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Kinetics of Base-Catalyzed 2,4,6-Trinitrotoluene Transformation

Deborah R. Felt, Steven L. Larson, and Lance D. Hansen

August 2001

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Kinetics of Base-Catalyzed 2,4,6-Trinitrotoluene Transformation

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Preface

The work reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS.

This report was prepared by Ms. Deborah Felt of Applied Research Associates, Inc. (Southern Division); Mr. Lance Hansen of the Environmental Engineering Branch (EEB), Environmental Laboratory (EL), ERDC; Dr. Steven L. Larson of the Environmental Chemistry Branch (EEC), Environmental Laboratory (EL), ERDC. Chemical analyses were performed by the Environmental Chemistry Branch of ERDC. We gratefully acknowledge the support provided by Dr. Edward Valente, Department of Chemistry, Mississippi College, and Dr. John Cullinane, Environmental Laboratory, ERDC. The study was conducted under the direct supervision of Mr. Danny Averett, Chief, EEB, and Dr. Richard E. Price, Chief, Environmental Processes and Engineering Division, and under the general supervision of Dr. James R. Houston, Director, ERDC, and Acting-Director, EL. At the time of publication of this report, COL John W. Morris III, EN, was Commander and Executive Director of ERDC.

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1 Introduction

This technical report is one in a series of reports that deals with the chemistry and technology of the base-induced transformation of 2,4,6-trinitrotoluene (TNT). Kinetic studies in aqueous solutions, which are the focus of this paper, help establish reaction rates and activation energies, which in turn are used to design effective remediation systems. In another study in our laboratory, TNT transformation products were characterized by challenging radiolabeled ^{14}C TNT with a basic solution and following the transformation products using gel permeation chromatography. Most of the transformation products were polar (98 percent) and varied in molecular weight from 6,000 to <100 Daltons. These results indicated that polymerization and ring cleavage had occurred during the OH-TNT reaction. The results from the gel permeation chromatography study are fully described in Felt, Larson, and Hansen (2001). In a separate study, explosives-contaminated soils were challenged with lime using different moisture contents and mixing protocols. A treatment using 30 percent moisture content was the most effective at degrading TNT, with no significant difference indicated between mixing protocols. A technical report outlining the soil results is in draft. Future work will include pilot-scale treatments, evaluation of the effect of soil structure on treatment efficiency, studies using radiolabeled TNT in soils, and identification of individual reaction products.

Contamination of groundwater, surface water and soil by explosives has occurred at military sites throughout the world as a result of manufacture of explosive compounds, assembly of munitions, and deployment of explosives containing devices (Roberts and Hartley 1992; Jenkins, Thorne, and Walsh 1994; Pennington et al. 1995). Listed as a priority pollutant, TNT is toxic to humans, plants and animals (Rosenblatt et al. 1991; Smith 1991; Won, DiSalvo, and Ng 1976; Palazzo and Leggett 1986; and Simini et al. 1995). TNT remediation methods, such as incineration, composting, bioremediation, and ultraviolet (UV) light, have been used with mixed success (Pennington et al. 1995; Dillert et al. 1995; Lang et al. 1998; Spain 1995). The transformation of TNT in basic solutions has long been established (Urbanski 1964) and could potentially be part of a rapid, low-cost, and minimally resource-intensive technology to remediate TNT contamination. The rate of TNT transformation when exposed to UV (Dillert et al. 1995), to iron (II) (Brannon, Price, and Hayes 1998), or to a combination of UV light, ozone, and electrohydraulic discharge (Lang et al. 1998) is enhanced

at alkaline pH. Dunnivant and Schwarzenbach (1992) reported that TNT degradation caused by Natural Organic Matter (NOM) was increased at elevated pH. Degradation intermediates of TNT were polymerized in alkaline conditions during anaerobic bioremediation of soils (Funk et al. 1993) and at elevated temperatures (Saupe, Garvnes, and Heinze 1997). Research is needed to evaluate the efficacy of using base-induced transformation of TNT as part of a remediation technology and to identify the preliminary parameters necessary for practical implementation of this technique. In order to design a remediation technology to degrade TNT efficiently, it is necessary to determine the minimum pH level necessary to achieve TNT transformation. The mechanism of the OH-TNT reaction is unknown and chemical kinetics studies were necessary to determine the kinetics of the OH-TNT reaction. Kinetic studies help establish reaction rates, activation energies, and other information concerning the reaction mechanisms that directly affect a possible remediation technology. This information is needed to guide engineers in predicting the time requirements for effective remediation and designing effective remediation systems.

The objectives of this study were to validate TNT transformation in basic solutions and to determine the kinetics of the OH-TNT reaction in order to evaulate the efficacy of base-induced TNT transformation for use as a remediation alternative. Three experiments were performed to meet these objectives: (a) TNT transformation was validated in basic solutions and experimental parameters were determined. (b) Effects of neutralization and pH level on the OH-TNT reaction were determined. (c) Kinetic experiments executed at three temperatures were used to calculate activation energies. Results from these experiments will yield an understanding of the OH-TNT reaction that enables engineers to design effective explosives remediation systems.

