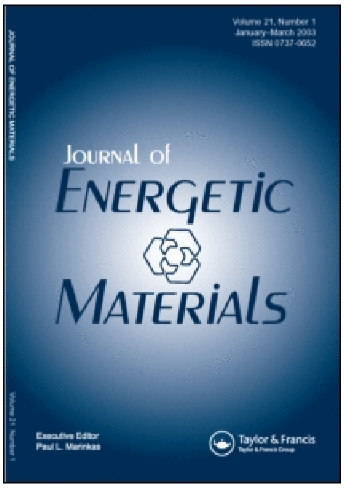

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The hydrolysis of the α, β, and ε polymorphs of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane(CL-20) was investigated in dilute buffered aqueous solutions over a pH range of 4–10 and at 35, 43, 50, 58 and 65°C, with starting concentrations of CL-20 at one half the solubility limit for the respective temperature. In all cases, an overall first-order kinetic behavior was observed. The rate constants, half-lives, activation energies, and Arrhenius pre-exponential factors were determined. The latter was found to vary linearly with pH.

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Based on these findings, general formulas for the hydrolysis kinetics of the three polymorphs were developed.

Keywords: arrhenius equation, CL-20, HNIW, hydrolysis, kinetics, polymorphs

Introduction

The highly energetic polycyclic nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, more commonly known as CL-20) was synthesized in the 1980s [1]. It has a potential application in propellant formulations, as it meets the stringent munitions sensitivity requirements, such as minimum combustion signature, and as its energetic properties are superior to those of cyclotetramethylenetetranitramine (HMX) and cyclotrimethylene-trinitramine (RDX) [2]. Structurally, CL-20 consists of a rigid isowurtzitane cage with a nitro group ($-NO_2$) attached to each of the six bridging nitrogen atoms (Fig. 1). Relative to HMX and RDX, CL-20 has a higher molecular weight, density, heat of formation, and number of $N-NO_2$ bonds. Unlike RDX and HMX, which have no C–C bonds, CL-20 has three slightly elongated C–C bonds; e.g., the C1–C4 bond is 0.159–0.160 nm [3], whereas an ordinary sp^3 C–C single bond is 0.154 nm [4]. Under ambient conditions CL-20 can exist in four stable polymorphs (α, β, γ, ε), the structures and densities of which have been established by X-ray crystallography. A labile ζ form, existing only at high pressure, has been identified and described in phase diagram studies [5–7]. The ε-polymorph is preferred for industrial applications because

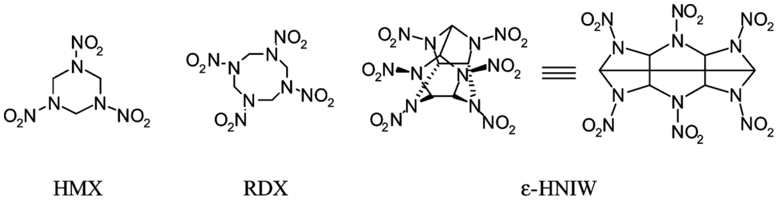

Figure 1. Structures of RDX, HMX, and ε-HNIW (CL-20).

of its high crystal density and stability at ambient conditions [8]. As CL-20 is under consideration to replace HMX and RDX, it is a potential emerging contaminant of the same category as the latter two energetic compounds. Its environmental toxicity effects on living organisms have been and continue to be investigated [9,10]. The energetic properties of CL-20 have been thoroughly studied; however, very little is known about its chemical behavior, particularly its fate in aqueous solutions, which bears upon its stability and fate in the environment.

The fate of an organic compound in aquatic environment is determined, among other factors, by its water solubility and chemical and biological reactivity. For many organic compounds, abiotic hydrolysis is of primary importance as a decomposition reaction. Some hydrolyses occur so rapidly that the greater concern is about the transformation products rather than for the parent substance [11]. In other cases, compounds can be resistant to hydrolysis. Lastly, a compound may have an intermediate reactivity that may necessitate a stability assessment of both the parent substance and its hydrolysis products. The importance of abiotic hydrolysis in the environment can be determined quantitatively from data on hydrolysis rate constants and half-lives.

