Aqueous solubility and alkaline hydrolysis of the novel high explosive hexanitrohexaazaisowurtzitane (CL-20)

Pelin Karakaya[a], Mohammed Sidhoum[a,*], Christos Christodoulatos[a],
Steve Nicolich[b], Wendy Balas[b]

[a] *Center for Environmental Systems, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, NJ 07030, USA*
[b] *US Army TACOM-ARDEC, Energetics & Warheads Division, Picatinny Arsenal, NJ 07806, USA*

Abstract

The recently developed polycyclic nitramine CL-20 is considered as a possible replacement for the monocyclic nitramines RDX and HMX. The present study reports aqueous solubility data for CL-20, as well as the kinetic parameters for its alkaline hydrolysis with sodium hydroxide below and above its solubility limits. Aqueous solubility of CL-20 was measured in the temperature range of 4–69 °C and the data were fitted to a generalized solubility model. Alkaline hydrolysis experiments were conducted at 15, 20, 30 and 40 °C, with hydroxide concentrations ranging from 0.25 to 300 mM. Like RDX and HMX, alkaline hydrolysis of CL-20 follows second-order kinetics. CL-20 alkaline hydrolysis was found to proceed at a significantly faster rate than RDX. The temperature dependency of the second-order rate constants was evaluated using the Arrhenius model. The activation energy for CL-20 was found to be within close range of the activation energies reported for RDX and HMX.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

HNIW (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane), more commonly called CL-20, is a novel high-density cyclic nitramine, synthesized for use as an energetic component in propellant formulations [1]. It meets stringent munitions sensitivity requirements and has a higher energy content than the conventionally used cyclotetramethylenetetranitramine (HMX) and cyclotrimethylenetrinitramine (RDX) [2,3]. CL-20 has recently shifted to commercial production and is now in exploratory and advanced development [4]. Its energetic properties have been thoroughly studied. However, there has been very little research regarding the treatment of the generated waste during industrial CL-20 production activities and the potential remediation of contaminated sites.

The molecular structures of CL-20, RDX and HMX are shown in Fig. 1. The basic structure of CL-20 consists of a rigid isowurtzitane cage with a nitro group attached to each of the six bridging nitrogen atoms within the cage. CL-20 has a higher molecular weight, heat of formation, number of $N-NO_2$ bonds, and density (2.044 g/cm^3 for the ε-polymorph) than RDX and HMX [5]. In contrast to the aforementioned nitramines that have no C−C bonds in their structures, CL-20 bears three slightly elongated C−C bonds [6]. It can exist in four stable polymorphic forms (α, β, γ, ε) under ambient conditions, the structures and densities of which have been established by X-ray crystallography [3]. Among these, the ε-polymorph is preferred for its highest crystal density and stability at ambient conditions [7].

The instability of high explosives to strong bases is well known [8]. Because most energetic materials are synthe-

---

* Corresponding author. Tel.: +1 201 216 5310; fax: +1 201 216 8303.
E-mail address: msidhoum@stevens.edu (M. Sidhoum).
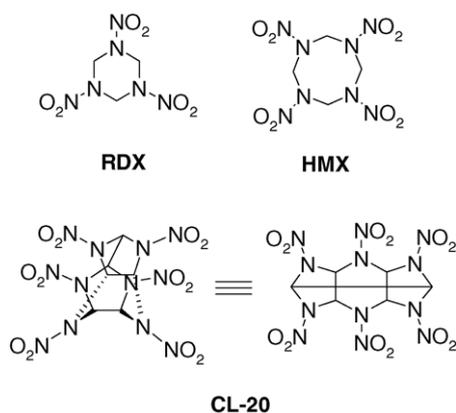
Fig. 1. Molecular structures of CL-20, HMX, and RDX.

sized in acidic media, they are vulnerable to hydrolysis. Energetic materials, such as nitrate esters, nitroaromatics, and nitramines, usually decompose to form nitrates, nitrites, ammonia, nitrogen, hydrogen, organic acids, and formaldehyde. Intermediates formed during the course of the hydrolysis of some energetic materials can provide reaction pathways to other nitro derivatives and addition products that are still energetic [9]. The by-products resulting from the alkaline hydrolysis of energetic materials could possibly be disposed of directly [8] or can be further treated biologically [10]. Several researchers have investigated the kinetics of the alkaline hydrolysis of nitrated energetic compounds such as RDX, HMX, TNT and nitrocellulose [11–17]. To date there have been no studies on the kinetics of the alkaline hydrolysis of CL-20. The objectives of the research presented herein are to establish the aqueous solubility of CL-20 within a temperature range, correlate its solubility behavior, and determine its kinetics under alkaline hydrolysis conditions above and below solubility limits as a possible process of treatment and/or remediation schemes, and compare the hydrolytic behavior to that of RDX.

2. Experimental

2.1. Reagents and chemicals

CL-20 was manufactured by A.T.K. Thiokol Propulsion (Brigham City, UT) and supplied by Picatinny Arsenal, NJ. Data provided by Thiokol, indicated that the CL-20 had a purity greater than 99% (determined by HPLC) had an ε-polymorph content greater than 98% (determined by Fourier Transform Infrared Spectroscopy), and the average particle size was 2 μm with a uniformity coefficient of 1.47. RDX synthesized and supplied by the U.S. Army TACOM/ARDEC (Picatinny, Arsenal, NJ) had an HMX content of 10% (w/w) as production related impurity. The solvents used, acetonitrile and acetone, were HPLC grade (Aldrich Chemical Co., Milwaukee, WI). Sodium hydroxide stock solution (10N), and reagent grade hydrochloric acid

and sulfuric acid were purchased from Fischer Scientific.