2 Materials and Methods

Representative samples, 3 mL, TNT solution (100 ppm) were challenged with 7 mL of 1 molar (M) potassium hydroxide (KOH) solution (sample) or 7 mL water (control). Triplicate aliquots (500 µL) from each sample and control were taken at predetermined times (1, 5, 10, 30, 60, 120, and 180 min) and added to 500 µL 1 M phosphate buffer solution. The aliquots were further diluted 1:1 with acetonitrile and analyzed for TNT concentration using a modified EPA method 8330 (Dillert et al. 1995). Representative samples (25 µL) were injected on a high performance liquid chromatography (HPLC) equipped with a diode array detector (DAD) set at 254 nm and C-18 reverse-phase column. An isocratic mobile phase of 50 percent methanol and 50 percent 0.01 M phosphate buffer ± 1.5 percent methanol was used to protect the column from the high pH level. Methanol was added to the buffer to retard microbial growth. The flow rate was 0.5 mL/min and the run time was 40 min. TNT retention time for these conditions was 17 min. The method detection limit was 0.095 ppm TNT and detector response was linear between 0.1 and 5 ppm TNT.

Effects of Neutralization and pH Levels

Triplicate samples of TNT solution (102 ppm) were challenged with potassium hydroxide solution and immediately diluted 1:1 with a phosphate buffer (pH 7) to determine if neutralizing the samples would quench the reaction. Samples were then diluted 1:1 with acetonitrile:water. Multiple injections (25 µL) of the sample and unchallenged control solution were made over an 18-hr period using the method and instrument parameters previously described.

Triplicate samples (1 mL) TNT solution (100 ppm) were challenged with l mL KOH solutions at various pH levels. Samples were taken after reaction times of 1 min and 24 hrs, diluted 1:1 with acetonitrile, and aliquots (25 (L) were analyzed using the method and instrument parameters previously described.

Kinetics Experiments

Triplicate samples of a TNT solution (102 ppm) were challenged with equivalent volumes containing an excess of base (1 M KOH) at three different temperatures (25, 10, and 0 °C). Representative samples (500 µL) of the reaction mixtures were taken at predetermined times, diluted 1:1 with acetonitrile, and TNT concentrations were monitored using the method and instrument parameters previously described. The zero time samples were TNT solution diluted 1:1 with water with no addition of base to simulate the composition of the reaction. Mean TNT concentrations were plotted versus time.

3 Results and Discussion

TNT concentrations were analyzed over time after TNT solutions were challenged with hydroxide solutions. Results of TNT concentration versus time for TNT samples challenged with hydroxide and TNT controls at room temperature (24 °C) are presented in Figure 1.

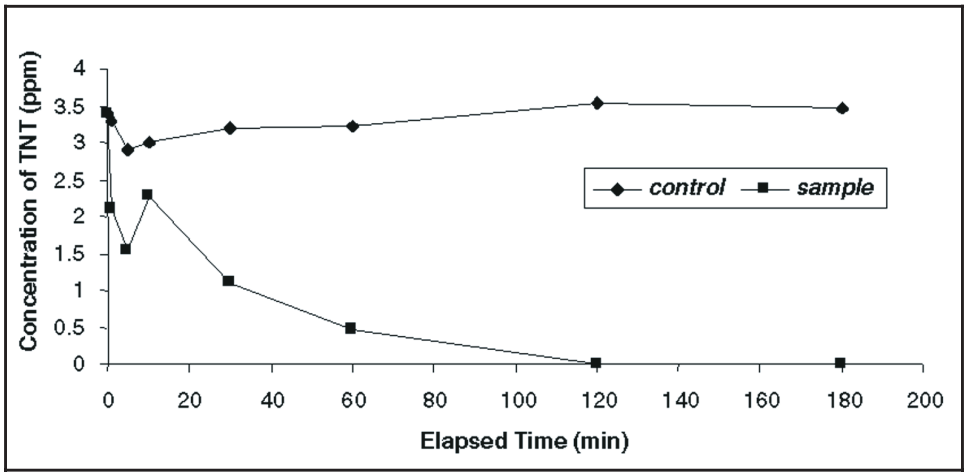

Figure 1. TNT concentration versus time for samples challenged with hydroxide and controls at 24 °C

The elapsed times in Figure 1 represent the time in minutes that elapsed (the reaction time) from the time of the addition of the base to the sample until analysis for TNT using HPLC. Relative to controls, TNT concentrations in the base-treated samples quickly declined and TNT was undetectable after 120 min. This indicates that TNT is transformed in basic solutions under these conditions. This reaction time (120 min) is favorable to the time required to complete TNT degradation using other efficient remediation technologies, photochemical oxidation or electrohydraulic discharge reactors, without the expensive equipment and highly trained personnel to operate them (Lang et al. 1998; Schmelling and Gray 1995). TNT transformation was further indicated by a color change during the reaction. Aqueous TNT solutions at the initial concentration (100 ppm) are clear. The challenged sample changed color, from clear to a brownish yellow color, immediately after the base was introduced. After 1 hr, the color had changed again, to pink.