Initially, the objective of this study was to establish the hydrolytic behavior of ε-CL-20 over a wide range of pH and temperature, following the EPA Guidelines OPPTS 835.2130 [12], and to determine the kinetic parameters.

The EPA guidelines explicitly state that when a compound under investigation is poorly soluble in water it may be introduced into it as a solution in a water-miscible organic solvent, such as acetonitrile, provided that the organic solvent does not exceed 1% by volume of the starting solution. However, we found that when ε-CL-20 is recrystallized from a stock acetonitrile solution, it no longer comprises the original ε polymorph but is a mixture of the α and β polymorphs. Since the phenomenon of conformational isomerism implies that the crystals of the different CL-20 polymorphs are built of different conformer HNIW molecules [2], it was reasonable to expect that, when in solution, these conformers would display different hydrolytic kinetic behavior. The work was then expanded to investigate the hydrolysis of all three polymorphs—α, β, and ε—under the conditions originally chosen for the ε polymorph. Most importantly, that involved the preparation of the pure α and β polymorph solids from the available ε polymorph in order to prepare the starting solutions by dissolving the solids, thereby avoiding the use of an organic solvent.

In general, the kinetics of the hydrolysis of a substance follows a pseudo-first-order rate law:

$$\frac{d[C_t]}{dt} = -k'[C_t] \tag{1}$$

where k' is the pseudo-first-order rate constant and C_t is the concentration of the test substance. It is traditionally assumed that, in aqueous solutions, three hydrolytic decomposition pathways are possible for a given substance: (1) acid (H^+) catalysis; (2) base, or alkaline (OH^-) catalysis; and (3) noncatalyzed nucleophilic attack of water (neutral). When all three pathways are operative, k' is given by:

$$k' = k_H[\mathrm{H}^+] + k_N + k_{OH}[\mathrm{OH}^-] \tag{2}$$

where k_H, k_N, and k_{OH} are the pseudo-first-order rate constants for the hydrolysis under acidic, neutral, and basic conditions, respectively.

According to Eq. (2), to determine the dependence of k' on pH at a fixed temperature T_j it is necessary to obtain the values of k_H, k_N, and k_{OH}. This is done by determining k' at a minimum of three different pH levels for at least three fixed temperatures and solving the resulting system of equations for the unknowns k_H, k_N, and k_{OH} [12] or applying nonlinear regression analysis to the experimental data. The slope of a plot of k' versus pH can show the relative importance of the three hydrolytic mechanisms [13], which can, in turn, indicate the predominant hydrolytic pathway(s). The temperature dependence of the hydrolytic constants can be described by the Arrhenius equation:

$$\frac{d\ln k}{d(1/T)} = -\frac{E_a}{R} \tag{3}$$

where R is the universal gas constant ($8.314\,\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$), T is the absolute temperature (K), and E_a is the activation energy (J/mol) of the reaction. This equation is useful for interpolation and extrapolation purposes, since a plot of $\ln(k)$ versus $1/T$ is often a nearly straight line [14].

An alternative to the above method, which was used in the present work, is to establish any pH-dependent trend in the E_a and the Arrhenius pre-exponential factor A and hence derive an empirical formula describing the hydrolytic process.

Experimental

Chemicals

Commercial-grade CL-20 (ε-HNIW) was manufactured by 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); its ε polymorph content was greater than 98% (determined by infrared spectrometry); and the average particle size was 2 μm with a uniformity coefficient of 1.47. Acetonitrile, ethyl acetate, acetone, and chloroform (all HPLC grade) and stock solution 0.97 *M* NaOH were purchased from Aldrich. Potassium hydrogenphthalate (PHP), potassium dihydrogenphosphate (KH_2PO_4), and sodium tetraborate decahydrate ($Na_2B_4O_7\cdot 10H_2O$) were purchased from Fisher Scientific. Deionized (DI) water was obtained by purification of tap water through a Millipore Quantum^{TM} Ultrapure Organex Cartridge.