2.2. Analytical methods

CL-20 and RDX were analyzed with a reverse-phase HPLC system (Varian Inc., Walnut Creek, CA) equipped with a photodiode array detector. A Symmetry Shield™ RP-18 (3.9 mm × 150 mm) 5 μm column (Waters®, Milford, MA) was used. The HPLC method is based on the U.S. EPA Standard Method 8330, which was originally developed for the analysis of nitroaromatic and nitramine explosives [2]. The chromatographic conditions for CL-20 consisted of an isocratic binary mobile phase of water and acetonitrile (40:60, v/v) pumped at a flow rate of 1.0 mL min^{-1} and spectrophotometric detection at 229 nm. CL-20 eluted as a symmetrical peak with a retention time of 4.1 min. The chromatographic conditions for RDX analysis were as follows: an isocratic ternary mobile phase consisting of water, methanol, and acetonitrile (50:40:10, v/v/v) at a flow rate of 1.0 mL min^{-1} and spectrophotometric detection at 236 nm. The retention time for RDX was 3.5 min.

Stock solutions of CL-20 were prepared in acetonitrile. Calibration standards (0.5–250 mg/L) prepared by diluting the stock solutions with deionized water (1:1, v/v) were analyzed immediately. The detection limit for CL-20 was 0.2 mg/L. RDX stock solutions were prepared in acetone. Calibration standards (0.25–5 mg/L) were prepared by diluting the stock solutions with deionized water (1:1, v/v). Since the RDX had an HMX content of 10%, the standard measurements were multiplied by a correction factor of 0.9. The detection limit for RDX was 0.15 mg/L.

Nitrite (NO_2^-) and nitrate (NO_3^-) ions were analyzed using a reverse-phase HPLC system (Varian Inc., Walnut Creek, CA) equipped with a photodiode array detector. The ions were separated using a Dionex Ionpac AS16 column with a mobile phase of 5 mM NaOH pumped at a flow rate of 1.2 mL min^{-1} and spectrophotometric detection at 215 nm. The nitrite and nitrate ions eluted at 6.7 and 9.9 min, respectively. The detection limit for both nitrite and nitrate ions was 1 mg/L.

Hydroxide ion concentrations were determined by titration with hydrochloric acid using a Metrohm Titrino 702 SM titrator (Brinkmann Instruments Inc., Westbury, NY).

2.3. Measurement of aqueous solubility

The aqueous solubility of CL-20 was measured at temperatures ranging from 4 to 69 °C. Solutions were prepared by adding excess amounts of the solid compound (0.15 g) in flasks containing deionized water (300 mL). Experiments were conducted in a water bath and the temperature was controlled within ±0.5 °C. A stainless steel three-blade propeller rotated by an overhead lab stirrer (Stirpak model 4554-10, Cole Parmer) was used to stir the mixture at 150 rpm. Once thermodynamic equilibrium was established at a given tem-

perature (48 h), three samples (2 mL each) were withdrawn with a syringe, filtered through 0.2 μm polypropylene filters (Whatman Puradisc 25-PP) and immediately diluted with acetonitrile (1:1, v/v) to avoid precipitation. To overcome CL-20 adsorption losses during filtration, it was necessary to discard the first 0.5 mL of the filtered samples. To avoid re-crystallization of CL-20, the hardware used for sampling and filtration was equilibrated at the test temperature.

2.4. Aqueous hydrolysis experiments

Batch hydrolysis experiments were carried out at four temperatures (15, 20, 30 and 40 °C) below solubility limits (homogeneous alkaline hydrolysis) and above solubility limits (heterogeneous alkaline hydrolysis) using NaOH concentrations ranging from 0.25 to 300 mM. The temperature of the reaction medium was regulated using a water bath (Fisher Scientific, Model Isotemp-210).

2.4.1. Homogeneous alkaline hydrolysis experiments

De-ionized water (495 mL) containing dissolved reactant was placed in a 1 L beaker. The stainless steel three-blade propeller rotated by an overhead Cole Parmer Stirpak 4554-10 lab stirrer set at 150 rpm was centered and lowered into the beaker and raised to a height of 1 cm above the beaker bottom. Next, 5 mL of concentrated NaOH solution of appropriate molarity were added to the solution.

2.4.2. Heterogeneous alkaline hydrolysis experiments

Deionized water (from 291 to 297 mL) containing reactant powder was placed in a 600 mL beaker. The propeller was centered and lowered into the beaker and the stirrer was adjusted to 1000 rpm. The high mixing speed was required to minimize CL-20 particles flotation. Next, 3–9 mL of concentrated NaOH solution of appropriate molarity, were introduced into the solution to yield a 300 mL reaction volume.

Samples (2 mL) withdrawn periodically from the reaction mixture were added to test tubes containing appropriate amounts of H_2SO_4, to neutralize the sample. The purposes of neutralization are (1) to quench the base hydrolysis reaction and (2) to protect the HPLC column from alkaline conditions. The neutralized samples were further diluted with acetonitrile (1:1, v/v) and analyzed immediately.

3. Results and discussion

3.1. Aqueous solubility of CL-20

Aqueous solubility data for CL-20 measured at 13 temperatures are presented in Table 1 and plotted in Fig. 2. The results show that solubility of CL-20 increases remarkably with temperature. Accordingly, there is about a 17.5-fold increase in solubility as temperature rises from 4 to 69 °C.

Table 1
Aqueous solubility of CL-20 as a function of temperature

Temperature (°C)	Solubility of CL-20[a]	
	(mg/L)	(mole fraction)
4	2.27 (0.09)[b]	9.33×10^{-8}
15	2.96 (0.12)	1.22×10^{-7}
19.5	3.44 (0.06)	1.41×10^{-7}
25	4.33 (0.04)	1.78×10^{-7}
30	5.49 (0.02)	2.26×10^{-7}
35	6.96 (0.01)	2.86×10^{-7}
39	8.10 (0.06)	3.33×10^{-7}
45	11.30 (0.25)	4.64×10^{-7}
50	14.16 (0.47)	5.82×10^{-7}
55	17.37 (0.17)	7.14×10^{-7}
60	23.98 (0.41)	9.85×10^{-7}
65	32.36 (1.03)	1.33×10^{-6}
69	39.68 (0.25)	1.63×10^{-6}

[a] Averages of triplicate measurements.
[b] Values in parentheses are standard deviations.