Sample chromatograms indicated a reaction intermediate that formed quickly after reaction initiation and then slowly degraded over time. This correlates with the color changes that were noted during the reaction. A chromatogram of a base-challenged TNT sample is compared to that of TNT standard in Figure 2. A large peak was identified at a retention time of 3.5 min in the base-challenged sample. This feature was not in evidence in the control chromatogram, as shown in Figure 2, and was presumed to indicate an unknown polar reaction product. The transformation products were determined to be 98 percent polar in a separate study that characterized the chemical properties of TNT transformation products using solvent-solvent extraction (Felt, Larson, and Hansen, in preparation). The peak height of this feature decreased over time indicating follow-on secondary degradation. These results indicate that TNT in basic solution quickly transforms to yield a colored intermediate product, then the intermediate product slowly degrades to form the final colored product(s).

Effects of Neutralization and pH Levels

The minimum pH level necessary to achieve base-induced TNT transformation and effects on TNT transformation by lowering pH levels were determined in order to establish basic design parameters of a remediation system. Figure 3 shows TNT concentrations versus time of a base-challenged sample immediately diluted with pH 7 buffer compared to an unchallenged TNT control.

TNT concentrations in the unchallenged stock solution remained the same, but TNT concentrations in the buffered sample continued to decline over time. The feature at 3.5 min identified previously in a base-challenged sample was also evident in the sample chromatograms of the neutralization experiments. The rate of TNT transformation in the buffered sample was similar to unneutralized samples in that the rate was very fast initially and was much slower over the remainder of the test. This indicates that lowering the pH after initiation of the OH-TNT reaction did not quench the reaction and TNT continued to degrade in the buffered system. This implies that remediation systems would not have to be maintained at high pH levels for extended periods of time, but could be neutralized after the base was introduced into the system and TNT would continue to degrade. Base-induced TNT transformation may be possible at lower initial pH levels, which would translate to lower remediation costs and be more readily accepted by remediation experts. In order to determine the minimum pH level necessary to attain TNT transformation, TNT solutions were challenged with basic solutions at different pH levels. Figure 4 shows TNT concentrations versus time of TNT stock solutions that were challenged with hydroxide at various pH levels and sampled at 1 min and 24 hr.