CL-20 Polymorphs

The ε polymorph of CL-20 was dried in a vacuum desiccator until constant weight before use.

The β polymorph was prepared from ε-CL-20 by a procedure adapted from Kim et al. [8]. One gram of ε-CL-20 was dissolved in 2.5 g ethyl acetate. Next, 10 g of chloroform were added with constant stirring. Instantaneous precipitation of the β polymorph occurred. After 1 min, the precipitate was removed by quick vacuum filtration to avoid the concomitant crystallization of the ε polymorph. The crystals were washed with DI water and dried in a vacuum desiccator until constant weight before use.

The α polymorph of CL-20 was prepared by vacuum-assisted crystallization from a solution of ε-CL-20 in acetone.

The purity of all polymorphs was confirmed by X-ray diffractometry (Rigaku-TXR 3000 apparatus using Cu-Kα radiation). The scanning rate (2θ/time) was 1°/min over a range of 5–50°.

Procedures

Hydrolysis kinetic experiments were conducted with CL-20 below solubility limits. Five sets of experiments were run at temperatures of 35, 43, 50, 58, and 65°C.

For all polymorphs and temperatures, five pH levels of hydrolysis were investigated. Thus, a total of 90 hydrolysis experiments were run.

The standard buffers were prepared as follows:

pH 4.00: 500 mL 0.1 *M* PHP, 10 mL 0.1 *M* HCl, and DI water to 1.0 L
pH 5.50: 500 mL 0.1 *M* PHP, 366 mL 0.1 *M* HCl, and DI water to 1.0 L
pH 7.00: 500 mL 0.1 *M* KH_2PO_4, 291 mL 0.1 *M* NaOH, and DI water to 1.0 L
pH 8.00: 500 mL 0.025 *M* sodium tetraborate, 205 mL 0.1 *M* HCl, and DI water to 1.0 L
pH 9.00: 500 mL 0.025 *M* sodium tetraborate, 46 mL 0.1 *M* HCl, and DI water to 1.0 L
pH 10.00: 500 mL 0.025 *M* sodium tetraborate, 183 mL 0.1 *M* NaOH, and DI water to 1.0 L

All stock buffers and glassware were autoclaved at 180°C for 1 h before use.

Saturated aqueous solutions of the three CL-20 polymorphs (ε, α, and β) were prepared at the five chosen hydrolysis temperatures by shaking 100 mg of solid CL-20 polymorph in 500-mL Erlenmeyer flasks for 48 h. The saturated solutions of the respective CL-20 polymorphs were vacuum-filtered through

0.2-µm Whatman membrane filters at the corresponding temperatures to remove excess solids. Each saturated solution was diluted 1:1 by volume with DI water to prepare CL-20 stock solutions for the hydrolysis runs. Next, after warming to the required temperature, 100 µL of the appropriate stock buffer was added to the 100-mL reaction flasks. The sets of reaction flasks were incubated in the dark in a G24 Environmental Incubator-Shaker (New Brunswick Scientific Company, Inc., Edison, NJ).

Sampling and Analysis

CL-20 disappearance was monitored by HPLC at room temperature. The HPLC method was based on the U.S. EPA Standard Method 8330 [12], which was originally developed for analysis of nitroaromatic and nitramine explosives. Measurements of CL-20 concentration were performed in a Varian high-performance liquid chromatograph with a 9065 Polychrom UV detector, 9095 autosampler, and 9010 pump. A Symmetry Shield™ RP-18 (3.9 mm × 150 mm) 5 µm column (Waters®, Milford, MA) was used. The mobile phase was an isocratic binary mixture of water and acetonitrile (40:60 v:v) pumped at a flow rate of 1.0 mL min^{-1}.
. The analytical wavelength for spectrophotometric detection was 229 nm. Under these conditions, CL-20 elutes as a symmetric peak with a retention time of 3.5 min. The HPLC method used does not distinguish among CL-20 conformers in solution.

