species absorption in the range 250−800 nm, although some slight parent absorption bleaching was noted for wavelengths less than 300 nm. Therefore, the hydroxyl radical reaction rate constant with $R^1R^2N{-}NO_x$ was determined as for NDMA previously,[33] using SCN^- competition kinetics[37] based on the competing reactions

$$ {}^{\bullet}OH + R^1R^2N{-}NO_x \rightarrow \text{products} \quad (5)$$

$$ {}^{\bullet}OH + SCN^- (+SCN^-) \rightarrow OH^- + (SCN)_2^{\bullet-} \quad (6)$$

and monitoring the $(SCN)_2^{\bullet-}$ absorption at 475 nm. As the nitrosamine/nitramine reaction transients do not absorb at this wavelength, this hydroxyl radical competition can be analyzed to give the following analytical expression:

$$\frac{[(SCN)_2^{\bullet-}]_o}{[(SCN)_2^{\bullet-}]} = 1 + \frac{k_5[R^1R^2N{-}NO_x]}{k_6[SCN^-]} \quad (7)$$

where $[(SCN)_2^{\bullet-}]_o$ is the final yield of $(SCN)_2^{\bullet-}$ measured for only the blank SCN^- solution, and $[(SCN)_2^{\bullet-}]$ is the reduced yield of this transient when the $R^1R^2N{-}NO_x$ is present. Therefore, a plot of $[(SCN)_2^{\bullet-}]_o/[(SCN)_2^{\bullet-}]$ (or a parameter directly proportional to this intermediate concentration ratio) against the ratio $[R^1R^2N{-}NO_x]/[SCN^-]$ should give a straight line of slope k_5/k_6. On the basis of the established rate constant

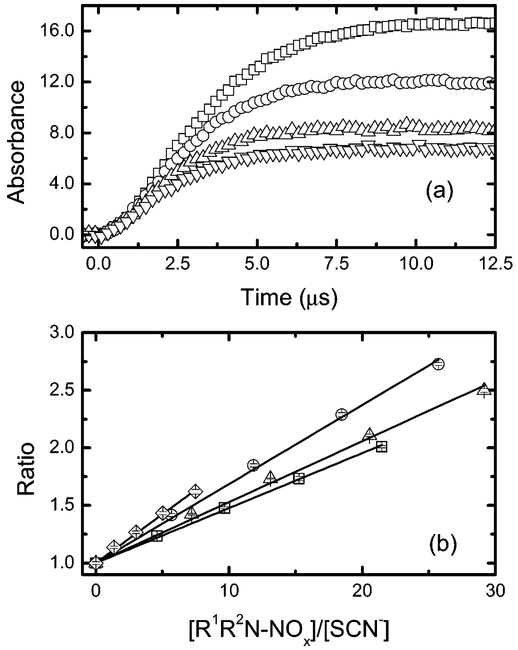

Figure 1. (a) Kinetics of $(SCN)_2^{\bullet -}$ formation at 475 nm for N_2O-saturated 5.28×10^{-5} M SCN^- containing 0 (□), 3.80×10^{-4} (○), 6.92×10^{-4} (△), and 1.54×10^{-3} (▽) M dimethylnitramine at natural pH and room temperature. (b) Competition kinetics plot for hydroxyl radical reaction with methylethylnitrosamine (□), diethylnitrosamine (○), dimethylnitramine (△), and diethylnitramine (◊) using SCN^- as a standard. Solid lines are weighted linear fits, corresponding to slopes of 0.0471 ± 0.0005, 0.0666 ± 0.0007, 0.0528 ± 0.0004, and 0.0821 ± 0.0020, respectively.

for hydroxyl radical reaction with SCN^-, $k_6 = 1.05 \times 10^{10}$ M^{-1} s^{-1},[37] the k_5 rate constant can then be calculated.

Typical kinetic data obtained at 475 nm are shown in Figure 1a, for dimethylnitramine. As expected, a decrease in the maximum $(SCN)_2^{\bullet -}$ absorption intensity is observed when increased amounts of $(CH_3)_2N{-}NO_2$ was added. The transformed plot shown in Figure 1b gives a weighted linear fit corresponding to a reaction rate constant of $k = (5.44 \pm 0.20) \times 10^8$ M^{-1} s^{-1}. Comparison data obtained for methylethylnitrosamine, diethylnitrosamine, and diethylnitramine are also shown in this plot. The calculated rate constants for all the nitrosamines and nitramines of this study are given in Table 1, in comparison to analogous literature data. It is important to note that the errors quoted for all measured rate constants in this work are the combination of the measurement precision and the initial compound purity.