The aqueous solubility of CL-20 is significantly lower than that of RDX, which is expected due to the more symmetrical and significantly less polar molecular structure of CL-20 and agrees with the predictions of Qasim et al. [18]. The obtained solubility data are slightly higher than those reported by Monteil-Rivera et al. [19].

From thermodynamic considerations, the following general solubility equation can be written for solutions where pure solids do not ionize or dissociate [20]:

$$\ln(x) = A + \frac{B}{T} + C \ln(T) \qquad (1)$$

where x is the solubility expressed in mole fraction at the prevailing absolute temperature T (K). The correlation constants A, B, and C obtained by non-linear analysis of the solubility data versus temperature data ($R^2 = 0.9991$) are −511.12, 19063.26 K and 75.76, respectively.
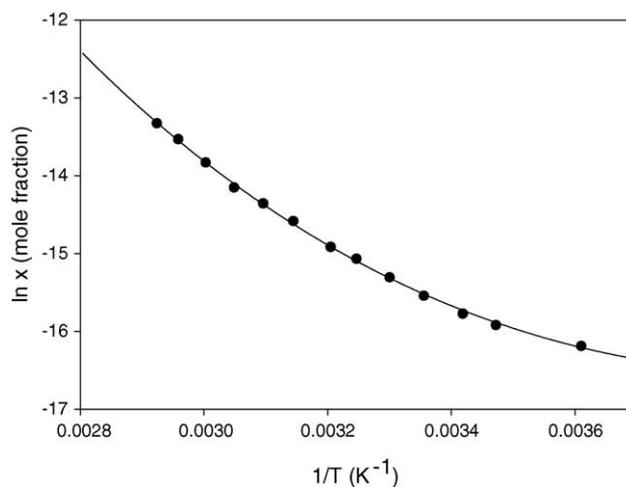
Fig. 2. Aqueous solubility of CL-20 expressed in mole fraction as a function of temperature: (●) experimental data; (—) Eq. (1) fitted to the data.

3.2. Kinetics of alkaline hydrolysis of CL-20

The rate of reaction of energetic materials under alkaline conditions depends on the concentrations of the base and the energetic compound. It has been suggested that the alkaline hydrolysis of the nitramines HMX and RDX proceeds via the E2-elimination mechanism, which is a common elimination mechanism in organic chemistry and follows a second-order rate law [12,21,22]. E2 is a bimolecular elimination mechanism, where two groups are lost simultaneously from adjacent atoms so that a new double (or triple) bond is formed. One group leaves with its electrons and the other without, the latter most often being a proton being pulled off by a base. The former is referred to as the leaving group. The mechanism thus takes place in one step and kinetically is second order; first order in substrate and first order in base [23].

Accordingly, the kinetics of alkaline hydrolysis of CL-20 using a strong base (NaOH) is represented as follows:

$$\frac{dC_{CL-20}}{dt} = -k_2 C_{CL-20} C_{NaOH} \tag{2}$$

where C_{CL-20} is the CL-20 concentration, C_{NaOH} the base concentration, and k_2 the second-order rate constant. Because the consumption of NaOH cannot be accurately or conveniently measured during the time course of the reaction, it is difficult to determine the second-order rate constant (k_2) directly. However, by adjusting the experimental conditions, a pseudo-first order rate constant (k_1) can be obtained. This situation can be realized, by either maintaining the NaOH concentration constant throughout the reaction, or at least sufficiently in excess such that any change in the concentration of the base is negligible compared to the change in concentration of CL-20. Under such experimental conditions, Eq. (2) is reduced to the following pseudo-first order rate equation:

$$\frac{dC_{CL-20}}{dt} = -k_1 C_{CL-20} \tag{3}$$

where k_1 is given by:

$$k_1 = k_2 C_{NaOH} \tag{4}$$

By monitoring the CL-20 concentration during the time course of the reaction at a given NaOH concentration and temperature, one can obtain k_1 using the integrated form of Eq. (3):

$$\ln C_{CL-20} = \ln C_{CL-20}^0 - k_1 t \tag{5}$$

where C_{CL-20}^0 is the initial concentration of CL-20. According to Eq. (5), the slopes of the semi-logarithmic plots of the concentration–time data yield the rate constant k_1. Next, by varying the NaOH concentration at a given temperature, the second-order rate constants can be calculated using Eq. (4).

A series of kinetic runs for the homogeneous CL-20 alkaline hydrolysis were carried out with initial CL-20 concentrations of about 3 mg/L ($\sim 6.85 \times 10^{-3}$ mM) and NaOH concentrations ranging from 0.25 to 10 mM. The experiments

were performed at 15, 20, 30 and 40 °C. Data for the CL-20 homogeneous alkaline hydrolysis are presented in Fig. 3. In these studies, the molar ratio of NaOH to CL-20 ranged from 36.5:1 to 1460:1. To validate the assumption that base concentration remains constant throughout the experiments, the NaOH concentration in the solution was measured at the end of the experiments (when CL-20 is depleted). At the lowest NaOH concentration used (0.25 mM at 40 °C), the NaOH consumption was found to be negligible (about 3%); which supports the pseudo-first order kinetics assumption under the present experimental conditions.

Another set of experiments was conducted to examine the kinetics of heterogeneous CL-20 alkaline hydrolysis, with initial CL-20 concentrations at about 500 mg/L (~ 1.14 mM) at 15, 20, 30 and 40 °C. The obtained data are shown in Fig. 4. In these experiments, the NaOH concentration was varied from 25 to 300 mM, which corresponds to molar ratios of NaOH to CL-20 ranging from 21.9:1 to 262.8:1. For the experiments conducted with NaOH concentrations of 300, 200, 100, and 50 mM, the NaOH consumption was measured as 1.6%, 2.4%, 5%, and 9.5%, respectively. However, at the lowest NaOH concentration studied (25 mM at 40 °C), the decrease in NaOH concentration during heterogeneous alkaline hydrolysis was about 19%. Overall, it was considered that the changes in NaOH concentrations are within acceptable limits for the application of the pseudo-first order kinetics assumption.