Samples from the 35°C series were prepared by placing 1.0 mL sample in 2.0-mL screw-top glass vials (12 × 32 mm, with polypropylene/PTFE septa, by Varian); these were analyzed immediately. However, to avoid precipitation of CL-20, samples for analysis from the remaining temperature sets were prepared by diluting 0.5 mL of the corresponding reaction solutions with 0.5 mL of acetonitrile warmed to the corresponding reaction temperature. All samples were analyzed immediately (within 10 min of preparation).

Results and Discussion

The key purpose of the buffers in the hydrolyses was to ensure that the reaction rates would not be affected by the various potential end-products of CL-20 degradation, to wit nitrite ion, formaldehyde, formic acid, ammonia, etc. The subject is treated more in-depth by Fournier et al. [15].

Figure 2 shows six typical time-concentration profiles of the hydrolysis of a CL-20 polymorph, in this case *β*-CL-20 at 50°C. The time-concentration profiles in all investigated conditions support the assumption that CL-20 disappearance follows first-order behavior with respect to CL-20 concentration. First-order curves fitted to the experimental data exhibit excellent correlation, as demonstrated by the R^2 values reported in Tables 1–3. Thus, the assumption of pseudo-first-order kinetics with respect to CL-20 concentration is strongly supported by nonlinear regression analyses performed on time-concentration data for all polymorphs at all temperatures and pH levels.

The temperature-corrected pH values for each buffer were calculated using the pH-temperature relationships reported by

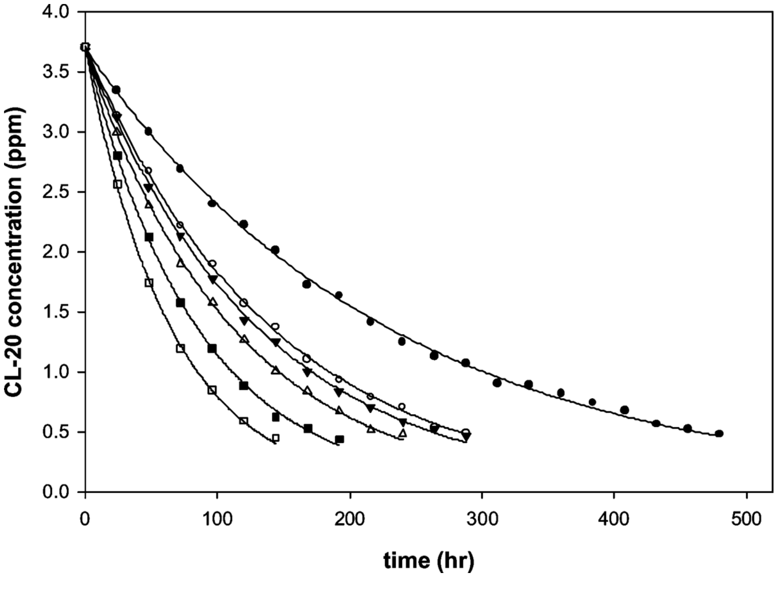

Figure 2. Hydrolysis of α-CL-20 at 50°C (●: data at pH 4; ○: data at pH 5.5; ▼: data at pH 7; △: data at pH 8; ■: data at pH 9; □: data at pH 10;—: exponential decay models).

Bates [16]. For all buffers, the correction factors were found to be negligible, and no corrections were necessary. Nonlinear regression analyses with one independent variable (time) were performed on all 90 sets of data to obtain the pseudo-first-order rate constants. The calculated first-order apparent rate constants for the α, β, and ε-CL-20 hydrolyses and the corresponding standard errors and regression coefficients are presented in Tables 1, 2, and 3, respectively. Based on these findings, it can be seen that the buffer-controlled hydrolysis of the α, β, and ε polymorphs of CL-20 in sub-solubility conditions is adequately described by a pseudo-first-order kinetic expression.