The hydroxyl radical reaction rate constants are seen to increase with increasing complexity of alkyl substitution for both the nitrosamines and the nitramines of this study. The previously determined rate constant for hydroxyl radical reaction with NDMA (4.30×10^8 M^{-1} s^{-1})[33] is consistent with this trend.

A survey of the literature did not give any oxidation rate constants for the $R^1R^2N{-}NO_x$ species in this study. However, further insight into the mechanism of the primary oxidation reaction for these compounds can be obtained by comparison of literature values for hydroxyl radical reaction with structurally similar chemicals in water (see Table 1). It is recognized that the different functionalities will activate/deactivate molecules to a different extent. A detailed study[39] of 2-methyl-2-nitrosopropane, $(CH_3)_3C{-}NO$, gave an absolute value for its hydroxyl radical addition reaction of 2.5×10^9 M^{-1} s^{-1}. As this rate constant is significantly faster than our values, it suggests that hydroxyl adduct formation for $R^1R^2N{-}NO_x$ would not be a major reaction pathway. The lack of adduct formation with the $R^1R^2N{-}NO_x$ compounds is not surprising, since the N−N bond shows a barrier to internal rotation that corresponds to partial double bond character, thus decreasing the likelihood of reaction at the nitroso nitrogen. Unfortunately, comparison of our rate constants with methylamine (1.8−4.1 × 10^9 M^{-1} s^{-1};[40] 5.7 × 10^9 M^{-1} s^{-1} [41]) is complicated because of the wide range of values and the mix of radical transients ($^\bullet CH_2NH_2$ and $CH_3N^\bullet H$) reported. The hydroxyl radical reaction with trimethylamine to give a mixture of $[(CH_3)_3N]^{\bullet +}$ and $^\bullet CH_2N(CH_3)_2$ has been reported as 1.3×10^{10} M^{-1} s^{-1}.[42] All these amine rate constants are significantly faster than our values for $R^1R^2N{-}NO_x$, suggesting that the presence of the electron-withdrawing $-N{-}NO_x$ group lowers the dative stabilization of the formed carbon-centered radical by the nitrogen lone pair. Reaction of the hydroxyl radical with aromatic nitroso chemicals such as nitrosobenzene[43] (1.8×10^{10} M^{-1} s^{-1}) again is much faster, consistent with the proposed mechanism of ring-adduct formation for aryl compounds.

The conclusion of all these comparisons is that hydroxyl radical reaction with the $R^1R^2N{-}NO_x$ species is most likely to occur by hydrogen atom abstraction from one of its alkyl groups, with the faster rate constants for the ethyl-substituted moieties consistent with the greater stability of the formed secondary carbon-centered radicals. To confirm this hypothesis, we investigated this primary reaction mechanism of the hydroxyl radical using 2-methyl-3-nitrosopropane (MNP) spin-trapping EPR techniques.[44]

The steady-state irradiation (∼190 Gy) of a mixture of 2×10^{-3} M MNP and 1.0×10^{-2} M dimethylnitramine in N_2O-saturated water at natural pH gives the spin-trap spectrum shown in Figure 2a. The EPR spectrum in Figure 2a does not exhibit any large nitrogen couplings from the parent radical, and therefore we can eliminate any spin adduct species from nitrogen-centered radical species, $(CH_3)_2N^\bullet$, $(CH_3)_2N^\bullet{-}NO_2$, or $(CH_3)_2N{-}^\bullet NO_2$, reacting with MNP. This is in contrast to previous photolysis/EPR data reported for dimethylnitramine crystals where both $(CH_3)_2N^\bullet$ [45] and $(CH_3)_2N^+{-}^\bullet NO_2$[46] were reported. Similarly, one can eliminate the addition of an oxygen-centered radical. No MNP−OH adduct species was observed, indicating that the hydroxyl radical had quantitatively reacted with the dimethylnitramine, as expected. This EPR spectrum is indicative of a carbon-centered radical from the nitramine adding to the MNP at the nitrogen atom, yielding a nitroxide signal with a nitrogen splitting of 16.8 G and a proton splitting of 10.7 G to two equivalent protons. These data are consistent with the hydroxyl radical abstracting a hydrogen atom from a methyl group of this nitramine, consistent with the previous findings for NDMA.[33]