From the concentration–time profiles (Figs. 3 and 4), it is clear that the rate of alkaline hydrolysis of CL-20 depends on alkali strength. For example at 20 °C and 3 mg/L of initial CL-20, 85% of the compound reacts with 10 mM NaOH within 5 min; however with 1 mM NaOH, it requires about 65 min to achieve the same degree of transformation. The temperature effect on the rate of alkaline hydrolysis of CL-20 is also illustrated in Fig. 3. For instance at 1 mM NaOH and 3 mg/L of initial CL-20, when the temperature is increased from 20 to 30 °C, the time required for the same extent of removal (85%) drops from 65 to 12 min.

The CL-20 concentration–time profiles were used to obtain the relevant kinetic parameters for homogeneous and heterogeneous alkaline hydrolysis, by applying non-linear regression analysis. The computed pseudo-first order rate constants (k_1) and corresponding standard errors are presented in Table 2. The experimental data correlate closely with the pseudo-first order kinetic model with excellent correlation coefficients.

The k_2 values were obtained as the slopes of the plots k_1 versus NaOH concentration (Fig. 5). The second-order rate constants obtained at homogeneous conditions (k_2^{hom}) and at heterogeneous conditions (k_2^{het}), by single-parameter linear regression for the temperatures studied and the corresponding correlation coefficients are presented in Table 3. The values of k_2^{hom} are significantly higher than those obtained for k_2^{het}, with ratios of 109, 112, 122 and 137 at temperatures of 15, 20, 30 and 40 °C, respectively. The lower k_2^{het} values may be attributed to mass transfer limitations that commonly
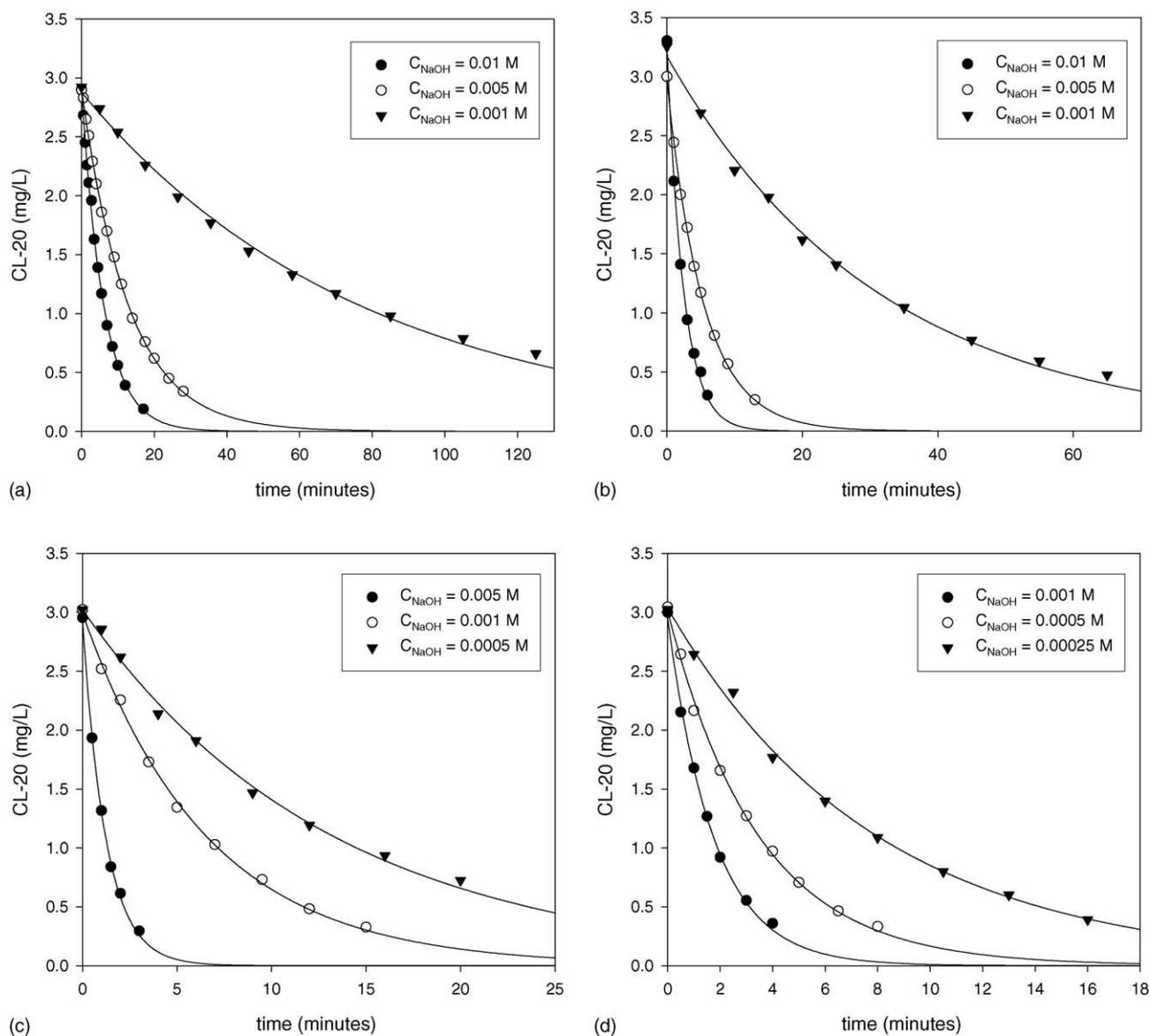
Fig. 3. Concentration–time profiles of CL-20 homogeneous alkaline hydrolysis at (a) 15 °C, (b) 20 °C, (c) 30 °C and (d) 40 °C, at various alkalinities.