A comparison of the rate constants makes it evident that, under identical hydrolytic conditions, the relative stability of the three CL-20 polymorphs decreases in the order $\varepsilon > \beta > \alpha$. For the investigated hydrolytic conditions, the ε polymorph exhibits the longest half-life of all: over six months at 35°C and pH 4, which is about 17 and 6 times longer than the half-lives of the α and β polymorphs, respectively. The buffered hydrolysis of all CL-20 polymorphs is overall much slower than the hydrolysis of CL-20 in rigorously alkaline conditions [17]. This indicates that water alone will not be a major factor in the CL-20 degradation in the environment. The slow rate of decomposition of CL-20 in water is easily explained by the far lower basic properties of water as a proton-abstracting agent in E2 elimination reactions, compared to the hydroxide ion in alkaline hydrolysis of CL-20 [17]. In addition, it must be noted that even though the E2 mechanism is described by a second-order kinetic expression (rate $= k'$[base][substrate]), the basic agent here, water, is in such a great excess relative to the substrate (CL-20), that it is safely included in the observed rate constant k'. The overall reaction thereby exhibits a first-order time-concentration profile, as it is observed in all cases investigated in this work.

Table 4 shows the Arrhenius parameters obtained from a linear least-squares fit to a plot of the natural logarithm of the apparent rate constants ($\ln k'$) versus the reciprocal of the absolute temperature ($1/T$) for the three CL-20 polymorphs at the six pH levels. A very good correlation is observed in all cases, based on the high R^2 values. The obtained hydrolytic

Table 1
Apparent first-order rate constants $k'(\mathrm{h}^{-1})$
for the hydrolysis of α-CL-20 at different pH levels and temperatures

pH	35°C	43°C	50°C	58°C	65°C
4	$2.73\cdot10^{-3}$ $(4.69\cdot10^{-5})$[a] $\mathrm{R}^2 = 0.9973$	$1.13\cdot10^{-2}$ $(4.566\cdot10^{-5})$ $\mathrm{R}^2 = 0.9985$	$1.47\cdot10^{-2}$ $(3.068\cdot10^{-5})$ $\mathrm{R}^2 = 0.9967$	$1.92\cdot10^{-2}$ $(3.412\cdot10^{-5})$ $\mathrm{R}^2 = 0.9976$	$2.24\cdot10^{-2}$ $(4.176\cdot10^{-5})$ $\mathrm{R}^2 = 0.9899$
5.5	$2.85\cdot10^{-3}$ $(4.6\cdot10^{-5})$ $\mathrm{R}^2 = 0.9977$	$1.19\cdot10^{-2}$ $(4.305\cdot10^{-5})$ $\mathrm{R}^2 = 0.9971$	$1.51\cdot10^{-2}$ $(3.806\cdot10^{-5})$ $\mathrm{R}^2 = 0.9949$	$1.98\cdot10^{-2}$ $(4.415\cdot10^{-5})$ $\mathrm{R}^2 = 0.9948$	$2.31\cdot10^{-2}$ $(4.706\cdot10^{-5})$ $\mathrm{R}^2 = 0.9957$
7	$2.96\cdot10^{-3}$ $(4.173\cdot10^{-5})$ $\mathrm{R}^2 = 0.9982$	$1.24\cdot10^{-2}$ $(4.244\cdot10^{-5})$ $\mathrm{R}^2 = 0.9989$	$1.59\cdot10^{-2}$ $(4.380\cdot10^{-5})$ $\mathrm{R}^2 = 0.9991$	$2.09\cdot10^{-2}$ $(4.441\cdot10^{-5})$ $\mathrm{R}^2 = 0.9974$	$2.46\cdot10^{-2}$ $(4.839\cdot10^{-5})$ $\mathrm{R}^2 = 0.9985$
8	$3.17\cdot10^{-3}$ $(6.515\cdot10^{-5})$ $\mathrm{R}^2 = 0.9962$	$1.33\cdot10^{-2}$ $(5.066\cdot10^{-5})$ $\mathrm{R}^2 = 0.9987$	$1.72\cdot10^{-2}$ $(3.298\cdot10^{-5})$ $\mathrm{R}^2 = 0.9969$	$2.25\cdot10^{-2}$ $(4.304\cdot10^{-5})$ $\mathrm{R}^2 = 0.9891$	$2.65\cdot10^{-2}$ $(4.811\cdot10^{-5})$ $\mathrm{R}^2 = 0.9919$
9	$3.49\cdot10^{-3}$ $(7.144\cdot10^{-5})$ $\mathrm{R}^2 = 0.9964$	$1.46\cdot10^{-2}$ $(4.623\cdot10^{-5})$ $\mathrm{R}^2 = 0.9991$	$1.87\cdot10^{-2}$ $(3.738\cdot10^{-5})$ $\mathrm{R}^2 = 0.9988$	$2.41\cdot10^{-2}$ $(4.609\cdot10^{-5})$ $\mathrm{R}^2 = 0.9979$	$2.89\cdot10^{-2}$ $(4.806\cdot10^{-5})$ $\mathrm{R}^2 = 0.9954$
10	$3.68\cdot10^{-3}$ $(6.263\cdot10^{-5})$ $\mathrm{R}^2 = 0.9972$	$1.55\cdot10^{-2}$ $(3.298\cdot10^{-5})$ $\mathrm{R}^2 = 0.9975$	$1.98\cdot10^{-2}$ $(3.407\cdot10^{-5})$ $\mathrm{R}^2 = 0.9899$	$2.54\cdot10^{-2}$ $(4.092\cdot10^{-5})$ $\mathrm{R}^2 = 0.9968$	$3.06\cdot10^{-2}$ $(4.903\cdot10^{-5})$ $\mathrm{R}^2 = 0.9989$