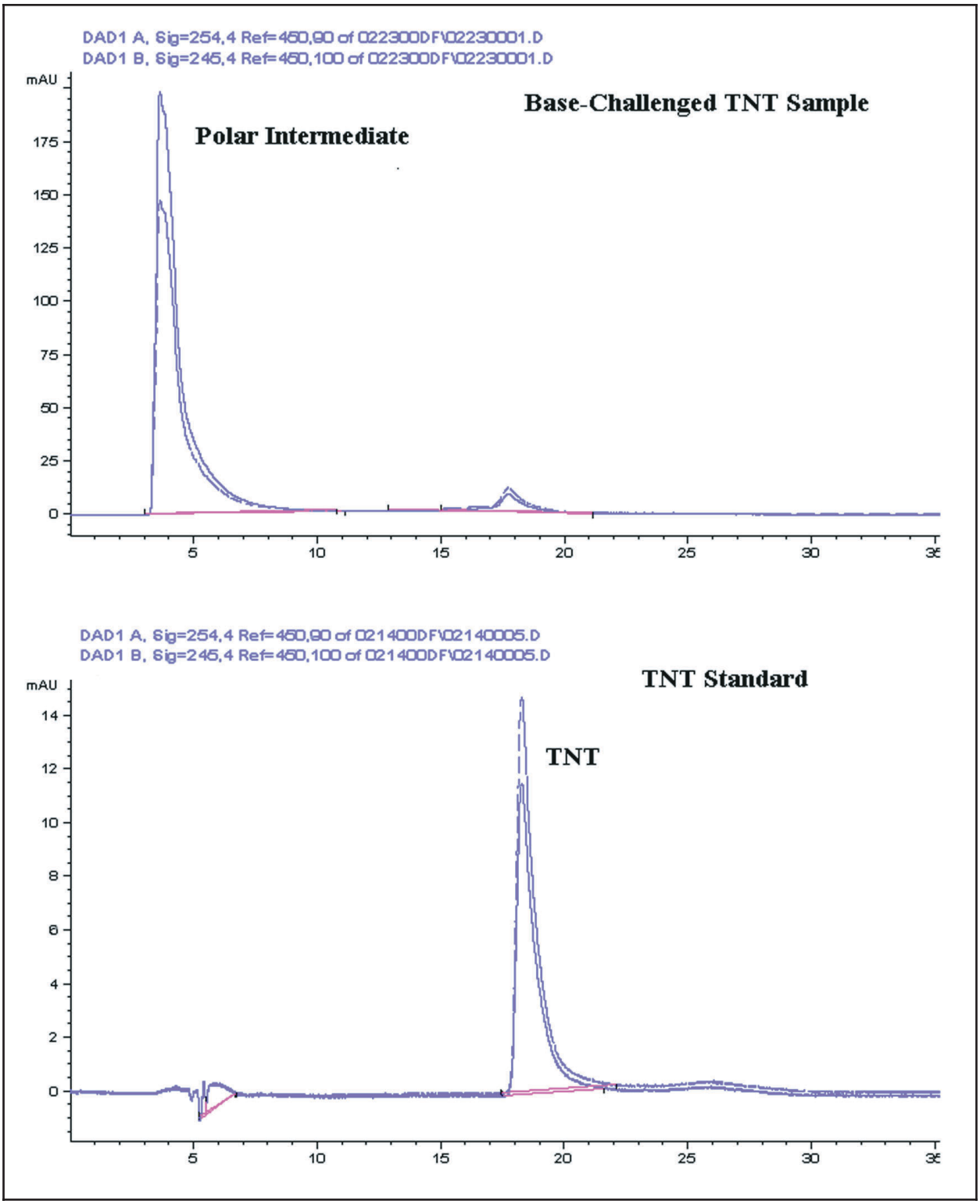

Figure 2. Chromatogram of base-challenged reaction mixture compared to the TNT standard

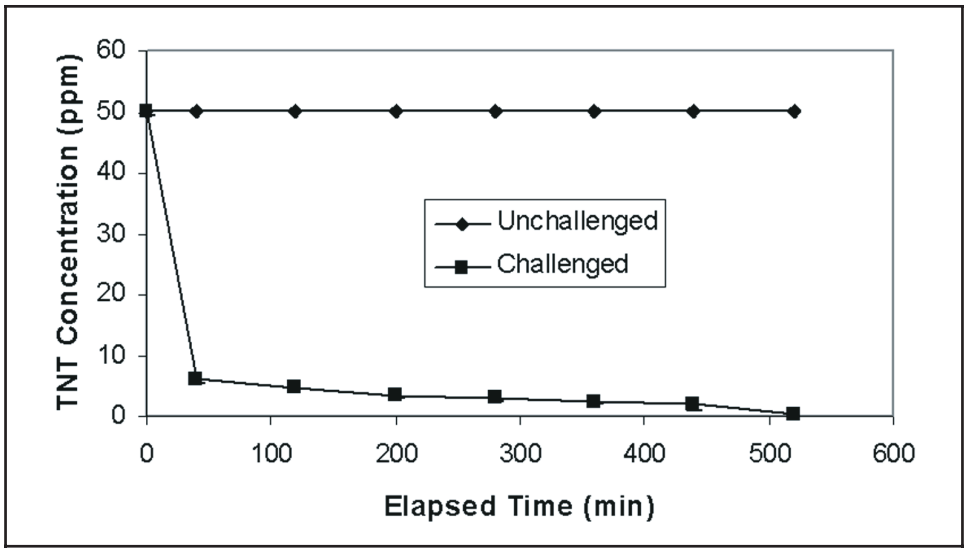

Figure 3. Hydroxide-challenged sample diluted with pH 7 buffer versus unchallenged control

