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Physicochemical Parameters of Insensitive Munition Constituent Methylnitroguanidine (MeNQ) of Importance to Environmental Fate and Transport

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Abstract: 1-methyl-3-nitroguandine (MeNQ) is being pursued as an insensitive munition to replace legacy munitions such as TNT and RDX. This study was intended to determine the basic physicochemical properties of MeNQ as well as potential environmental fate pathways. The solubility of MeNQ was determined to be 12.92 ± 0.52 g/L and aqueous photolysis was found to efficiently degrade the munition, where its quantum yield and half-life were found to be 0.009 and 0.59 days, respectively. Hydrolysis was an insignificant degradation pathway resulting in 8.1 % degradation at pH 4, 2.6 % at pH 7, and 6.2 % at pH 9 after five days at an elevated temperature. Volatilization at environmentally relevant conditions was found to be insignificant as the molecule thermally degrades, leading to an inability to calculate Henry's Constant for volatilization from water. Spectroscopic (UV-vis, FTIR, NMR) and analytical (HPLC) studies were undertaken and are shown alongside the parent molecule, NQ, for comparison to characterize the emerging munition.

Keywords: N-methyl-N-nitroguanidine · MeNQ · physicochemical properties · photolysis, hydrolysis · environmental fate

1 Introduction

2,4,6-Trinitrotoluene (TNT) and 1,2,3-trinitro-1,3,5-triazine (RDX) are well known for being used in a wide variety of explosives for the U.S. military, but a history of unintended detonations have caused the Department of Defense to pursue the use of insensitive munitions (IMs) as alternatives. 1-methyl-3-nitroguandine (MeNQ) is being investigated as a possible component to be used in the replacement of TNT and RDX in propellants/warheads [1, 2]. Very little is known about MeNQ and its environmental fate and transport.

Many IM constituents, including MeNQ, have been shown to degrade via UV-irradiation but this can result in degradation products that are more toxic than their parent compound. For example, nitroguanidine (NQ) is an insensitive munition that has a very similar structure and chemical properties as MeNQ. NQ was found to be relatively harmless to fish and aquatic invertebrates [3], but after photolysis, its toxicity is multiple orders of magnitude higher [3–5]. The LC50 of NQ towards *Ceriodaphnia dubia* was found to be 1,170 mg/L before photolysis and 0.76 mg/L after extensive photolytic degradation [3]. The toxicity of the photolysis product mixture was determined to be due to oxidative stress based on a toxicogenomics approach [4]. Efforts to determine the photolytic products found a mixture of nitrate, nitrite, ammonia, guanidine, nitrosoguanidine, cyanoguanidine, cyanamide, and cyanide [6–8]. Although nitroso compounds are highly carcinogenic it was found to not elicit a response in the acute trials lasting

48 hours [6]. The acute toxicity response could only partially be explained by nitrite, cyanide, and, to a lesser extent, ammonia [6].

A handful of studies have focused on the toxicity of MeNQ. Reinke [2] did an extensive toxicology study involving oral exposures to rats (*Rattus norvegicus*), Lotufo et al. [9] studied toxicological effects of MeNQ on fathead minnows (*Pimephales promelas*), and Gust et al. [10] performed dermal exposures on leopard frogs (*Rana pipiens*). A more comprehensive assessment was recently detailed [11]

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where the number of species was further expanded to include leopard frog tadpoles, larval midges (*Chironomus dilutus*), blackworms (*Lumbriculus variegatus*), hydrozoans (*Hydra littoralis*), amphipods (*Hyalella azteca*), and cladocerans (*Daphnia pulex*) gaining a more comprehensive toxicity assessment. These studies found that MeNQ was not toxic to their target species, was unlikely to bioaccumulate with a $\log_{know}$ of -0.83 [9], but noted changes in microbial communities [10]; however, when MeNQ was UV-treated, its degradation products had higher toxicity than the parent compound [9, 11].

Degradation of MeNQ by means other than photolysis is not reported in the literature. Very little literature regarding MeNQ exists to predict its environmental fate and characterization of the molecule. With the potential use of MeNQ as a component in munitions, it is likely that through manufacture, testing, and training exercises it will be present in soils and nearby ground/surface waters. More information regarding the fate of MeNQ in the environment is necessary before it can be integrated in the Army's arsenal. This study aims to determine basic physicochemical properties, potential degradation pathways, and analytical measurements of MeNQ.