[a] The numbers in parentheses are the standard errors.

Table 2

Apparent first-order rate constants k′ (h^{-1})

for the hydrolysis of β-CL-20 at different pH levels and temperatures

pH	35°C	43°C	50°C	58°C	65°C
4	$8.70 \cdot 10^{-4}$ $(8.241 \cdot 10^{-6})$[a] $R^2 = 0.9952$	$3.46 \cdot 10^{-3}$ $(1.232 \cdot 10^{-5})$ $R^2 = 0.9955$	$4.55 \cdot 10^{-3}$ $(6.738 \cdot 10^{-5})$ $R^2 = 0.9859$	$6.18 \cdot 10^{-3}$ $(1.009 \cdot 10^{-5})$ $R^2 = 0.9997$	$6.65 \cdot 10^{-3}$ $(4.571 \cdot 10^{-5})$ $R^2 = 0.9856$
5.5	$1.20 \cdot 10^{-3}$ $(1.03 \cdot 10^{-5})$ $R^2 = 0.9994$	$5.11 \cdot 10^{-3}$ $(3.475 \cdot 10^{-5})$ $R^2 = 0.9951$	$6.80 \cdot 10^{-3}$ $(3.825 \cdot 10^{-5})$ $R^2 = 0.9965$	$8.45 \cdot 10^{-3}$ $(3.667 \cdot 10^{-5})$ $R^2 = 0.9959$	$9.19 \cdot 10^{-3}$ $(1.829 \cdot 10^{-5})$ $R^2 = 0.9991$
7	$1.47 \cdot 10^{-3}$ $(3.025 \cdot 10^{-5})$ $R^2 = 0.9962$	$6.04 \cdot 10^{-3}$ $(2.962 \cdot 10^{-5})$ $R^2 = 0.9947$	$8.01 \cdot 10^{-3}$ $(4.437 \cdot 10^{-5})$ $R^2 = 0.9895$	$9.85 \cdot 10^{-3}$ $(2.940 \cdot 10^{-5})$ $R^2 = 0.9984$	$1.15 \cdot 10^{-2}$ $(3.792 \cdot 10^{-5})$ $R^2 = 0.9963$
8	$1.68 \cdot 10^{-3}$ $(5.215 \cdot 10^{-5})$ $R^2 = 0.9945$	$7.14 \cdot 10^{-3}$ $(4.875 \cdot 10^{-5})$ $R^2 = 0.9981$	$9.57 \cdot 10^{-3}$ $(3.862 \cdot 10^{-5})$ $R^2 = 0.9968$	$1.31 \cdot 10^{-2}$ $(2.270 \cdot 10^{-5})$ $R^2 = 0.9973$	$1.43 \cdot 10^{-2}$ $(2.809 \cdot 10^{-5})$ $R^2 = 0.9981$
9	$1.83 \cdot 10^{-3}$ $(4.128 \cdot 10^{-5})$ $R^2 = 0.9985$	$9.31 \cdot 10^{-3}$ $(4.293 \cdot 10^{-5})$ $R^2 = 0.9937$	$1.24 \cdot 10^{-2}$ $(3.297 \cdot 10^{-5})$ $R^2 = 0.9977$	$1.67 \cdot 10^{-2}$ $(1.605 \cdot 10^{-5})$ $R^2 = 0.9981$	$1.78 \cdot 10^{-2}$ $(3.295 \cdot 10^{-5})$ $R^2 = 0.9951$
10	$2.15 \cdot 10^{-3}$ $(3.269 \cdot 10^{-5})$ $R^2 = 0.9967$	$1.20 \cdot 10^{-2}$ $(3.994 \cdot 10^{-5})$ $R^2 = 0.9929$	$1.60 \cdot 10^{-2}$ $(4.395 \cdot 10^{-5})$ $R^2 = 0.9959$	$2.15 \cdot 10^{-2}$ $(1.809 \cdot 10^{-5})$ $R^2 = 0.9939$	$2.29 \cdot 10^{-2}$ $(3.875 \cdot 10^{-5})$ $R^2 = 0.9971$