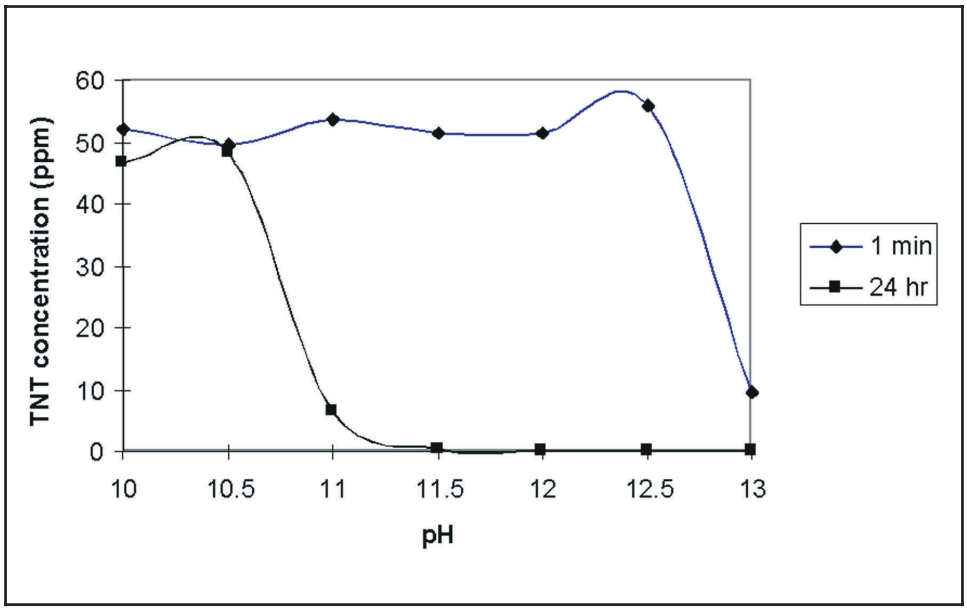

Figure 4. TNT stock solution challenged with hydroxide at various pH levels

TNT quickly degraded at pH 13 compared to the other pH levels. TNT concentrations were relatively unchanged after 1 min for samples challenged with pH levels up to 13, but TNT concentration was reduced significantly in samples challenged with pH 11-13 after 24 hr. Some degradation was obvious at all pH values in the range of 10.5-13 after 24 hr, with sharp TNT reduction starting at pH 11. This indicates that lower pH levels could be used in remediation systems to initiate TNT transformation, but the treatment time would be longer compared to a system that used > pH 11. Studies following TNT transformation at lower pH levels over extended

time periods would further define the minimum conditions (pH level and time) needed to complete TNT remediation.

Kinetics Experiments

The changes in TNT concentrations with respect to time were studied in order to determine the kinetic parameters that govern the base hydrolysis of TNT in aqueous solution. When the concentrations of TNT for aqueous base hydrolysis are plotted versus reaction time, a number of general trends are noted at three different temperatures as shown in Figure 5. For each temperature, two components are observed. A very fast initial decrease in TNT concentration was followed by a slower rate of degradation that continued to complete TNT destruction.

A summary of TNT concentrations versus time for OH-TNT for three different temperatures is presented in Table 1. The notation, ND (not detected) in the table, indicates that the TNT level was below the method detection limit.

Table 1
Summary of TNT Analysis for the Reaction of TNT with Hydroxide

25 °C			10 °C			0 °C		
Elapsed Time min	Avg TNT ppm	Standard Deviation	Elapsed Time min	Avg TNT ppm	Standard Deviation	Elapsed Time min	Avg TNT ppm	Standard Deviation
0	56.05	6.84	0	53.83	8.35	0	54.94	1.57
1	9.49	2.92	1	6.29	1.18	1	0.71	0.18
2	6.44	1.23	2	5.06	1.03	2	1.62	0.08
5	3.6	0.87	5	4.32	0.34	5	2.55	0.05
10	1.76	0.25	10	3.55	0.73	10	2.82	0.32
15	1.11	0.13	15	4.33	0.50	—	—	—
20	0.72	0.04	20	2.72	2.02	20	2.24	0.22
40	ND	ND	45	3.41	1.24	45	1.54	0.24
			90	1.90	0.58	90	1.22	0.33
			120	1.93	0.47	120	0.96	0.06
			180	1.64	0.62	180	0.87	0.09
			240	1.01	0.65	240	0.47	0.41
			360	0.21	0.08	360	0.60	0.19
			480	0.15	0.05	—	—	—
			1,080	ND	ND	1,080	1.33	0.04
			1,440	ND	ND	1,440	0.23	0.02
						1,800	0.19	0.08
						2,880	ND	ND

Elapsed time from addition of base to HPLC injection.