Table 2
Pseudo first-order rate constants k_1 (min^{-1}) and corresponding correlation coefficients (R^2) for alkaline hydrolysis of CL-20 for different NaOH concentrations and temperatures

C_{NaOH} (mM)	15 °C	20 °C	30 °C	40 °C
Homogeneous alkaline hydrolysis				
10	0.1639 (0.0025)[a] $R^2 = 0.9987$	0.4086 (0.0103) $R^2 = 0.9982$		
5	0.0776 (0.0007) $R^2 = 0.9994$	0.1869 (0.0025) $R^2 = 0.9993$	0.8089 (0.0160) $R^2 = 0.9991$	
1	0.0129 (0.0003) $R^2 = 0.9961$	0.0320 (0.0009) $R^2 = 0.9962$	0.1531 (0.0030) $R^2 = 0.9986$	0.5696 (0.0155) $R^2 = 0.9979$
0.5			0.0763 (0.0022) $R^2 = 0.9963$	0.2902 (0.0064) $R^2 = 0.9982$
0.25				0.1273 (0.0032) $R^2 = 0.9975$
Heterogeneous alkaline hydrolysis				
300	0.0427 (0.0020) $R^2 = 0.9898$	0.1051 (0.0115) $R^2 = 0.9750$		
200	0.0319 (0.0012) $R^2 = 0.9945$	0.0686 (0.0021) $R^2 = 0.9952$	0.2501 (0.0155) $R^2 = 0.9853$	
100	0.0156 (0.0006) $R^2 = 0.9928$	0.0437 (0.0005) $R^2 = 0.9991$	0.1531 (0.0070) $R^2 = 0.9860$	0.4281 (0.0643) $R^2 = 0.9027$
50			0.0709 (0.0017) $R^2 = 0.9972$	0.1731 (0.0068) $R^2 = 0.9915$
25				0.1151 (0.0019) $R^2 = 0.9988$

[a] Numbers in parentheses are standard errors.
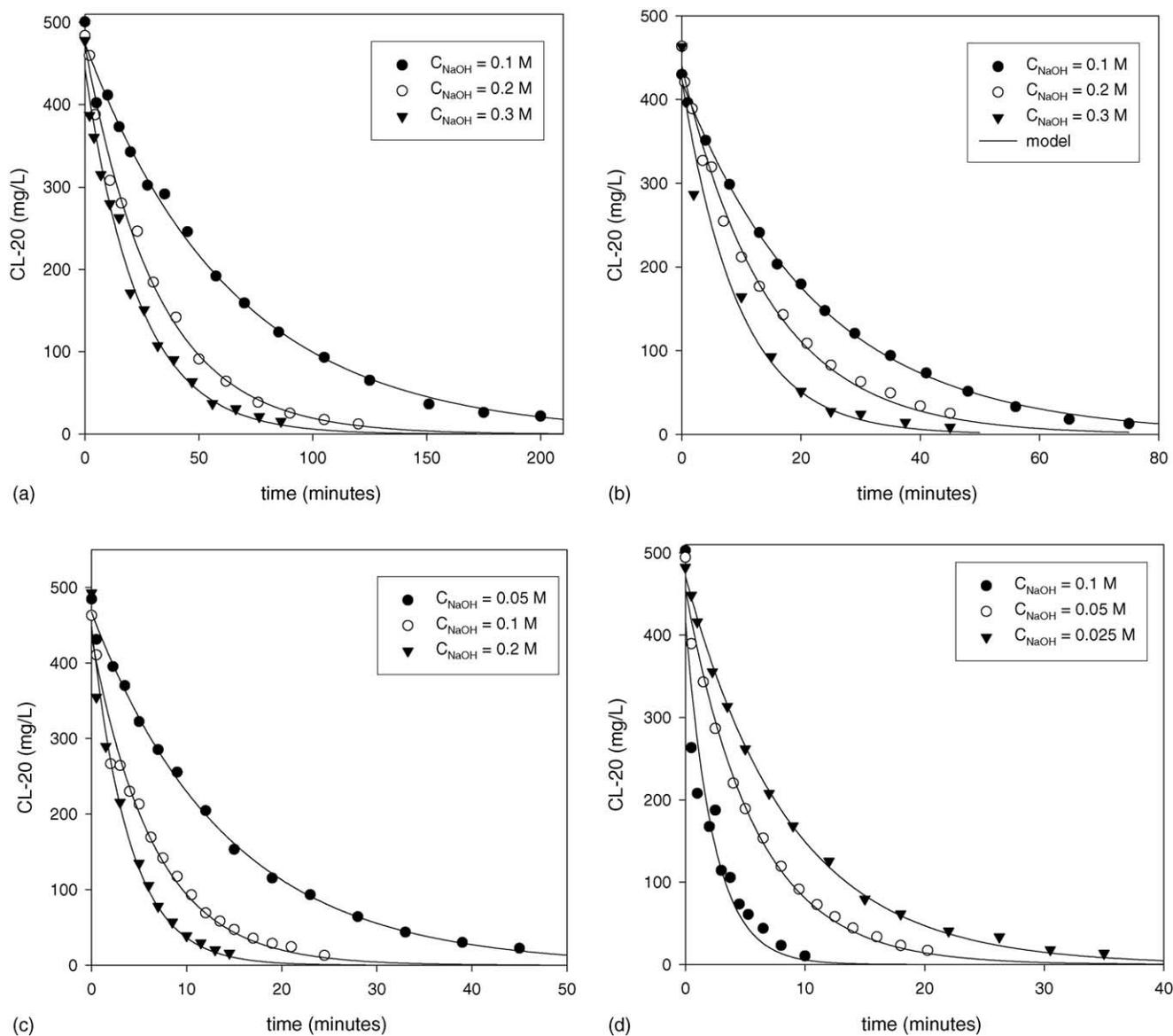
Fig. 4. Concentration–time profiles of CL-20 heterogeneous alkaline hydrolysis at (a) 15 °C, (b) 20 °C, (c) 30 °C and (d) 40 °C, at various alkalinities.

occur in heterogeneous reactions, which indicate that the heterogeneous hydrolysis of CL-20 may not be under chemical kinetic control.

The values of k_2^{hom} for alkaline hydrolysis of CL-20 are considerably greater than those for the alkaline hydrolysis of RDX and HMX reported by Heilmann et al. [12]. For example at 20 °C, the obtained k_2^{hom} for CL-20 is 40.10 M^{-1} min^{-1}, whereas the corresponding values

for HMX and RDX were calculated as 6.70×10^{-3} and 0.15 M^{-1} min^{-1}, respectively using the Arrhenius parameters provided by these researchers.