2 Experimental Section

2.1 Chemicals

All water used throughout these experiments was purified by a Milli Q water purification system giving a resistivity of >18.2 MΩ cm. All reagents were used as received except for MeNQ ($\sim25\%$ water), which was purchased from Sigma Aldrich and oven-dried before use in the preparation of calibration standards. Pyridine ($\geq99.9\%$), 4-nitroacetophenone (98 %), sodium phosphate monobasic dihydrate ($\geq99.9\%$), sodium acetate ($>99\%$), boric acid (99.9999 %), and dimethyl sulfoxide-d_6 (DMSO-d_6) (100 % 99.96 atom % D) were obtained from Sigma Aldrich. Analytical standards of NQ, 1,000 µg/L, were purchased from Restek (Catalog # 31602). Methanol and acetonitrile (Optima HPLC or LC-MS grade) were obtained from Fisher Scientific.

2.2 Instrumentation

An Agilent Cary-8454 UV-Vis was used for determining molar absorption coefficients in quartz cuvettes. An Agilent 1200 Series HPLC system equipped with a quaternary pump, Agilent 1200 Series Diode Array Multiple Wavelength Detector, and Synergi 4 µM Hydro-RP 80 Å C18 column with polar end-capping (250×4.6 mm; Phenomenex) was used for chromatographic analysis. The HPLC method for MeNQ quantitation for hydrolytic experiments (260 nm; ret time = 7.5 min) was a 50 µL injection with an isocratic mobile phase of 100 % water at a flow rate of 1.1 mL/min.

Bruker Daltonics Data Analysis software were used for peak integrations. Quantitation of experimental results was determined against a standard prepared from the commercially available MeNQ dried in an oven at 80 °C to a constant mass and dissolved in water. For PNAP (285 nm; ret time = 3.85 min), the mobile phase was 25:75 % water: methanol at a flow rate of 1.1 mL/min. Chromatographic characterization of MeNQ in the presence of NQ utilized an isocratic mobile phase of 51:45:4 water: methanol: ACN, with a run time of 10 min, flow rate of 1.0 mL/min, injection volume of 50 µL, oven temperature of 25 °C, and detection at 254 nm and 267 nm (reference wavelength: 360 nm) (adapted from EPA Method 8330B [12]). Agilent Chem-Station OpenLab software was used for data analysis. A Thermo Scientific Nicolet iS50 FTIR spectrometer with Smart iTX accessory with diamond crystal was used for all infrared spectroscopy. For each spectra, the background was subtracted and 16 scans were averaged. Data were recorded every 0.482 cm^{-1}. Thermogravimetric analysis and differential scanning calorimetry were conducted with a Netsch STA 449 F1 Jupiter calibrated against benzoic acid. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance 300 MHz NMR spectrometer with a 5 mm BBO probe using DMSO-d_6 as the solvent collected at room temperature.

2.3 Solubility Testing

The solubility of MeNQ in water was determined as described by [13]. Solid MeNQ was oven-dried and stored in amber vials with Teflon septum screw caps. The flask method was utilized without a preincubation period and concentrations were determined via HPLC. A percent difference of less than 15 % was necessary for the experiment to be considered satisfactory.

2.4 Hydrolytic Stability Testing

MeNQ hydrolytic stability was determined as described in [14]. Triplicate MeNQ solutions were prepared in buffered high purity water at pH 4 (sodium acetate), pH 7 (sodium phosphate monobasic dihydrate), and pH 9 (borate); pH was confirmed by pH electrode (Oakton PC700). Initial MeNQ concentrations were determined by HPLC, solutions were stoppered, wrapped in aluminum foil, placed in a water bath on a temperature-controlled heating plate at 50 °C, and left in the dark for five days. Afterward, solutions were allowed to reach room temperature and were again analyzed by HPLC to determine their concentrations. A compound was considered hydrolytically stable if degradation was less than 10 %.