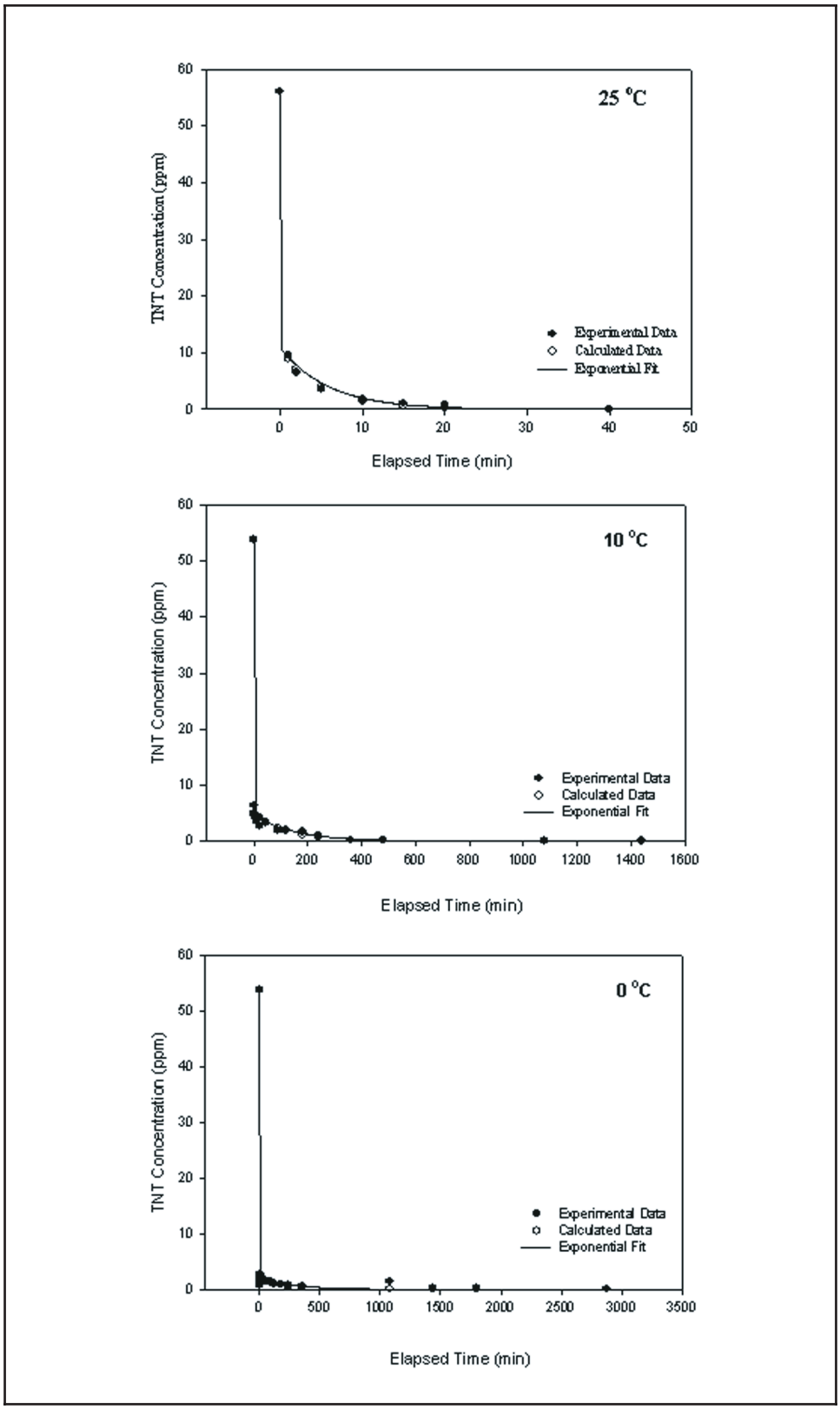

Figure 5. TNT concentration versus reaction time using hydroxide

The rapid initial reduction in concentration did not seem to be affected by cooler temperatures because the rate was consistent for the three temperatures. The slower, secondary reduction rate decreased as the temperature decreased. It took longer for the reaction to go to completion (TNT concentration below detection limit) as the temperature was lowered; that is <40 min at room temperature; <18 hr at 10 °C; and <48 hr at 0 °C. This indicates that the secondary rate was temperature-dependent. The kinetics experiments suggest the OH-TNT reaction has two components with two rates: a fast component that occurs immediately after the addition of the base to the TNT solution, followed by a slower secondary component. This result is collaborated by results from a study that separated radiolabeled ^{14}C TNT transformation products using gel permeation chromatography into molecular weight ranges (Felt, Larson, and Hansen 2001). The results indicated a multistep reaction mechanism, evidenced by the fact that the transformation products have varied molecular weights, ranging from 6,000 to <100 Daltons. The transformation products having the same molecular weight would indicate a single-step mechanism. It has been suggested that TNT radicals or ions are being formed during the initial stage of OH-TNT reaction, as these types of reactions are temperature-independent. Further studies must be conducted to confirm this.

Mathematical Model

Kinetics data were fitted to a second order exponential nonlinear regression equation to provide a mathematical model of the OH-TNT reaction.

$$\text{function} = Ae^{-bx} + Ce^{-dx} \tag{1}$$

The variables A and C are the amplitudes for the initial fast decay and the second slower decay with time constants k_1 and k_2, respectively. Nonlinear regression was performed on the experimental data shown in Table 1 and theoretical data were generated for comparison with observed data calculated using the nonlinear regression, as shown in Figure 5. The double exponential decay equation fits TNT transformation by hydroxide, as determined by experimental means, to a model with two distinct reaction rates: a very fast initial rate followed by a much slower rate. Rate constants, rate coefficients, and activation energies were then predicted using this model for the OH-TNT reaction. The reaction rates calculated for the kinetics data at three temperatures using the second order exponential non-linear regression equation, Equation 1, are summarized in Table 2.

Table 2
Reaction Rates Calculated for Kinetics Data Using Second Order Exponential Nonlinear Regression Equation

Temperature °C	First Coefficient *A*	First Rate Constant k_1	Second Coefficient *C*	Second Rate Constant k_2	r^2	k_1/k_2
25	45.23	6951.38	10.81	0.203	0.9992	34,243
10	49.06	200	4.77	0.00819	0.9977	24,420
0	51.86	10	1.97	0.00440	0.9980	2,273

The reaction rates fit the nonlinear regression function, which suggests the OH-TNT reaction follows pseudo-first order kinetics with regard to TNT concentration,

$$-d(TNT)/dt = k(TNT) \tag{2}$$

which upon integration gives,

$$\ln(TNT)_t = \ln(TNT)_0 - kt \tag{3}$$

Hydroxide is required to initiate the reaction, however the hydroxide concentration is in great excess compared to TNT and remains essentially constant over the course of the reaction. The plot of natural logarithm (ln) (TNT) against time is a straight line indicating the OH-TNT reaction is first-order with respect to TNT.