We have also observed that in homogeneous alkaline hydrolysis, one hydroxide ion is required for every reacting CL-20 molecule; whereas four hydroxide ions are consumed per CL-20 molecule under heterogeneous conditions. This finding suggests that the homogeneous and heteroge-

Table 3
Second-order rate constants (k_2) and corresponding correlation coefficients (R^2)

Temperature (°C)	k_2^{hom} (M^{-1} min^{-1})	k_2^{het} (M^{-1} min^{-1})
15	16.1897 (0.3215)[a] $R^2 = 0.9977$	0.1481 (0.0055) $R^2 = 0.9769$
20	40.0992 (1.1061) $R^2 = 0.9957$	0.3544 (0.0164) $R^2 = 0.9607$
30	161.3619 (1.3225) $R^2 = 0.9997$	1.3119 (0.0792) $R^2 = 0.9591$
40	568.7810 (9.8810) $R^2 = 0.9974$	4.1404 (0.2377) $R^2 = 0.9733$

[a] Numbers in parentheses are standard errors.
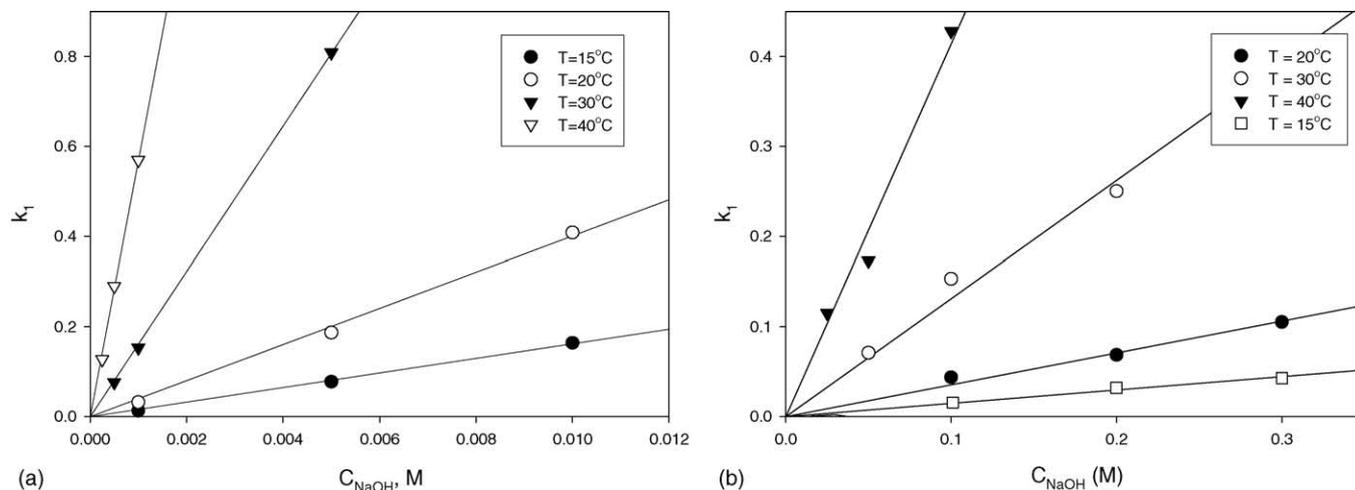
Fig. 5. Linear regression analysis using Eq. (4) for (a) homogeneous and (b) heterogeneous alkaline hydrolysis of CL-20. The second-order rate constants (k_2) are calculated from the slopes of the curves.

neous alkaline hydrolysis reaction mechanisms may be different.

3.3. Temperature dependency of the rate constants

The temperature dependency of k_2 can be represented by the Arrhenius law:

$$k_2 = A\,e^{-E/RT} \tag{6}$$

where A is the frequency factor or Arrhenius constant, E the activation energy (kJ/mol) of the reaction, R the gas constant ($8.314 \times 10^{-3}\,kJ\,mol^{-1}\,K^{-1}$), and T (K) the absolute temperature. This expression fits the experimental data well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency [24]. The parameters A and E are determined from a linear least square fit of the natural logarithm of the obtained average second-order rate

constants (Table 3) against the reciprocal of the absolute temperature as shown in Fig. 6. The value of the activation energy, E, was calculated as 105.64 kJ/mol for homogeneous alkaline hydrolysis ($R^2 = 0.9979$). The apparent activation energy for the heterogeneous reaction was calculated as 98.81 kJ/mol ($R^2 = 0.9970$). These activation energies differ only by 6.47%, and can therefore be considered similar, which indicates that the external mass transfer limitations were overcome by the mixing speed used in the heterogeneous experiments. The activation energy values obtained for the CL-20 base hydrolysis are within close range of those reported by Heilmann et al. [11,12] for RDX (99.9 kJ/mol) and HMX (111.9 kJ/mol) and the heterogeneous activation energy reported by Christodoulatos et al. [16] for nitrocellulose (100.9 kJ/mol). The Arrhenius pre-exponential constants for the homogeneous and heterogeneous reactions