2.5 Outdoor Photolysis Testing

Outdoor photolysis experiments were conducted as described in EPA method 835–2210 [15]. Quartz test tubes with Teflon-lined septum screw caps (LuzChem, 11.11 mm ID, ~13 mL capacity) were placed on a matte black sample holder at a 30° incline from horizontal with the top of the samples pointed due north. All samples were prepared in the laboratory under unreactive red light and were transported to the environmental field stand (approximately 20' high in an open field) while covered with aluminum foil. MeNQ samples were one part-per-million, confirmed by HPLC. The *p*-nitroacetophenone-pyridine (PNAP-PYR) actinometer was used in this experiment to calculate quantum yield by standard methodology [15]; the concentration of PNAP was 10 μM while the concentration of pyridine was calculated to be 0.04655 μM based on MeNQ's estimated half-life from a preliminary experiment. Foil-wrapped control samples were also placed on the stand with the PNAP-PYR and MeNQ samples and showed no appreciable degradation. A sample was taken by removing a PNAP-PYR tube, control tube, and MeNQ tube at 12:00 PM every day from the stand and wrapping them in foil to be transported back to the lab for analysis by HPLC.

2.6 Estimation of Vapor Pressure by Thermo-Gravimetry

Thermogravimetric analysis and differential scanning calorimetry were performed after calibration with benzoic acid over the range 50–570 °C as previously described [16]. Estimation of the vapor pressure was conducted using a MatLab script that can be found in the supplemental information. An empty aluminum oxide crucible was tared and then loaded with ~10 mg of MeNQ. The heating profile started at 55 °C with a temperature ramp of 10 °C/min until reaching 600 °C. The sampling rate was set to 3.0 seconds with all samples run under nitrogen gas flow to avoid combustion.

3 Results and Discussion

3.1 Spectroscopic Characterization and Chromatographic Analysis of MeNQ

The spectra for MeNQ are shown in Figure 1 alongside those for NQ for ease of comparison. The UV-vis spectrum of MeNQ, collected at 6, 5, and 3 mg/L, shows an increased absorption of natural sunlight as the λ_{max} peak for the N-NO_2 absorption has been shifted from 264 nm for NQ to 267 nm for MeNQ. The FTIR transmission spectra for both munitions are shown in Figure 1, where the spectrum for NQ matches the spectrum collected by Oyumi, et al. [17]. The spectrum for MeNQ has many similarities to that of NQ. Both spectra show the amine symmetric (ν_s) and asymmetric (ν_{as}) stretches at 3450–3100 cm^{-1}, the nitro stretches for each at 1550–1475 cm^{-1} (asymmetric) and 1360–1290 cm^{-1} (symmetric), but the MeNQ shows the characteristic C–H stretches in the range 2850–2950 cm^{-1}.

The ^{1}H spectrum (Figure 2A) shows the methyl group in MeNQ having a chemical shift of 2.55 ppm and splitting of the N–H protons due to the asymmetry of the molecule in the range of 6.7–8.4 ppm (Figure 2A inset), whereas the N–H protons in NQ result in a single peak at 7.28 ppm. The N–H peaks in MeNQ are split into 3 peaks, showing the tautomerization of the molecule from the more stable nitro-imine to the nitroamine is more pronounced than in NQ. Integration of these peaks shows a ratio of 0.9:0.145 showing the nitroamine accounts for 14% of the distribution. The tautomerization of MeNQ to the nitroamine is favored more substantially than that of NQ which solely exists as the nitroimine [18]. The ^{13}C NMR spectrum (Figure 2B) of MeNQ shows the methyl peak having a chemical shift of 28.31 ppm and the guanidinyl carbon having a chemical shift of 160.57 ppm, slightly upfield of the peak for NQ at 161.27 ppm, referenced to the d_6-DMSO peak at 40 ppm. These results are consistent with other methylated guanidine derivatives.

HPLC analysis by methods adapted from EPA Method 8330B [12] shows MeNQ elutes from the C18 column at 2.95 minutes, close to that of NQ at 2.87 minutes, causing the molecules to co-elute at the concentrations used in this study. Due to the high solubility/polarity of these molecules, asymmetry is observed with fairly significant tailing on the peaks (Figure 3). Detection by DAD was achieved by monitoring the signal at 254 nm, typical for aromatics and other conjugated systems; however, sensitivity was increased by monitoring closer to the λ_{max}, 267 nm, for the MeNQ, and could be further enhanced by injecting greater volumes of the sample or using more concentrated samples. For samples where the identity of MeNQ or NQ may be ambiguous, or the explosives are both present, the ratio of the peak heights (267 nm/254 nm) rather than integrated areas, a qualitative measure permissible by EPA Method 8330B [12] due to the co-elution, yields a differentiable response for the two related explosives. For example, NQ has a 267/254 ratio of 1.36, and for MeNQ the ratio is 1.57.

