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Kinetics of the Alkaline Hydrolysis of High Explosives RDX and HMX in Aqueous Solution and Adsorbed to Activated Carbon

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Aqueous alkaline hydrolysis of bulk quantities and wastewater contaminated with high explosives is a promising technology for treatment and disposal of the worldwide surplus of munitions. We investigated the hydrolysis kinetics of the high explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) for temperatures ranging from 50 to 80 °C and in the pH range from 10 to 12. The experimental data were described using a pseudo-first-order model with subsequent calculation of second-order rate constants from experiments with excess hydroxide concentration. The temperature dependency of the rate constants was evaluated using the Arrhenius model. The activation energies were determined to be $E_{RDX} = 99.9 \pm 1.9$ kJ mol^{-1} and $E_{HMX} = 111.9 \pm 0.8$ kJ mol^{-1}. The rate of HMX hydrolysis is much slower than the rate of RDX hydrolysis and may become rate limiting in the treatment of RDX/HMX mixtures. The alkaline hydrolysis of RDX yields 1.6 M NO_2^-, 1.5 M $HCOO^-$, 0.1 M CH_3COO^-, 1.1 M HCHO (*11*), 0.9 M NH_3, 1.1 M N_2O, and 0.34 M N_2 per mol of RDX hydrolyzed. Acetate ion (CH_3COO^-) is a previously unknown end product of the alkaline hydrolysis of RDX. A mass balance showed a recovery of 94% carbon and 90% nitrogen. During GC/MS analysis of the end products, no further unknown products could be found. In batch desorption studies, it was also shown that RDX-laden activated carbon can be regenerated using alkaline hydrolysis ($T = 80$ °C, pH 12) and that the desorption of the hydrolysis products is complete.

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Introduction

The interest in military waste has recently increased due to growing environmental concerns and the end of the Cold War. The environmental fate and health impacts of high explosives waste and their appropriate treatment technologies are yet to be identified. Byrd and Humphreys (*1*) report a U.S. demilitarization inventory at the end of fiscal year 1992 of 313 000 000 kg of high explosives (e.g., RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; TNT, 2,4,6-trinitrotoluene). The current nuclear weapons dismantling efforts by the U.S. Department of Energy will generate another 50 000 kg/year of excess high explosives waste through the year 2000. In addition to bulk high explosives, contaminated groundwater and process water from closed military bases, former production plants, contaminated soil, and weapon dismantling facilities will need to be treated. Problems related to contaminated sites and demilitarization activities also exist in Europe and the former Soviet Union, with some of the sites dating back to World War II.

The heterocyclic nitroorganic compounds RDX (CAS Registry No. 121-82-4) and HMX (CAS Registry No. 2691-41-0) are some of the most important high explosives. Both are major components in nuclear and conventional weapons. Today, they are widely used as part of high-performance explosives in the United States, such as plastic bonded explosives PBX-9011 (90% HMX), -9404 (94% HMX), -9407 (94% RDX), and -9501 (95% HMX) (*2*) and LX-04-1 (85% HMX), -07-2 (90% HMX), -09-0 (93% HMX), -10-0 (95% HMX), -11-0 (80% HMX), and -14-0 (95.5% HMX) (*3*). Recently, HMX has replaced its homologue RDX in importance in the United States, and it is more prevalent in recently manufactured explosive devices. This is due in part to HMX's greater yield and resistance to unwanted detonation.

RDX and HMX have important health and toxicity effects. RDX is a class C possible human carcinogen and has adverse effects on the central nervous system in mammals (*4*). HMX also has central nervous system effects but only in higher concentrations (*5*). Generally, less is known about HMX, and further chronic carcinogenicity and toxicity studies are needed.

Currently high explosives are being destroyed by open burning/open detonation (*1*, *6*). In fiscal year 1992, 80% of the U.S. Department of Defense's annual demilitarization tonnage of 56 000 000 kg was destroyed this way (*1*); however, due to environmental and legal concerns, this technology will soon be unavailable. Combustion of high explosives can lead to various unwanted toxic products. Holl and Schneider (*7*) documented a pyrolytic reaction under critical conditions (delayed ignition; low ignition heat; accidental smolder fire) that leads to the formation of large amounts of hydrocyanic acid (HCN) during RDX combustion.

Process waters or groundwaters contaminated with high explosives from dismantling activities or contaminated sites generally have been treated by adsorption onto activated carbon (*8*). The laden carbon cannot be thermally regenerated because of explosion risk and must be disposed as hazardous waste. Burning of the spent carbon has now been banned for the same reasons as mentioned for open

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burning/open detonation, and other disposal methods are expected to become more difficult and more expensive due to more stringent regulations.

The U.S. Departments of Energy and of Defense are now combining their efforts to identify possible future technologies for demilitarization. Alkaline hydrolysis has been identified as an alternative treatment technology; however, additional basic research is necessary before commercial or industrial facilities can be successfully constructed.

Several researchers have investigated the kinetics of the alkaline hydrolysis of RDX (*9*−*12*). Hoffsommer *et al.* (*11*) identified end products and a rate-determining E2-elimination mechanism as the initial step of the alkaline hydrolysis of RDX. Identified end products and by products are NO_2^-, N_2, NH_3, N_2O, $HCOO^-$, CH_2O, and H_2. The formaldehyde is subject to a *Canizarro* reaction at the elevated pH and produces formate (*13*). The reaction was also confirmed to be second-order with respect to RDX and OH^- concentrations. Second-order rate constants were calculated from pseudo-first-order rate data (for excess OH^-).