Fig. 6. Arrhenius plot of calculated second-order rate constants (k_2): (■) heterogeneous; (□) homogeneous; (—) model.
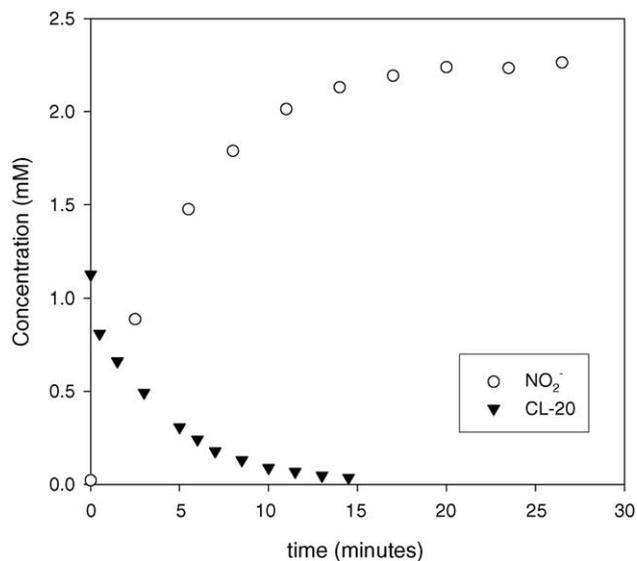
Fig. 7. Dynamics of nitrite ion generation during CL-20 removal during alkaline treatment with 0.2 M NaOH solution at 30 °C.
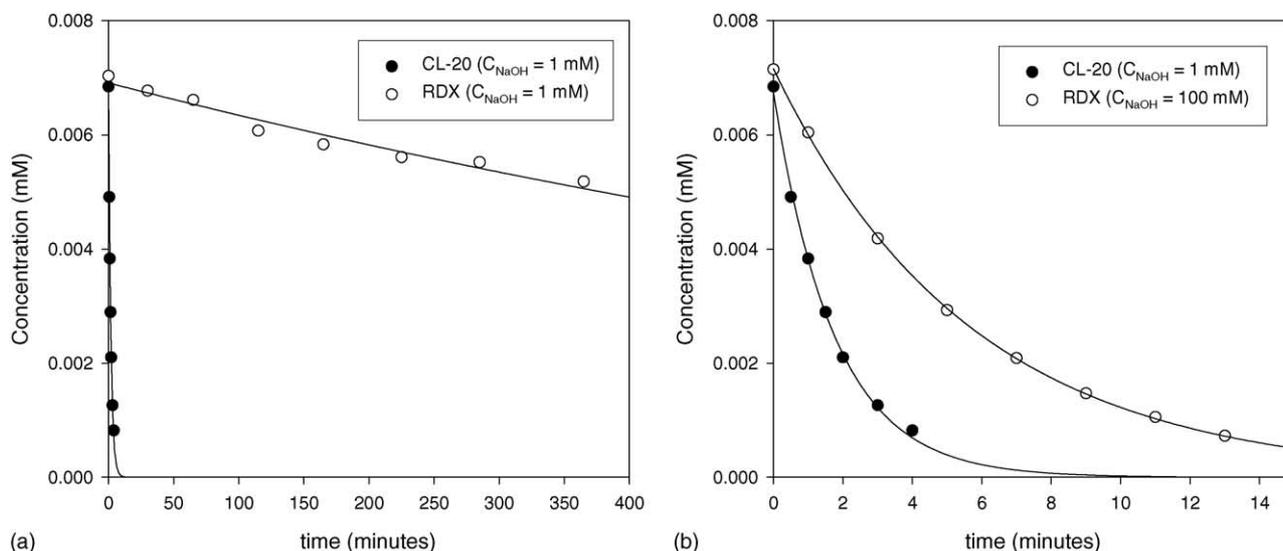
Fig. 8. Comparison of alkaline hydrolysis concentration–time profiles of CL-20 and RDX at 40 °C: (a) homogeneous conditions with 1 mM NaOH; (b) homogeneous conditions, when the NaOH concentration for RDX is increased to 100 mM.

are significantly different; 2.52×10^{20} and 1.34×10^{17}, respectively.

3.4. Nitrite production

It has been suggested that denitration is the primary step in the degradation mechanism of cyclic nitramines, which involves proton abstraction by hydroxide ion and simultaneous loss of NO_2^- [21,25]. The concentrations of nitrite and nitrate ions were monitored during the alkaline hydrolysis experiments. It was observed that alkaline treatment of CL-20 yields a NO_2^- to initial CL-20 molar ratio of 2:1, while the amount of NO_3^- generation was insignificant. This result is in agreement with the findings of Balakrishnan et al. [25]. A typical plot of NO_2^- formation during the time course of the heterogeneous alkaline hydrolysis of CL-20 system is presented in Fig. 7.

3.5. Comparison with RDX

Experiments were conducted to compare the destruction of CL-20 and RDX by alkaline hydrolysis, at 40 °C, in separate reaction vessels. Alkaline hydrolysis of CL-20 was found to occur at remarkably faster rates as compared to RDX. Results presented in Fig. 8a indicate that, at similar initial nitramine molar concentrations (6.85×10^{-3} mM of CL-20 and 7.03×10^{-3} mM of RDX) and 1 mM NaOH, CL-20 totally reacts in less than 10 min, while at 365 min; only 26% of RDX has been consumed by the reaction. When the NaOH concentration used for RDX base hydrolysis is increased to 100 mM while maintaining the NaOH at 1 mM for the CL-20 reaction, the rate of CL-20 disappearance is still greater than the one for RDX (Fig. 8b). The significantly higher CL-20 degradation rates as compared to RDX can be attributed to

CL-20 having elongated bonds and a more strained structure, which theoretically makes its degradation easier than RDX [18]. The k_2^{hom} for RDX was calculated as $1.80 \, \text{M}^{-1} \, \text{min}^{-1}$ with a standard error of 0.0094, which is comparable to the values calculated based on the kinetic parameters that were reported by other researchers ($2.00 \, \text{M}^{-1} \, \text{min}^{-1}$ [12], $1.61 \, \text{M}^{-1} \, \text{min}^{-1}$ [21] and $1.50 \, \text{M}^{-1} \, \text{min}^{-1}$ [22]).

4. Conclusions

Alkaline hydrolysis is a simple and effective treatment technology for energetic materials including CL-20. The alkaline hydrolysis of CL-20 above and below solubility limits follows second order kinetics. Homogeneous alkaline hydrolysis rates of CL-20 are higher than heterogeneous rates, and the reaction is faster in comparison to the alkaline hydrolysis of RDX. The activation energy for CL-20 undergoing alkaline hydrolysis is within close range of the reported activation energies for other nitrated energetic compounds. Only partial product analyses of the decomposition of CL-20 under alkaline hydrolysis have been presented in the literature [25]. Further studies are necessary to evaluate mass transfer effects on the alkaline hydrolysis rates of CL-20; to identify the numerous intermediates and end products of the alkaline reactions whose identity is yet unknown; and the reaction mechanisms under homogeneous and heterogeneous conditions.