3.2 Environmental Fate and Transport Testing

The solubility of MeNQ was determined to be 12.92 ± 0.52 g/L, four- to five-fold more soluble than NQ with solubility in the range of ~3.0 g/L [19] and 2.6 g/L [20] under similar conditions. Probing the volatility and melting point of MeNQ with TGA/DSC, shown in Figure 4, resulted in an estimation of the vapor pressure of 1×10^{-17} Pa, roughly ten orders of magnitude lower than NQ [16], and the melting range of MeNQ was found to be 155 °C (from the onset of melting) which is lower than that of NQ [21]. Although MeNQ was found to thermally degrade rather than vapor-
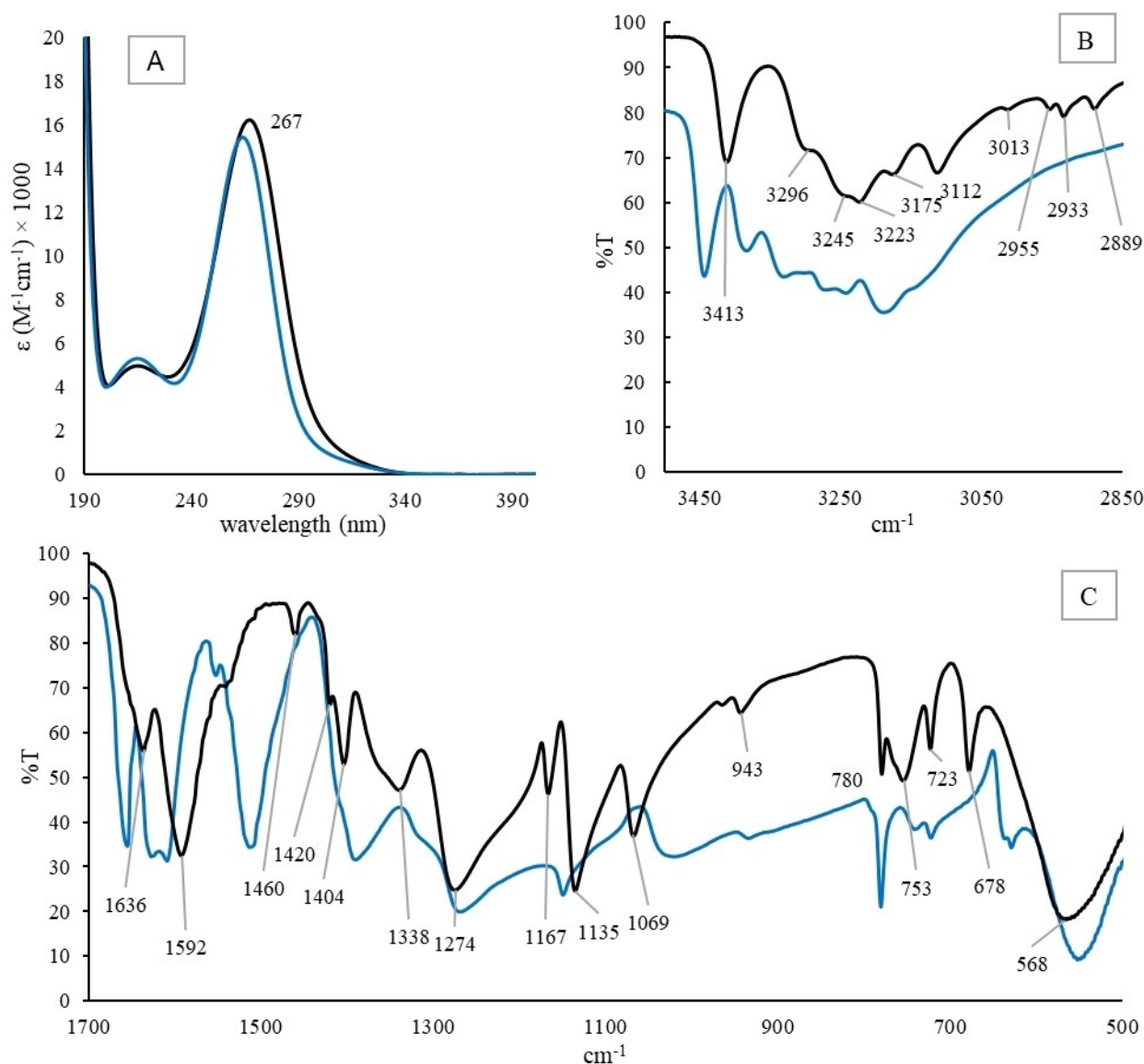
Figure 1. Molar absorptivity coefficient determined from the average of 3 concentrations (A) and FTIR (B and C) spectra of MeNQ (black) and NQ (blue). Only labels for MeNQ are included on the FTIR spectra for clarity. Individual spectra for each compound can be found in the Supplemental Information.