Less research has been performed on the alkaline hydrolysis of HMX; however, we anticipate some similarities to the alkaline hydrolysis of RDX. Epstein *et al.* (*9*) concluded that the alkaline hydrolysis of HMX is second-order. Croce *et al.* (*12*), in their study on rate enhancement effects in the presence of cationic micelles, proposed that the alkaline hydrolysis of HMX follows the same basic mechanism as RDX with regard to the almost similar activation parameters for HMX and RDX that were obtained in these and the Hoffsommer *et al.* (*11*) rate studies. Nevertheless, Croce *et al.* (*12*) report aqueous standard solutions containing 6, 9, and 12 mg of HMX/L, which are above the solubility limit of 5 mg of HMX/L (*14*), which we confirmed. Possible heterogeneous effects in their study need special interpretation. All these investigations were at temperatures ranging from 0 to 45 °C.

Current research is under way at the Los Alamos National Laboratory. The emphasis in these investigations is on the heterogeneous alkaline hydrolysis of solid HMX and other bulk high explosives (*15*). Spontarelli *et al.* demonstrated that many propellants, explosives, and pyrotechnics can be base hydrolyzed at temperatures ranging from 60 to 150 °C.

To develop an economical treatment scheme for HMX- and RDX-contaminated waters, additional basic research is necessary. HMX and RDX are sparingly soluble in water (solubility limits at 25 °C: ∼5 mg of HMX/L [*14*] and ∼50 mg of RDX/L [*2*]). Direct treatment of the wastewater with base hydrolysis is not economical. An alternative treatment process using granular activated carbon (GAC) adsorption of HMX and RDX and subsequent off-line regeneration of the laden GAC through alkaline hydrolysis is a potentially viable process (Figure 1). The contaminated water is first treated through HMX and RDX adsorption onto GAC, which concentrates the contaminants on the carbon and reduces the volume of material to be treated with alkaline hydrolysis. The laden carbon is regenerated with alkaline hydrolysis and can be reused to treat another charge of contaminated water. The end products are thought to be low molecular weight compounds that can easily be degraded in regular wastewater treatment plants with nitrification/denitrification stages. This treatment scheme is complementary to the earlier proposal of Hesselmann *et al.* (*16*) that used carbon adsorption with solvent and biological carbon regeneration.

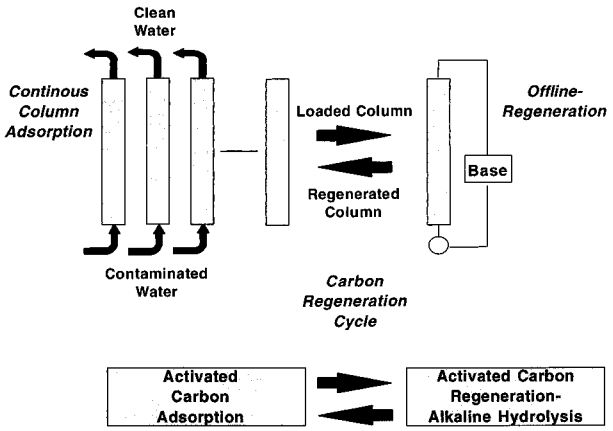

FIGURE 1. Treatment scheme for waters contaminated with high explosives.

In this paper, we investigate the chemical kinetics of the alkaline hydrolysis of HMX and RDX under aqueous homogeneous conditions. Because the rates of the alkaline hydrolysis increase at higher temperatures and pressures, and these conditions seem more feasible for industrial operation, we investigate the kinetics of the alkaline hydrolysis of HMX and RDX at elevated temperatures ranging from 50 to 80 °C. The pH varied on the range 10−12. The results are meaningful for treatment of explosives-contaminated waters and bulk high explosives. We also investigated the principal viability of activated carbon regeneration by alkaline hydrolysis with batch studies. Our research on a continuous process (Figure 1) is ongoing.

Materials and Methods

Analytical Section. High-Performance Liquid Chromatography (HPLC). Dissolved HMX and RDX were analyzed using high-performance liquid chromatography with a variable wavelength UV-detector (HPLC/UV, Hewlett-Packard Series 1050) set to 236 nm. A mobile phase consisting of 40% water, 30% methanol, and 30% acetonitrile (vol %) was used at a flow rate of 1 mL/min. (All solvents were HPLC grade, Fisher Scientific, Springfield, NJ.) An Adsorbosphere-C18 10-μm reversed-phase column (Alltech, Deerfield, IL) with prefilter element and guard column (C18 5-μm, Alltech) was used. The injection volume was set to 20 μL using the autosampler. Peaks were detected at retention times between 3.5 and 3.7 min (HMX) and between 4.1 and 4.3 min (RDX). The peak area was a linear function of the concentration between 0.1 and 5 mg/L (HMX) and between 0.1 and 40 mg/L (RDX). The amount of HMX impurity contained in the RDX was quantified. We found 0.1 mg/L to be the detection limit with this method. For the external calibration, at least three replications were performed for each standard concentration. The mean was then used for the calibration curve. All samples were filtered through sterile Acrodisc-13 0.2-μm syringe microfilters (Gelman Sciences, Ann Arbor, MI) before injection.