Activation Energies

Activation energies are required to predict residence times and other requirements for designing effective remediation systems. Activation energies were calculated by solving the Arrhenius equation,

$$k = Ae^{-E_a/RT} \quad \text{or} \quad \ln k = \ln A - (-E_a/R)\,1/T \tag{4}$$

The values of a rate constant (k_1) at different temperatures are related by

$$\ln k_2^1/k_1^1 = (-E_a/R)\left[1/(T_2 - T_1)\right] \tag{5}$$

where k_{21} and k_{11} are the rate constants for two temperatures T_2 and T_1. A plot of the natural log of k versus $1/T$ ($1/K$) gave a line with the slope of $-E_a/R$. The activation energy, E_a, was calculated using the following equation:

$$E_a \text{ (kJ / mole)} = -(2.303)R \text{ (slope)} \tag{6}$$

The plot is linear for the first, faster rate of the TNT-hydroxide reaction, k_1, as shown in Figure 6, with r^2 of 0.9982, an intercept of 80.10, and a slope of -21214.42 K. The calculated activation energy for the first phase of the reaction was 406.20 kJ/mol. Substituting the values for A and E_a into the equation yields:

$$k_1 = 80.10e^{-(406.20\ \text{kJ/mol})/(8.314\ \text{J/mol}\ K)T} \tag{7}$$

which can be used to solve for the reaction rate at any given temperature within the range studied. Figure 7 illustrates the Arrhenius plot for the calculated rate constants for the second, slower rate constant, k_2. The r^2 for this regression was 0.9229, an intercept of 41.10, and a slope of -12,805.21 K. Using the previous formulas, E_a is 245.18 kJ/mol and the rate equation is

$$k_2 = 41.10e^{(245.180\ \text{kJ/mol})/(8.314\ \text{J/mol}\ K)T} \tag{8}$$

Ratios of k_1/k_2 decline as the temperature goes down as shown in Table 2. A declining k_1/k_2 ratio with temperature indicates a differential temperature effect. This result indicates the two distinct steps in the overall reaction are each affected differently by temperature.

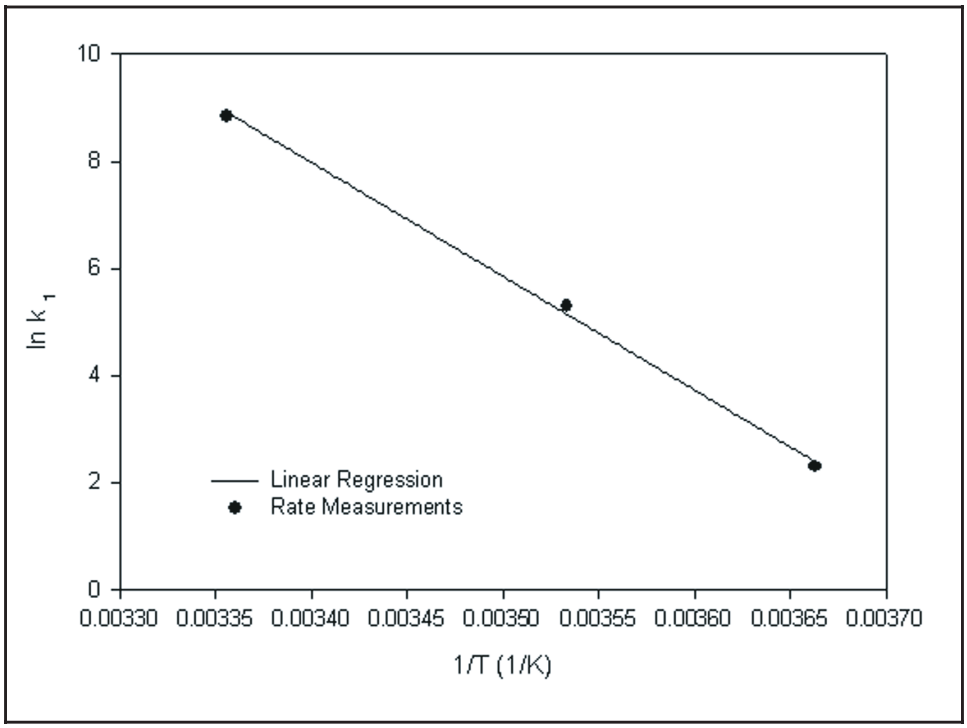

Figure 6. Arrhenius plots for the initial reaction using rate measurements for k_1 and k_2 for the HPLC data