Hydrated Electron Reactions. The rate constants for hydrated electron reaction with $R^1R^2N{-}NO_x$ were determined by fitting exponential decays to the pseudo-first-order kinetics of this species, monitored by its absorption at 700 nm, in pulse-electron irradiated, nitrogen-saturated solutions at natural pH (∼7). These solutions also contained 0.50 M *tert*-butyl alcohol, or 0.10 M methanol, to scavenge the hydroxyl radicals and hydrogen atoms,[37] converting them into relatively inert 2-methyl-2-propanol radicals

$$^\bullet OH/H^\bullet + (CH_3)_3COH \rightarrow H_2O/H_2 + {}^\bullet CH_2(CH_3)_2COH \qquad (8)$$

or $^\bullet CH_2OH$ radicals, respectively. Each kinetic trace was obtained by averaging the data of ∼10−15 individual pulses, with typical data shown in Figure 3 for dimethylnitramine. The decay of this absorption was found to be dependent upon the

TABLE 1: Rate Constants[a] ($M^{-1}\ s^{-1}$) for Hydroxyl Radical and Hydrated Electron Reaction with Nitrosamines and Nitramines Determined in This Study in Comparison to Analogous Literature Values

compound	structure	k ($^{\bullet}OH$)	k (e_{aq}^-)
methylethylnitrosamine	**$(CH_3)(C_2H_5)N{-}NO$**	**$(4.95 \pm 0.21) \times 10^{8}$**	**$(1.67 \pm 0.06) \times 10^{10}$**
diethylnitrosamine	**$(C_2H_5)_2N{-}NO$**	**$(6.99 \pm 0.28) \times 10^{8}$**	**$(1.61 \pm 0.06) \times 10^{10}$**
dimethylnitramine	**$(CH_3)_2N{-}NO_2$**	**$(5.44 \pm 0.20) \times 10^{8}$**	**$(1.91 \pm 0.07) \times 10^{10}$**
methylethylnitramine	**$(CH_3)(C_2H_5)N{-}NO_2$**	**$(7.60 \pm 0.43) \times 10^{8}$**	**$(1.83 \pm 0.15) \times 10^{10}$**
diethylnitramine	**$(C_2H_5)_2N{-}NO_2$**	**$(8.67 \pm 0.48) \times 10^{8}$**	**$(1.76 \pm 0.07) \times 10^{10}$**
NDMA	$(CH_3)_2N{-}NO$	4.30×10^{8} [33]	1.41×10^{10} [33]
2-methyl-2-nitrosopropane	$(CH_3)_3C{-}NO$	2.5×10^{9} [39]	6.2×10^{9} [39]
methylamine	$H_2N{-}CH_3$	$1.8{-}4.1 \times 10^{9}$ [40] 5.7×10^{9} [41]	9×10^{5} [40]
trimethylamine	$(CH_3)_2N{-}CH_3$	1.3×10^{10} [42]	
nitrosobenzene	$C_6H_5{-}NO$	1.8×10^{10} [43]	
hydroxylamine	$H_2N{-}OH$	9.5×10^{9} [47]	9.2×10^{8} [47]
N,*N*-diethylhydroxylamine	$(C_2H_5)_2N{-}OH$	1.3×10^{9} [48]	4.8×10^{7} [48]

[a] Rate constants determined in this study are in bold.

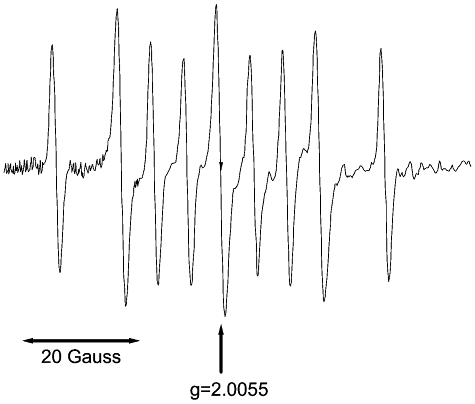

Figure 2. First derivative X-band (9.8 GHz) EPR spectrum of a nitrous oxide saturated aqueous solution containing 2.0×10^{-3} M MNP and 1.0×10^{-2} M dimethylnitramine, ^{60}Co-irradiated for 60 s (total dose ≈ 190 Gy), using 100 kHz field modulation of 1.6 G amplitude, and phase-sensitive detection. The magnetic field increases from left to right.