Ion Chromatography—Formate and Nitrite. The anions NO_2^- (nitrite) and $HCOO^-$ (formate) were analyzed using a Dionex ion chromatograph (basic chromatography module CMB-2, gradient pump GPM-1; Dionex, Sunnyvale, CA) with suppressed conductivity detection (conductivity detector CDM-1). An Ion Pac AS9-SC column (4 mm i.d.)

and a suppressor column were applied. The mobile phase consisted of 0.75 mM $NaHCO_3$ and 2 mM Na_2CO_3 dissolved/L of Milliq water at a flow rate of 2 mL/min. Samples were manually injected into a 50-μL sample loop. Peaks were detected at retention times between 1 and 1.1 min ($HCOO^-$) and between 1.7 and 1.8 min (NO_2^-), respectively. The peak area was a linear function of the concentration between 0.33 and 13.24 mg/L ($HCOO^-$) and between 0.33 and 13.33 mg/L (NO_2^-). We found 0.01 mg/L to be the detection limit with this method at neutral pH. For the external calibration, at least three data points were gathered for each standard concentration. The mean was then used for the calibration curve. All samples were filtered through sterile Acrodisc-13 0.2-μm syringe microfilters (Gelman Sciences) before injection. We found an influence of the pH value in the determination of $HCOO^-$ and NO_2^- concentrations with the described method. Therefore, standard curves were obtained for neutral pH and also pH 11 and pH 12.

Ion Chromatography—Acetate. Acetate ion (CH_3COO^-) analysis was performed on a Dionex 2110i ion chromatograph with an AS10 column and an AG10 guard column. The eluent was 70 mM NaOH at 1 mL/min. A suppressed conductivity detector was applied; sample size was 50 μL. The retention time for acetate ion with this method was 4.3 min. Standard curves were obtained for 2, 4, 6, 8, 12, 16 mg/L. The pH had no influence on the detection with this method in the observed pH range from neutral to pH 12.

Gas Chromatography/Mass Spectrometry (GC/MS). A Finnigan GC/MS system, consisting of a Finnigan gas chromatograph Model 9610 equipped with a Grob-type splitless injector and a Finnigan quadrupole mass spectrometer Model 4000 with an INCOS Model 2300 data system, was applied (Finnigan, Sunnyvale, CA). The GC/MS was operated with an electron energy of 70 eV, a source temperature of 240 °C, and a scan speed of 1 s $scan^{-1}$ from 50 to 550 amu. A 30-m DB5-MS (0.25 mm i.d., 25 μm film thickness, J&W Scientific, Folsom, CA) fused silica column was programmed for 4 min at 30 °C, then up to 300 °C at 6 °C/min, and hold at 300 °C for 60 min. The carrier gas was helium at a flow rate of 35 cm/s.

Liquid—Liquid-Extraction (LLE). Prior to GC/MS analysis, samples were extracted and concentrated with dichloromethane (Optima-grade, Fisher Scientific). A total of 1000 mL of the sample was contacted with 100 mL of dichloromethane in a Pyrex accelerated one-step extractor concentrator (Pyrex, Corning, NY). The concentrator tube was kept in a water bath at 80 °C. Recondensation of the recirculating dichloromethane was achieved with a condenser on top of the extractor body that was operated at 2—4 °C. After 5.5 h, the extraction was complete, and the bottom was concentrated to 1—5 mL. The sample volume was then further reduced by evaporation to 500 μL with 99.999% helium. The concentrated sample was transferred into an autosampler vial using a gas-tight syringe with attached luer-tip needle. The vial was closed and sealed with a Teflon-lined cap. The final sample concentration was 1:2000 with this method.

Ammonia. The ammonia concentration was measured with a Orion-95-12 (Orion Research, Boston, MA) ammonia electrode. The electrode was calibrated using the Orion-951006 standard solution (0.1 M NH_4Cl).

Experimental Section. Homogeneous Kinetics. Experiments were performed in a water bath at 50, 60, 70, 80 °C, which was held at constant temperature for at least 1 h prior to the start of an experiment. From a stock solution (approximately 4 mg of HMX/L or 36 mg of RDX/L, respectively) 1000 mL was placed into a reaction vessel (1000-mL Erlenmeyer) and heated in the water bath until constant temperature was reached. The mixture was stirred by an overhead motor stirring unit with a stainless steel mixer. The appropriate amounts of OH^- in order to reach a pH of 10—12 were added using a Eppendorf adjustable pipettor or a common pipet (23 mM NaOH with HMX); 1 M NaOH was used for the experiments with HMX (0.22, 2.1, 23 mM OH^-); 1 M and 10 M NaOH was used with RDX (1.5, 2.1, 10, 20 mmol); the volume change was evaluated for 23 mmol. A precision scientific timer was set simultaneously to the start of an experiment. Samples of 1 mL were taken at predefined times using 1-mL microsyringes and attached needles; sample collection time was 2 s; samples were immediately filtered into cooled (0 °C) HPLC vials. The pH was monitored and did not vary more than ±1%.

Ammonia Experiments. The ammonia concentration could not be determined in the experiments above because of the volatile character of ammonia (particularly at the elevated pH and temperature). To determine the ammonia production, separate experiments were performed: 40 mL of an aqueous RDX solution was put into a vial and 80 μL of 10 M NaOH (pH 12) or 80 μL of 1 M NaOH (pH 11), respectively, were added. The vials were immediately sealed with a Teflon-lined cap and put into a water bath at constant temperature. Selected vials were then taken from the water bath at precise time intervals and immediately cooled in an ice-bath ($T = 0$ °C). The ammonia concentration was then measured using an ammonia electrode.