ize, indicated by the multiple losses of mass during the heating by TGA, the vapor pressure could still be estimated using the Clausius-Clapeyron relationship. The very low vapor pressure of the munition indicates volatilization will not be appreciable under environmental conditions and precludes the calculation of Henry's Constant for atmospheric transport after dissolved in water. The lower melting point could be due to the lower amount of hydrogen bonding available in the lattice structure with the methyl group found in MeNQ.

Because the solubility of MeNQ was comparatively high for a munition, hydrolysis testing was conducted in environmentally relevant pH buffered solutions, but at 50 °C. Rais-

ing the temperature of the reactions beyond that of environmental relevance was chosen to increase the rate of hydrolysis if it were occurring. Trials from this five-day experiment showed 8.1 %, 2.6 %, and 7.2 % loss due to hydrolysis at pH 4, 7, and 9 respectively. Each of these losses is deemed to be an insignificant transformation as they did not reach the requisite 10 % degradation and testing was halted [14]. Identification of the hydrolytic products was not determined as the testing did not progress further than tier 1, however, the expected products would be methyl urea (from hydrolytic scission of the nitroimine), nitrourea (from hydrolytic scission of the methylamine), and/or methyl nitrourea (from scission of the amine) group [22].
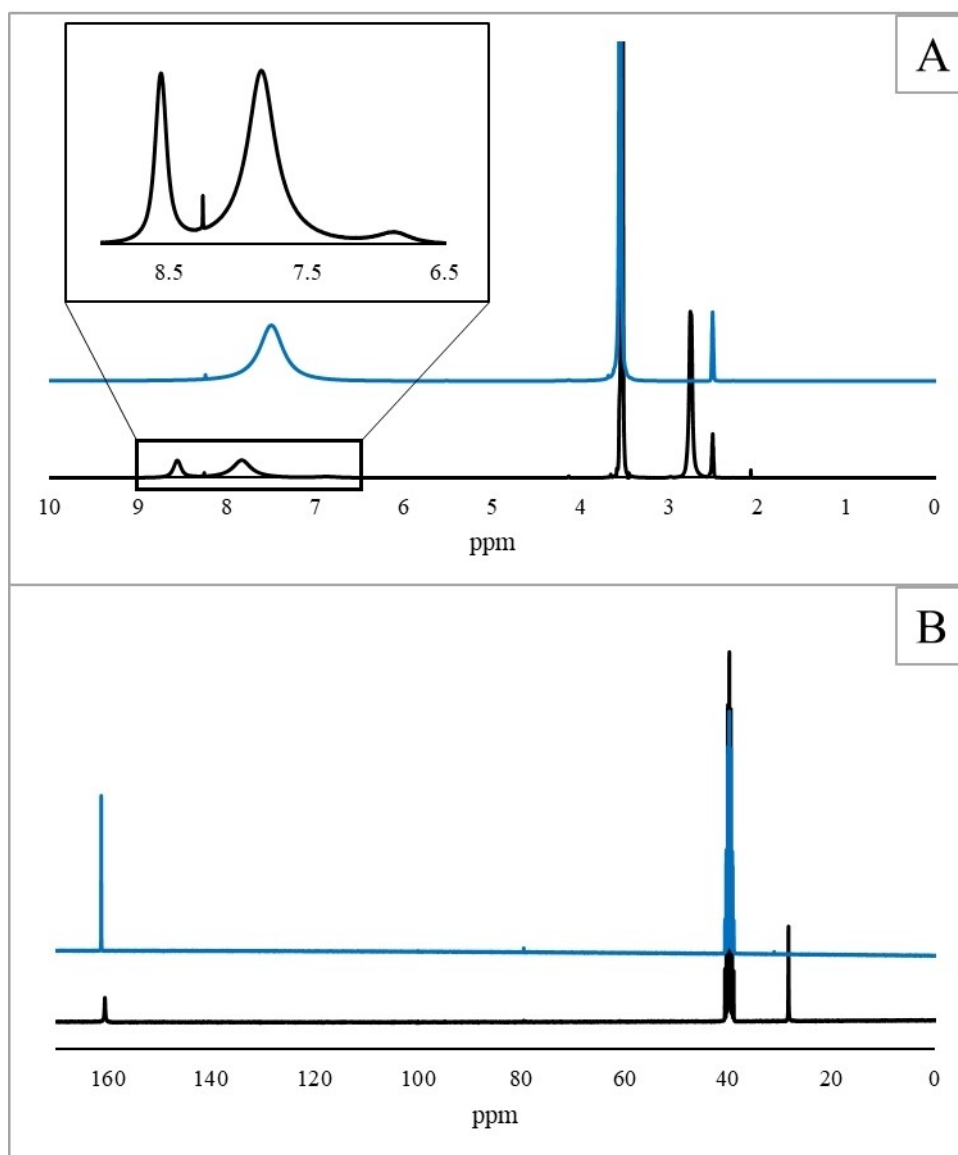
Figure 2. A) ^{1}H and B) ^{13}C NMR spectra of MeNQ (black) and NQ (blue), DMSO-d6 was used as the solvent. ^{1}H spectra show prominent water peak at 3.33 ppm as a result of solvent contamination.