References

[1] A.T. Nielsen, Caged polynitramine compound, U.S. Patent 5,693,794 (1997).

[2] S.L. Larson, D.R. Felt, L. Escalon, J.D. Davis, L.D. Hansen, Analysis of CL-20 in Environmental Matrices: Water and Soil, ERDC/EL TR-01-21, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 2001.

[3] A.T. Nielsen, A.P. Chafin, S.L. Christian, D.W. Moore, M.P. Nadler, R.A. Nissan, D.J. Vanderah, Synthesis of polyazapolycyclic caged polynitramines, Tetrahedron 54 (1998) 11793–11812.

[4] National Research Council, Advanced Energetic Materials, The National Academies Press, Washington, DC, 2004 (http://books.nap.edu/catalog/10918.html).

[5] B. D'Andrea, F. Lillo, A. Faure, C. Perut, A new generation of solid propellants for space launchers, Acta Astronautica 47 (2000) 103–112.

[6] G. Zhou, J. Wang, W.-D. He, N.-B. Wong, A. Tian, W.-K. Li, Theoretical investigation of four conformations of HNIW by B3LYP method, J. Mol. Struct. 589–590 (2002) 273–280.

[7] J.-H. Kim, Y.-C. Park, Y.-J. Yim, J.-S. Han, Crystallization behavior of hexanitrohexaazaisowurtzitane at 298 K and quantitative analysis of mixtures of its polymorphs by FTIR, J. Chem. Eng. Jpn. 31 (1998) 478–481.

[8] T. Spontarelli, G.A. Buntain, R.L. Flesner, J.A. Sanchez, P.J. Unkefer, An engineered system using base hydrolysis for complete destruction of energetic materials, in: Proceedings of the International Symposium on Energetic Materials Technology, American Defense Preparedness Association (ADPA), Orlando, FL, 1994.

[9] National Research Council, Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons, The National Academies Press, Washington, DC, 1999 (http://books.nap.edu/catalog/9660.html).

[10] K.-D. Zoh, J.I. Daniels, J.P. Knezovich, M.K. Stenstrom, Treatment of hydrolysates of the high explosives hexahydro-1,3,5-trinitro-1,3,5-triazine and octahydro-1,3,5-tetranitro-1,3,5,7-tetrazocine using biological denitrification, Water Environ. Res. 71 (1999) 148–155.

[11] H.M. Heilmann, M.K. Stenstrom, R.P.X. Hesselmann, U. Wiesmann, Kinetics of aqueous alkaline homogeneous hydrolysis of high explosive 1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane (HMX), Water Sci. Technol. 30 (1994) 53–61.

[12] H.M. Heilmann, U. Wiesmann, M.K. Stenstrom, Kinetics of the alkaline hydrolysis of high explosives RDX and HMX in aqueous solution and adsorbed to activated carbon, Environ. Sci. Technol. 30 (1996) 1485–1492.

[13] R.L. Bishop, R.L. Flesner, P.C. Dell'Orco, T. Spontarelli, S.A. Larson, Application of gas-liquid film theory to base hydrolysis of HMX powder and HMX-based plastic-bonded explosives using sodium carbonate, Ind. Eng. Chem. Res. 37 (1998) 4551–4559.

[14] R.L. Bishop, R.L. Flesner, P.C. Dell'Orco, T. Spontarelli, S.A. Larson, D.A. Bell, Base hydrolysis of HMX and HMX-based plastic-bonded explosives with sodium hydroxide between 100 and 155 °C, Ind. Eng. Chem. Res. 38 (1999) 2254–2259.

[15] D.R. Felt, S.L. Larson, L.D. Hansen, Kinetics of Base-catalyzed 2,4,6-trinitrotoluene Transformation, ERDC/EL TR-01-17, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 2001.

[16] C. Christodoulatos, T.-L. Su, A. Koutsospyros, Kinetics of the alkaline hydrolysis of nitrocellulose, Water Environ. Res. 73 (2001) 185–191.

[17] M. Emmrich, Kinetics of alkaline hydrolysis of 2,4,6-trinitrotoluene in aqueous solution and highly contaminated soils, Environ. Sci. Technol. 33 (1999) 3802–3805.

[18] M. Qasim, B. Flemming, L. Hansen, An approximation methods study and comparison of the chemical and physical properties of CL-20 and RDX for prediction of reactivities, Proc. Curr. Trends Comp. Chem. (2000) 184–187.

[19] F. Monteil-Rivera, L. Paquet, S. Deschamps, V.K. Balakrishnan, C. Beaulieu, J. Hawari, Physico-chemical measurements of CL-20 for environmental applications, comparison with RDX and HMX, J. Chromatogr. A 1025 (2004) 125–132.

[20] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York, 1987.

[21] J.C. Hoffsommer, D.A. Kubose, D.J. Glover, Kinetic isotope effects and intermediate formation for the aqueous alkaline homogeneous hydrolysis of 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX), J. Phys. Chem. 81 (1977) 380–385.

[22] M. Croce, Y. Okamoto, Cationic micellar catalysis of the aqueous alkaline hydrolyses of 1,3,5-triaza-1,3,5-trinitrocyclohexane and 1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane, J. Org. Chem. 44 (1979) 2100–2103.

[23] M.B. Smith, J. March, March's Advanced Organic Chemistry—Reactions, Mechanisms and Structure, 5th ed., Wiley, 2001.

[24] O. Levenspiel, Chemical Reaction Engineering, 2nd ed., Wiley, 1972.

[25] V.K. Balakrishnan, A. Halazs, J. Hawari, Alkaline hydrolysis of the cyclic nitramine explosives RDX, HMX, and CL-20: new insights into degradation pathways obtained by the observation of novel intermediates, Environ. Sci. Technol. 37 (2003) 1838–1843.