Gas Analysis. A 5-g sample of RDX was put into a gas-tight stainless steel reactor (Parr-Instruments, Moline, IL); the total reactor volume was 465 mL. The system was then sealed and evacuated with a vacuum system. Subsequently, 50 mL of 1.5 M NaOH were added into the sealed system. The solution was kept at a constant temperature ($T = 90$ °C) and continuously stirred. Gas samples were taken every 30 min until equilibrium was reached in the gas phase. The system pressure was measured. The total head space volume was 0.412 L. The gas samples were analyzed with a CEC 21-104 mass spectrometer (CEC, now Du Pont Corporation, Chicago, IL).

Regeneration Kinetics. A 0.13-g sample of dried (24 h at 105 °C) Filtrasorb-400 activated carbon (Calgon Corporation, Pittsburgh, PA) was contacted with 1 L of RDX solution (36 mg of RDX/L) in an Erlenmeyer flask until equilibrium was reached; the equilibrium solid phase concentration was $q_e = 187$ mg of RDX/g of activated carbon. The bulk liquid was then discharged, and the carbon was dried at ambient temperature. The dry loaded carbon was then added to an Erlenmeyer flask containing 1 L of a regeneration solution (20 mmol of OH^-/L; pH 12) that was kept constant at $T = 80$ °C for at least 1 h before the experiment. Timing commenced simultaneously. Samples were taken and analyzed for RDX, $HCOO^-$, and NO_2^- content.

Kinetic Models. In accordance with previous researchers (*11*), a second-order rate equation was fit to the experimental data. The second-order rate law can be reduced to a pseudo-first-order rate equation for constant OH^- concentration provided through excess base. Pseudo-first-order rate constants were obtained through a linear least-squares fit of the sample data to the pseudo-first-

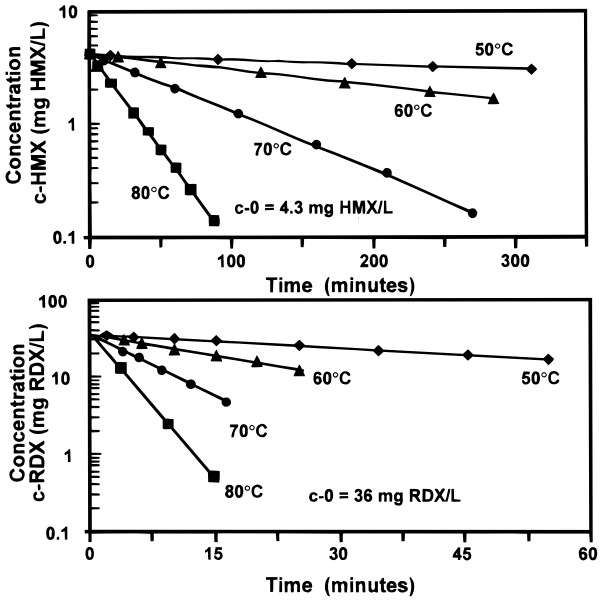

FIGURE 2. RDX and HMX hydrolysis at pH 11 for various temperatures.

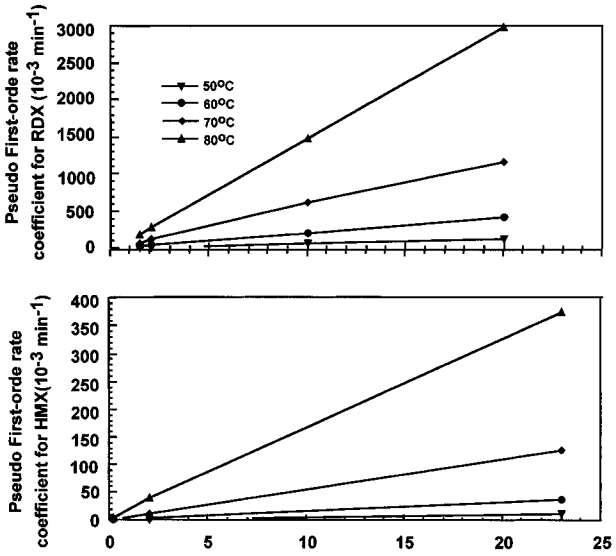

FIGURE 3. Pseudo-first-order reaction rate coefficient for RDX and HMX versus hydroxide concentration at various temperatures.

order model, as follows:

$$\ln \frac{c(t)}{c(t=0)} = -k_1 t = -k_2 c_{OH^-} t \qquad (1)$$

where c is the concentration of the respective compound and k_1 is the pseudo-first-order rate constant. The second-order rate constant can then be evaluated from the pseudo-first-order rate constants using the equation $k_2 = k_1/c_{OH^-}$ and performing several experiments at different OH^- concentrations. The temperature dependency of the kinetic constants was further evaluated using the Arrhenius equation:

$$\ln k_2(T) = \ln A - \frac{E}{RT} \qquad (2)$$

where A is the empirical Arrhenius factor or pre-exponential factor; E is the empirical activation energy; R is the gas constant; and T is the absolute temperature. The Arrhenius factor A and the constant E/R can be determined from a linear least-squares fit of the logarithm of the specific rate constants against the reciprocal of the absolute temperature (*17*). All error determination limits were obtained using standard error of the mean.