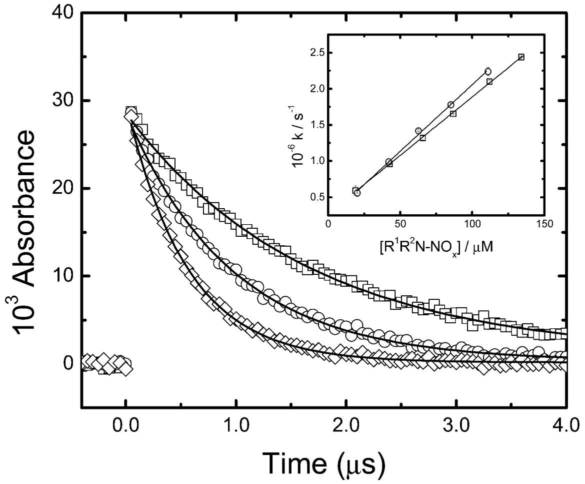

Figure 3. Typical kinetic decay profiles obtained for the hydrated electron absorbance at 700 nm for pulse-electron irradiated aqueous solution at natural pH containing 2.02×10^{-5} (□), 4.20×10^{-5} (○), and 8.52×10^{-5} (◊) M dimethylnitramine. Curves shown are the average of 10 individual pulses. Solid lines correspond to rate constant fitting with the pseudo-first-order values of 5.64×10^{5}, 1.43×10^{6}, and $2.33 \times 10^{6}\ s^{-1}$, respectively. Inset: Second-order rate constant determination for the reaction of the hydrated electron with diethylnitrosamine (□) and dimethylnitramine (○). Single-point error bars are one standard deviation, as determined from the average of at least three kinetic traces. Solid line corresponds to weighted linear fits, giving rate constants of 1.61×10^{10} and $1.91 \times 10^{10}\ M^{-1}\ s^{-1}$, respectively.

dimethylnitramine concentration (Figure 3 inset, along with analogous data for diethylnitramine), corresponding to a second-order rate constant for the reaction

$$e_{aq}^- + (CH_3)_2N{-}NO_2 \rightarrow \text{products} \qquad (9)$$

of $k = (1.91 \pm 0.07) \times 10^{10}\ M^{-1}\ s^{-1}$. This reaction is about 30 times faster than hydroxyl radical hydrogen atom abstraction for this compound. Similar measurements were performed for the other $R^1R^2N{-}NO_x$ of interest in this study, with all values again summarized in Table 1.

Comparison of all the $R^1R^2N{-}NO_x$ reductive rate constants with the value obtained for NDMA previously[33] ($1.41 \times 10^{10}\ M^{-1}\ s^{-1}$) shows that the nitrosamine reactions are fairly independent of alkyl substituent, indicating that most of the reaction occurs at the nitroso moiety, as expected. The rate constants for the nitramines are all slightly faster than for their corresponding nitrosamines, but again independent of substitution. Again, no specific rate constants for reduction of $R^1R^2N{-}NO_x$ species of this study were found in the literature. In comparison to the other analogous literature data, the $R^1R^2N{-}NO_x$ species rate constants are slightly faster than those measured for the 2-methyl-2-nitrosopropane[39] ($6.2 \times 10^{9}\ M^{-1}\ s^{-1}$) reaction, where this latter reaction is to give an initial electron adduct. The reaction of the hydrated electron with hydroxylamine[47] results in bond cleavage to give $^{\bullet}NH_2$ and OH^-; however, this rate constant ($9.2 \times 10^{8}\ M^{-1}\ s^{-1}$) is over an order of magnitude slower than determined here for $R_2N{-}NO_x$. Slower rate constants for hydrated electron reaction with methylamine[40] ($9 \times 10^{5}\ M^{-1}\ s^{-1}$) and *N*,*N*-diethylhydroxylamine[48] ($4.8 \times 10^{7}\ M^{-1}\ s^{-1}$) have also been reported.