Aqueous photolysis testing showed MeNQ, like NQ, has an appreciable absorbance of natural sunlight, and therefore the potential for photolysis to be a significant degradation pathway, to warrant further testing. The calculated minimum half-life (*i.e.*, if each photon absorbed resulted in a photolytic reaction, or a quantum yield of unity) based on the molar absorption coefficients obtained in Figure 1 would be on the order of 7.6 minutes. Preliminary experimentation resulted in an estimated half-life of 0.73 days under natural light which gave a calculated concentration of 0.04655 μM pyridine for use in the PNAP-PYR actinometer. Definitive experiments were conducted to find the quantum yield of MeNQ to be 0.009, very similar to the quantum yield of 0.01 for NQ [23], and a half-life of 0.587 days in the summer at 30° N latitude (Figure 5). The quantum yield of MeNQ was used to estimate the half-life for other seasons and is summarized in Table 1.

Table 1. Estimated half-life of MeNQ in other seasons of the year.

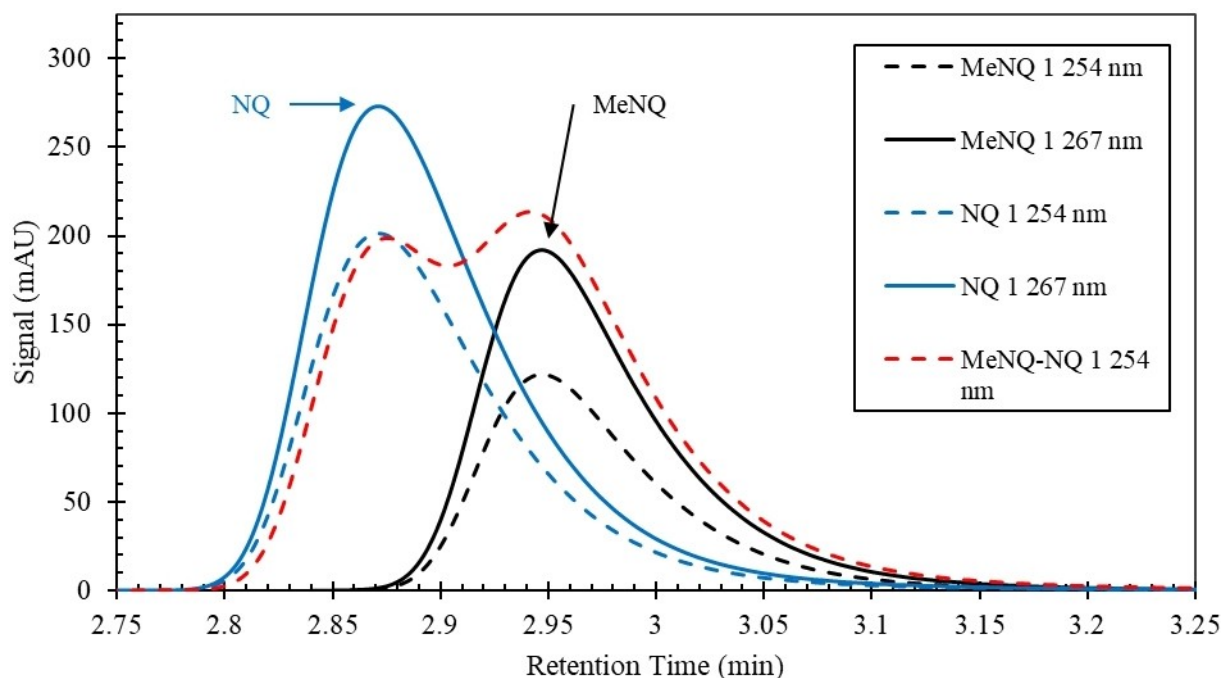| Season	Estimated Half-Life (days)
Fall	1.01
Winter	1.51
Spring	0.68

Figure 3. HPLC Chromatograms of NQ (blue), MeNQ (black), and a mixture of both (red). All sample concentrations were 2 mg/L in 1:1 water:ACN. Solid and dashed traces were monitored at 267 and 254 nm, respectively.
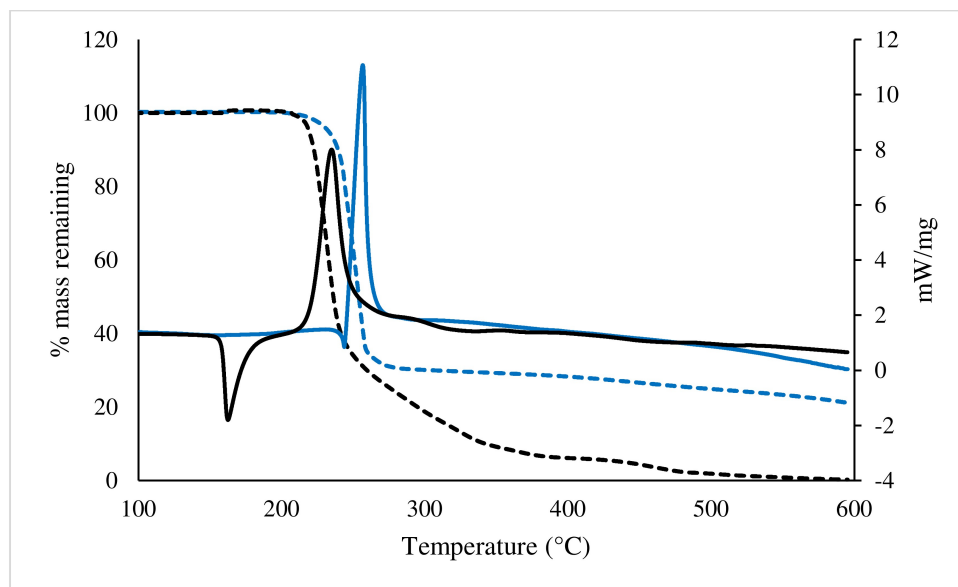

Figure 4. Thermal gravimetric analysis (dotted) and differential scanning calorimetry (solid) profiles of MeNQ (black) and NQ (blue).