Results and Discussion

Figure 2 shows a subset of the kinetic experimental results for HMX and RDX hydrolysis, and they are typical of all results. At 50 °C and pH 12, alkaline hydrolysis of HMX is very slow, and after more than 20 h less than 10% of the initial HMX was hydrolyzed. For higher pHs and temperatures, hydrolysis is much more rapid, and at pH 12 and 80 °C, alkaline hydrolysis is more than 99.9% complete after 100 min. RDX hydrolysis is much more rapid. At pH 12 and 80 °C, the hydrolysis is essentially complete after only a few minutes.

All experimental data could be fit accurately using the pseudo-first-order model (eq 1) and the linear least-squares fit method. Figure 3 shows the pseudo-first-order rate constants calculated from all results as a function of hydroxide concentration. Therefore, we consider the model applicable and deviations from constant OH^- concentration negligible for the respective process conditions. We obtained standard errors for the pseudo-first-order rate constants varying between ±0.4% ($k_{HMX,1}$ for 50 °C and 23 mM OH^-/L) and ± 3.1% ($k_{RDX,1}$ for 80 °C and 1.5 mM OH^-/L) of the rate constant with the majority of the error limits below 2% or 1% (Table 1). We found the subsequent calculation of the second-order rate constants from the pseudo-first-order rates to be precise (Table 2). The rates of the alkaline hydrolysis of RDX are approximately 11.5 times greater than the rates for the alkaline hydrolysis of HMX at similar temperatures. With increasing temperature however, the difference in rates is reduced and the isokinetic temperature is approximately 510 °C.

An increase in temperature of 10 °C produced an increase in the rate of 3.6−2.9-fold for the alkaline hydrolysis of HMX and 3.3−2.6-fold for RDX over the investigated temperature range. The evaluation of the temperature dependency of the calculated second-order rate constants using eq 2 is shown in an Arrhenius plot (Figure 4). The activation energy E over the range from 50 to 80 °C is constant as shown by the excellent correspondence between experimental and model data. We obtained values for the activation energies of $E_{RDX} = 99.9 \pm 1.9$ kJ mol^{-1} and $E_{HMX} = 111.9 \pm 0.8$ kJ mol^{-1}, respectively (Table 3). The precision is much less than the ±4 kJ mol^{-1} that is acceptable in common practice (*18*). We also found the Arrhenius parameter for RDX ($\ln A_{RDX} = 39.09 \pm 0.67$ L mol^{-1} min^{-1}) to be very close to the one of HMX ($\ln A_{HMX} = 40.93 \pm 0.27$ L mol^{-1} min^{-1}). This suggests a similar reaction mechanism for the hydrolysis of RDX and HMX. Kinetic coefficients at 50 and 80 °C, extrapolated from previous research over the range of 25−45 °C (*11*, *12*), are 20−22% lower for RDX and 3−27% lower for HMX than measured in this investigation.

The kinetics of NO_2^- and $HCOO^-$ formation are shown in Figure 5. Equilibrium is reached in approximately 6 h only for $T = 80$ °C and pH 12 (Figure 5d). In all other cases, the formation of $HCOO^-$ was incomplete after 360 min (Figure 5a−c). Therefore, all experiments were continued until a final equilibrium was reached after several days or weeks. The equilibrium concentrations are shown in Table 4. The molar yields are approximately 1.5 M $HCOO^-$ and 1.5 M NO_2^- formed/M RDX hydrolyzed. These results are significantly higher than those reported in previous re-

TABLE 1

Pseudo-First-Order Rate Constants of Alkaline Hydrolysis of HMX and RDX for Different OH^- Concentrations

	$k_{HMX.1}$ (10^{-3} min^{-1})		
T (°C)	0.22 mmol of OH^-/L	2.1 mmol of OH^-/L	23 mmol of OH^-/L
50	0.089 ± 0.002	0.99 ± 0.014	10.82 ± 0.04
60	0.35 ± 0.009	3.28 ± 0.027	38.45 ± 0.72
70	1.19 ± 0.022	11.87 ± 0.16	126.5 ± 1.26
80	3.62 ± 0.055	39.64 ± 0.25	374.9 ± 4.73

	$k_{RDX.1}$ (10^{-3} min^{-1})			
T (°C)	1.5 mmol of OH^-/L	2.1 mmol of OH^-/L	10 mmol of OH^-/L	20 mmol of OH^-/L
50	9.25 ± 0.075	12.98 ± 0.09	58.2 ± 0.77	127.2 ± 1.21
60	29.52 ± 0.23	41.45 ± 0.38	204.3 ± 1.33	412.8 ± 3.31
70	72.97 ± 1.75	122.8 ± 1.45	607.9 ± 5.65	1162 ± 16.7
80	190.9 ± 5.89	288.5 ± 5.83	1484 ± 26.0	2977 ± 43.4

TABLE 2

Calculated Second-Order Rate Constants of Alkaline Hydrolysis of HMX and RDX

T (°C)	$k_{HMX.2}$ (L mol^{-1} min^{-1})	$k_{RDX.2}$ (L mol^{-1} min^{-1})
50	$0.47 \pm 4.2 \times 10^{-4}$	6.35 ± 0.216
60	$1.68 \pm 8.7 \times 10^{-3}$	20.73 ± 0.053
70	5.50 ± 0.0137	58.71 ± 1.332
80	16.19 ± 0.221	150.62 ± 0.482