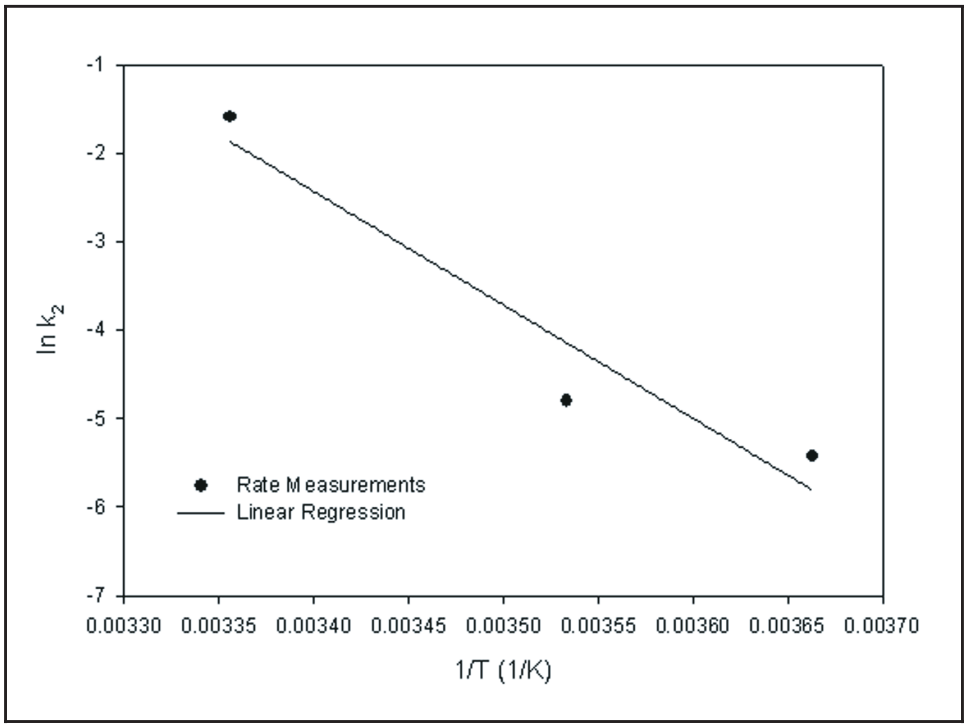

Figure 7. Arrhenius plots for the second, slower reaction using rate measurements for k_1 and k_2 for the HPLC data

4 Conclusions

The results of this three-phase experimental assessment indicate base transformation of aqueous/dissolved TNT is a potential technique for destruction of TNT in process waters from explosives handling facilities. This technique may also be used in conjunction with groundwater remediation activities that rely almost exclusively on engineered pump-and-treat systems. Proof-of-concept experiments validated apparently complete and rapid transformation of dissolved TNT when challenged by hydroxide in sufficient concentrations. Reaction-quenching experiments (neutralization) determined that once initiated, TNT transformation was autocatalytic and could not be inhibited by addition of acid to reduce pH levels. Temperature-dependent kinetics evaluations determined rate constants that can be used to develop preliminary designs of modified water treatment and remediation processes involving TNT-contaminated water.

In a separate study, TNT transformation products in aqueous solution were characterized using solvent-solvent extraction and gel permeation chromatography (Felt, Larson, and Hansen, in preparation). The majority of the transformation products were polar compounds (98 percent), indicating they may be more water-soluble than TNT. The transformation products varied in size from 6,000 to <100 Daltons, indicating a multistep reaction mechanism. Large molecular weight molecules indicate polymerization of the products, where small molecular weights indicate that the aromatic ring of TNT had been cleaved during the reaction. Polymers are less likely to be transported from the field site because of their relative size and small organic molecules are more likely to be utilized by bacteria as carbon sources. The results of these two studies provide basic mechanistic information about the OH-TNT reaction that can be used to design protocols for field application of ground water and soil remediation technologies.

Soil-slurry and bench-scale pan studies using explosives-contaminated soil have indicated that calcium hydroxide (lime) will quickly degrade TNT and RDX in contaminated soil. Future research to validate the use of this technology for soil remediation include pilot-scale (lysimeter) studies, studies using radiolabel tracers to track TNT transformation products in soils, toxicity studies, and the identification of individual transformation products using liquid chromatography-mass spectroscopy.

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14. ABSTRACT

Contamination of groundwater, surface water and soil by explosives has occurred at military sites throughout the world as a result of manufacture of explosive compounds, assembly of munitions, and deployment of explosives containing devices. Due to the adverse effects of explosives on humans and other natural receptors, a low cost means of decontaminating these areas of contamination is needed. Base-catalyzed transformation of explosives has shown promise as a rapid, low-cost, and minimally resource-intensive technology for detoxifying explosives in soil and water. In order to understand the mechanism of these reactions, a laboratory study has been performed to determine the kinetics of the degradation of 2,4,6-trinitrotoluene (TNT) with hydroxide in aqueous phase systems. Results presented include the validation of base-induced transformation of TNT, effects of neutralization and pH level on TNT transformation, kinetics of TNT degradation, and the dependence of the rate of TNT degradation on temperature. Understanding the effects of varying pH levels and kinetics of TNT transformation are parameters necessary for design of engineered remediation systems.

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