4 Conclusions

The values determined in this present work are summarized in Table 2 along with the literature values for NQ and the legacy munitions to be replaced by insensitive formulations. The solubility of both guanidine-based munitions is much greater than the two legacy munitions. Pho-

tolysis dominates the environmental fate for abiotic transformation as hydrolysis and volatilization will not compete on similar timelines. A detailed study of the hydrolytic rate was beyond the scope of the present study but undertaking the reaction at multiple temperatures would enable an Arrhenius analysis to estimate the rate and activation energies at ambient temperatures for comparison to NQ. Fur-
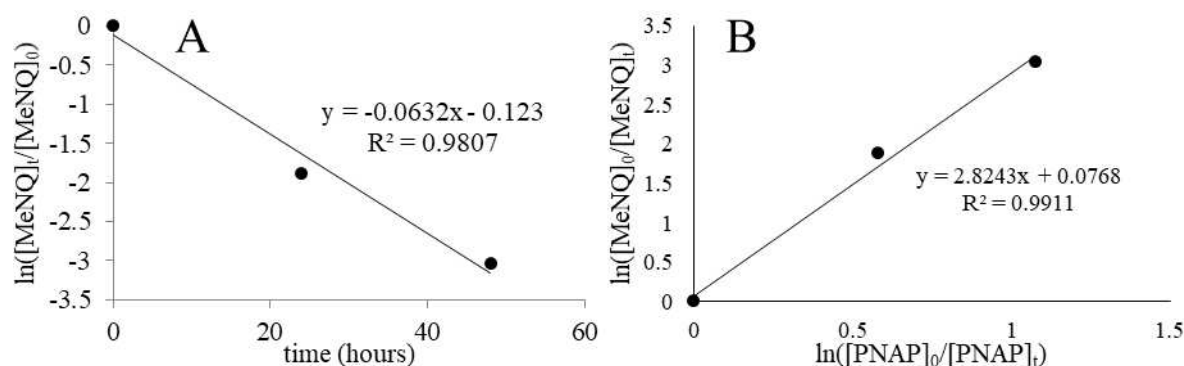
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Figure 5. Photolysis of MeNQ (A) and quantum yield determination against PNAP-PYR actinometer (B). After 72 hours of exposure no MeNQ remained and is omitted from the plots.

Table 2. Experimentally determined values of physicochemical parameters important for environmental fate and transport studies. a) calculated using $\log(P_v)^{exp} = -5.135$ mbar, b) this is the value determined at pH 10, c) taken as the onset of melting from DSC measurements.

Munition	Solubility	Hydrolysis rate constant	Photolysis quantum yield	Vapor pressure (MPa)	Melting point (°C)
MeNQ	12.92 ± 0.52 g/L	Negligible	0.009	1×10^{-20}	155[c]
NQ	2.6 ± 0.1 g/L [20]	2×10^{-8} s^{-1} [20]	0.01 [23]	1.65×10^{-10} [16]	232–240 [21]
RDX	0.0384–0.0389 g/L [25]	Negligible [Sikka, 1980]	0.18 [26]	8.52×10^{-11} [16]	205.5 [27]
TNT	0.1005 ± 0.002 [28]	0.00 [29][b]	0.0019 [30]	7.33×10^{-6} [31] [a]	80.9 [32]

thermore, it should be noted the hydrolytic rate constants for RDX and TNT are provided for the lowest pH values found in the literature to make comparisons to the buffered solutions utilized here. At greater pH values the hydrolysis of these munitions is sufficiently rapid for remediation purposes [24].

MeNQ has many similarities to NQ due to their similar chemical structure, but ^{1}H NMR analysis showed a greater degree of tautomerization of MeNQ compared to NQ. Quantification of MeNQ via HPLC analysis is possible with the methods outlined, and distinguishing MeNQ from NQ is possible by comparison with multiple wavelengths. MeNQ was found to melt at a considerably lower temperature than NQ and, rather than volatilize like NQ, MeNQ thermally degrades. This results in an estimated vapor pressure that is not environmentally relevant. MeNQ is 4 to 5 times more soluble in water but does not undergo hydrolysis at an appreciable rate for this to be an environmental sink for the munition. Aqueous photolysis, however, was determined to be a significant transformation process, and further work to determine the potential toxicity of the photolytically generated product mixture and identification of the products are warranted. Furthermore, biotic transformation studies of MeNQ are needed to determine if microbial degradation will compete with photolysis in the environment or poses a potential treatment solution for contaminated wastes.

Acknowledgements

Data Availability Statement

The data that supports this report's findings is available in the supplementary information.

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