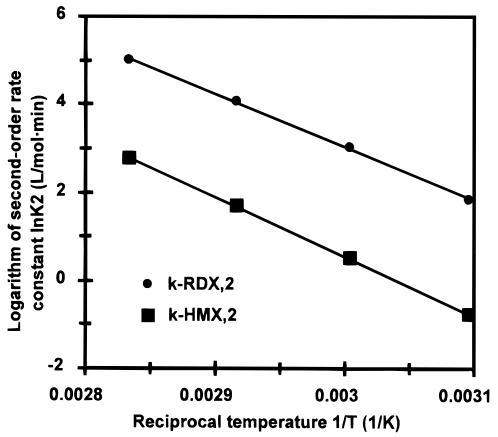

FIGURE 4. Arrhenius plot of second-order rate constants of the alkaline hydrolysis of HMX and RDX.

search. Hoffsommer *et al.* (*11*) reported molar yields of 1.1 M NO_2^-/M RDX and 0.7 M $HCOO^-$/M RDX. However, they conducted their study at lower temperatures, and the results indicate that the normalized molar yields may have been calculated before complete equilibrium was reached. We could not find a determinable variation trend with pH or temperature in the molar yield. It is also evident for all four conditions (Figure 5) that NO_2^- is a direct product from RDX formed during the first reaction step in timely accordance with RDX degradation and thus follows the same rate law.

For all other compounds, only equilibrium concentrations were determined (Tables 4 and 5). The normalized molar yield of NH_3 is 0.9 M/M RDX hydrolyzed for pH 12 at 50 and 80 °C as well as pH 11 and 80 °C. We also discovered acetate ion (CH_3HCOO^-) as an additional and previously unknown reaction product (*9*−*12*). The yield of 0.1 M CH_3HCOO^-/M RDX, however, is comparatively small. The analysis for gaseous products was performed in a 465-mL gas-tight reactor that was evacuated before the commencement of the experiment. A total of 5 g of RDX (0.0225 M) in 50 mL of 1.5 M NaOH at T = 90 °C produced a system pressure of 240.1 kPa at equilibrium. The gas analysis showed 75% N_2O and 23% N_2. The remaining 2% included small amounts of argon, oxygen, ammonia (1.5%), water, and methanol (0.1%). Using the ideal gas law, the total moles are calculated to 0.033 M. If the molar yield results from the gas analysis are rounded to 0.025 M N_2O and 0.0075 M N_2, the normalized molar yield is 1.1 M N_2O and 0.34 M N_2/M RDX hydrolyzed, respectively (Table 5). Using the previously discussed results, a mass balance for carbon and nitrogen can be calculated (Table 6). The recovery was close to 100%: 94% of the carbon and 90% of the nitrogen from RDX were found in the described products.

TABLE 3

Temperature Dependency of Second-Order Rate Constants of Alkaline Hydrolysis of HMX and RDX: Arrhenius Parameter and Activation Energy

	ln A (L mol^{-1} min^{-1})	E (kJ mol^{-1})
HMX	40.93 ± 0.27	111.9 ± 0.76
RDX	39.09 ± 0.67	99.92 ± 1.87

Nevertheless, the hydrolysate was further analyzed using liquid−liquid extraction (LLE) and GC/MS analysis. Any previously unknown organic intermediates, if present and extractable by dichloromethane and chromatographicable, will be detected with this method. The samples were concentrated from 1000 mL to 500 μL. In order to determine the origin of compounds in the analytical protocol, a comprehensive set of blank samples was extracted with LLE and analyzed with GC/MS. LLE system blanks (100 mL of dichloromethane with no sample recirculated for 5.5 h) as well as GC/MS system blanks (GC/MS injection of pure Optima-grade dichloromethane, Fisher Scientific) were run regularly to determine any system changes or contamination. Deionized water and HPLC-grade water blanks were extracted (LLE) and analyzed on the GC/MS to determine any contamination originating from the water. Furthermore, possible contamination from the base was determined with a set of base blanks (2 mL of 10 M NaOH in 1000 mL of deionized water or HPLC-grade water, respectively; NaOH and HPLC-grade water: Fisher Scientific). Subsequently, blanks of unhydrolyzed RDX and HMX in deionized and HPLC-grade water, respectively, were prepared and analyzed to determine impurities in RDX and HMX. Eventually, RDX and HMX hydrolysis samples were prepared with deionized and HPLC-grade water (40 mg of