By comparing our data in this way, we again postulate that as for NDMA the initial hydrated electron reaction occurs predominantly at the nitroso group. To resolve whether the reaction consists of only adduct formation

$$e_{aq}^- + R^1R^2N{-}NO_x \rightarrow [(CH_3)_2NO_x]^{\bullet -} \qquad (10)$$

or if any bond cleavage occurs

$$e_{aq}^- + R^1R^2N{-}NO_x \rightarrow R_2N^{\bullet} + NO_x^{\,-}/R_2N^{\bullet -} + NO_x \qquad (11)$$

we again performed spin-trap experiments, this time using 2.0×10^{-3} M DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) and 1.0×10^{-2} M nitramines under reducing conditions (N_2-saturated solution, 0.50 M *tert*-butyl alcohol). Typical spectral data obtained for diethylnitramine are shown in Figure 4. The spin-adduct spectrum for diethylnitramine/DMPO (central trace) was found to be a combination of the $DMPO{-}CH_2{-}C(CH_3)_2OH$

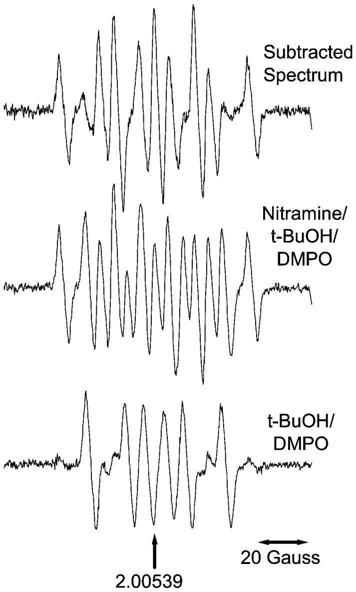

Figure 4. First derivative X-band (9.8 GHz) EPR spectra of solutions containing 2.0×10^{-3} M DMPO, ^{60}Co-irradiated for 60 s (total dose $\approx$ 190 Gy), using 100 kHz field modulation of 1.6 G amplitude, and phase-sensitive detection. The magnetic field increases from left to right. (Bottom) Nitrous-oxide-saturated aqueous solution containing 0.5 M *tert*-butyl alcohol: the six observed lines are due to the DMPO$-$CH$_2-$C(CH$_3$)$_2$OH EPR spectrum. (Middle) EPR spectrum from a nitrogen-deoxygenated aqueous solution containing 0.5 M *tert*-butyl alcohol and 1.0×10^{-2} M diethylnitramine. (Top) Spectral subtraction of normalized bottom trace from middle EPR spectrum, which yields the DMPO$-$H spin adduct radical spectrum (see text).

(bottom trace, obtained separately when only DMPO/*tert*-butyl alcohol was irradiated) and DMPO$-$H spectra (top trace).[44] This implies that reaction 10 is dominant in the reduction by the hydrated electron, with production of the reduced DMPO$-$H occurring by electron transfer from the transient (C$_2$H$_5$)$_2$N$-$NO$_2$ anion adduct

$$\mathrm{DMPO} + [(\mathrm{C_2H_5})_2\mathrm{N{-}NO_2}]^{\bullet-} \xrightarrow{H^+} \mathrm{DMPO{-}H} + (\mathrm{C_2H_5})_2\mathrm{N{-}NO_2} \quad (12)$$

as observed for NDMA previously.[33]

Summary

The measured hydroxyl radical rate constants were found to increase with increasing complexity of alkyl substitution for the nitrosamines and nitramines of this study. Our MNP spin-trap studies for dimethylnitramine confirm the expected carbon-centered radical formation, consistent with the findings for NDMA previously. In contrast, the hydrated electron rate constants are seen to be fairly independent of alkyl substitution, with the values for the nitramines slightly higher than for the corresponding nitrosamines. From DMPO spin-trap studies on diethylnitramine, it was observed that this reduction only resulted in the formation of a radical anion adduct. This finding has significant implications for AOT treatment of nitrosamine/nitramine contaminated waters; even though the reduction of these R^{1}R^{2}N$-$NO$_x$ species occurs much faster than oxidation, the transient produced is only an electron adduct, which might be capable of transferring the extra electron to another compound present in the water. This could regenerate the parent R^{1}R^{2}N$-$NO$_x$ species and reduce the overall efficiency of the AOT process.

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Supporting Information Available: A full description of the synthesis of the three nitramines and their characterization by ^{1}H NMR spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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