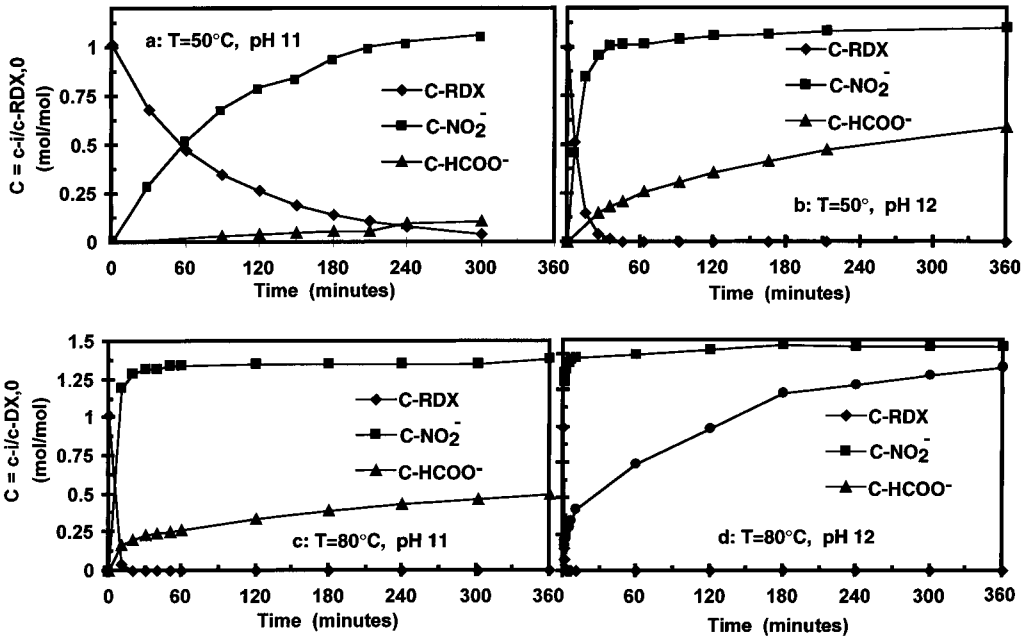

FIGURE 5. Kinetics of the alkaline hydrolysis of RDX: nitrite and formate formation (normalized concentration C = M product formed/M RDX hydrolyzed, t = 0 as a function of time).

TABLE 4

Normalized Molar Yields for Products of Alkaline Hydrolysis of RDX (Results from Liquid Analysis)[a]

	pH 11		pH 12	
	50 °C	80 °C	50 °C	80 °C
NO_2^-	1.5	1.5	1.3	1.6
$HCOO^-$	1.3	1.5	1.5	1.5
CH_3COO^-				0.1
NH_3		0.9	0.9	0.9

[a] M product formed/M RDX hydrolyzed.

TABLE 5

Normalized Molar Yields For Products of Alkaline Hydrolysis of RDX (Results from Gas Analysis)[a]

	normalized molar yield
N_2O	1.1
N_2	0.34

[a] M/M RDX hydrolyzed.

RDX or 4 mg of HMX, respectively, was stirred for 6 h in 1000 mL of water with 2 mL of 10 M NaOH at 80 °C). No further intermediates or end products could be discovered by GC/MS analysis from the alkaline hydrolysis of RDX and HMX.

In order to determine if alkaline hydrolysis is a feasible regeneration process for high "explosives-laden" activated carbon, we compared the batch homogeneous kinetics at 80 °C and pH 12 with batch desorption kinetics during alkaline hydrolysis regeneration of activated carbon under the same conditions. However, because the adsorbed RDX is rapidly destroyed during desorption at elevated pH and temperature, its concentration cannot be used to determine desorption kinetics. Therefore, NO_2^- and $HCOO^-$ were chosen as appropriate parameters to indicate desorption and hydrolysis rates during regeneration. NO_2^- is the first product formed during the alkaline hydrolysis of RDX, while $HCOO^-$ is more slowly produced because of its dual

TABLE 6

Carbon and Nitrogen Balance for Alkaline Hydrolysis of RDX ($C_3H_6O_6N_6$)

	$HCOO^-$ (M)	CH_3COO^- (M)	$HCHO$[a] (M)	sum (M)	RDX (M)	δ (M)	recovery (%)
carbon	1.5	0.2	1.1	2.8	3	−0.2	94
	NO_2^- (M)	NH_3 (M)	N_2O (M)	N_2 (M)	sum (M)	RDX (M)	δ (M)	recovery (%)
nitrogen	1.6	0.9	2.2	0.7	5.4	6	−0.6	90

[a] Data from ref 11.

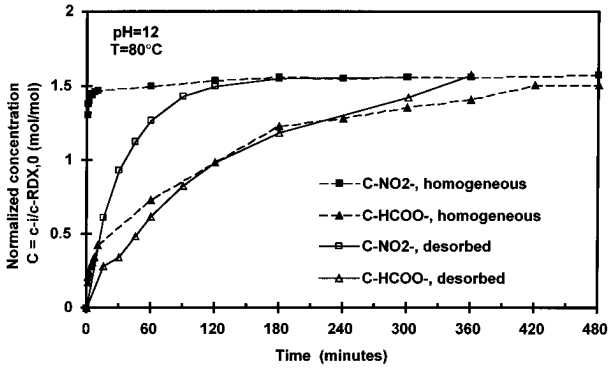

FIGURE 6. Comparison of the kinetics of nitrite and formate formation during aqueous homogeneous alkaline hydrolysis of RDX and regeneration of RDX-laden activated carbon.

formation from the ring cleavage and the fourth-order *Canizarro* reaction of formaldehyde. The ratios of NO_2^- and $HCOO^-$ produced per mole of RDX hydrolyzed can then be compared to solid-phase hydrolysis and desorption as well as to aqueous homogeneous conditions.

The results are shown in Figure 6. In the homogeneous experiment, 20 mM OH^- (pH 12) was added to an aqueous RDX solution (35 mg/L) that was stirred and heated (T = 80 °C). The regeneration experiment was carried out with 0.131 g of loaded activated carbon (q_e = 187 mg of RDX/g of activated carbon Filtrasorb-400), which was stirred in a

regeneration solution at 80 °C (20 mM OH^- or pH 12). NO_2^- is evidently produced much faster under homogeneous conditions than in desorption, which suggests limitation through diffusion. However, the $HCOO^-$ concentration during regeneration seems to be diffusion limited only in the beginning of the experiment. At the end of the experiment, the curves of the regeneration and the homogeneous experiments are almost the same, which indicates chemical limitation at this stage of the process. RDX could not be detected in the liquid phase at any time during the regeneration experiment.

Most importantly, however, the final yields are virtually the same for homogeneous conditions and regeneration conditions. The homogeneous reaction yields 1.6 M NO_2^- and 1.5 M $HCOO^-$/mol of RDX. The regeneration experiments yielded 1.6 M NO_2^- and 1.6 M $HCOO^-$/mol of RDX. The slight difference for $HCOO^-$ is likely due to experimental error. The regenerated carbon was furthermore contacted with 10 mL of acetonitrile in a 25-mL vial on a shaker table. No residual adsorbed RDX could be found in the bulk liquid after several days and weeks, respectively. This indicates that the alkaline hydrolysis of adsorbed RDX and subsequent desorption of hydrolysis products is complete.

We found excellent pseudo-first-order and second-order rate dependencies for the alkaline hydrolysis of HMX and RDX (Tables 1 and 2). For elevated temperatures ranging from 50 to 80 °C the reaction is second-order, and preliminary studies on the rate and reaction order of the alkaline hydrolysis of HMX and RDX at temperatures ranging from 0 to 45 °C (*9*−*11*) are verified for the higher temperature range. The temperature dependency of the rate constants is accurately predicted using the Arrhenius model (Figure 4; Table 3). The almost similar activation parameters for the alkaline hydrolysis of RDX and HMX also suggest that the reaction follows the same basic reaction mechanism.

The alkaline hydrolysis of RDX in the presence of hydroxide ions is approximately 10 times faster than the alkaline hydrolysis of HMX. Since HMX is a frequent contaminant in RDX, the compounds almost always occur together in explosives-contaminated wastewater and at contaminated sites. Therefore, the rate of the alkaline hydrolysis of HMX may be rate limiting in the design of a treatment system using alkaline hydrolysis; however, our results show that an increase in temperature has a higher influence on the rate of the alkaline hydrolysis of HMX than RDX. Higher temperatures (80 °C) may be preferable to further increased hydroxide concentrations (>25 mmol/L) for treatment of HMX using alkaline hydrolysis. The isokinetic temperature for the alkaline hydrolysis of RDX and HMX is approximately 510 °C.

The formation of $HCOO^-$ is obviously slow in comparison with RDX degradation and NO_2^- formation. This is due to the production of formate from both the ring cleavage and subsequently from the fourth-order *Canizarro* reaction of formaldehyde (HCHO) at the elevated pH (*11*), the latter one being slow (*13, 19, 20*). The carbon and nitrogen balance over the reaction time shows that RDX-h5 does not accumulate and is followed by the formation of complex intermediates from ring cleavage. The further mineralization of these intermediates is slow and rate-limiting. The reaction mechanism should be rewritten as shown in Figure 7. However, we could not prove the existence of any relatively nonpolar organic compounds by GC/MS analysis at equilibrium. We therefore conclude that none of these

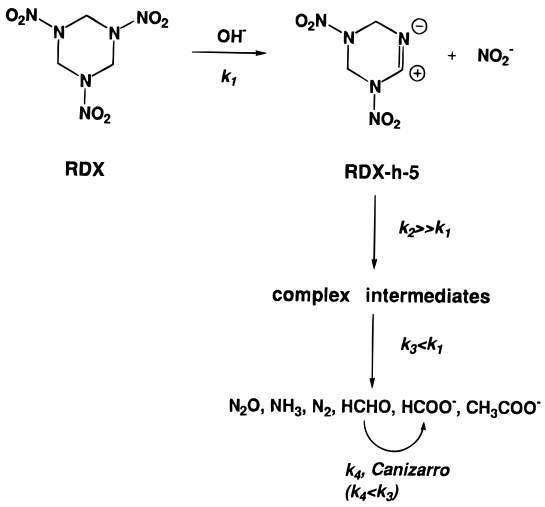

FIGURE 7. Proposed reaction mechanism for the alkaline hydrolysis of RDX.

complex intermediates are persistent but are completely reacted to the low molecular weight compounds as shown in Figure 7. Compared to previous research, the mass balance for carbon and nitrogen is improved. Hoffsommer *et al.* (*11*) recovered 77% nitrogen and 60% carbon. We recovered 90% of the nitrogen and 94% of the carbon, respectively.

Our objective in this study, which is part of our investigations of a novel physicochemical treatment scheme for explosives-contaminated waters (Figure 1), was to determine basic data for the chemical stage of the scheme (activated carbon regeneration by alkaline hydrolysis). The alkaline hydrolysis of RDX and HMX was rapid under homogeneous conditions. The application of the process for activated carbon regeneration led to 100% desorption of hydrolysis products, and no residual RDX could be extracted from regenerated activated carbon. Therefore, we consider the alkaline hydrolysis of HMX and RDX in presence of intermediate alkaline concentrations (2−25 mM OH^-/L) and elevated temperatures (above 50 °C) to be a feasible chemical regeneration process for high explosives-laden activated carbon as part of an off-line regeneration treatment scheme (Figure 1). Concentrating the high explosives on the activated carbon can make alkaline hydrolysis an economically feasible treatment method. The organic end products of the hydrolysis and byproducts should be treatable in conventional biological treatment processes. The high salinity that results from both the sodium hydroxide used for hydrolysis, and the acid needed for neutralization may require special handling and conditions

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