[a] The numbers in parentheses are the standard errors.

Table 3
Apparent first-order rate constants $k'(\mathrm{h}^{-1})$
for the hydrolysis of ε-CL-20 at different pH levels and temperatures

pH	35°C	43°C	50°C	58°C	65°C
4	$1.54{\cdot}10^{-4}$ $(4.587{\cdot}10^{-6})^a$ $\mathrm{R}^2 = 0.9983$	$6.60{\cdot}10^{-4}$ $(3.198{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9976$	$8.91{\cdot}10^{-4}$ $(6.824{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9967$	$1.17{\cdot}10^{-3}$ $(3.258{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9982$	$1.25{\cdot}10^{-3}$ $(3.760{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9868$
5.5	$1.58{\cdot}10^{-4}$ $(2.863{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9976$	$6.95{\cdot}10^{-4}$ $(4.483{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9969$	$9.39{\cdot}10^{-4}$ $(5.111{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9949$	$1.20{\cdot}10^{-3}$ $(7.863{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9895$	$1.28{\cdot}10^{-3}$ $(8.076{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9859$
7	$1.66{\cdot}10^{-4}$ $(4.617{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9981$	$7.11{\cdot}10^{-4}$ $(5.603{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9969$	$9.72{\cdot}10^{-4}$ $(1.167{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9991$	$1.27{\cdot}10^{-3}$ $(1.365{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9989$	$1.36{\cdot}10^{-3}$ $(9.095{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9800$
8	$1.82{\cdot}10^{-4}$ $(6.515{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9977$	$7.50{\cdot}10^{-4}$ $(5.444{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9937$	$1.03{\cdot}10^{-3}$ $(4.511{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9963$	$1.37{\cdot}10^{-3}$ $(2.371{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9945$	$1.48{\cdot}10^{-3}$ $(8.128{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9810$
9	$1.91{\cdot}10^{-4}$ $(7.144{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9964$	$8.32{\cdot}10^{-4}$ $(1.025{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9991$	$1.13{\cdot}10^{-3}$ $(4.824{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9966$	$1.43{\cdot}10^{-3}$ $(2.037{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9978$	$1.59{\cdot}10^{-3}$ $(4.466{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9925$
10	$2.08{\cdot}10^{-4}$ $(8.077{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9994$	$8.65{\cdot}10^{-4}$ $(3.982{\cdot}10^{-6})$ $\mathrm{R}^2 = 0.9975$	$1.19{\cdot}10^{-3}$ $(8.674{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9899$	$1.58{\cdot}10^{-3}$ $(6.077{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9949$	$1.68{\cdot}10^{-3}$ $(7.985{\cdot}10^{-5})$ $\mathrm{R}^2 = 0.9867$

[a] The numbers in parentheses are the standard errors.

activation energies are about 40% lower than those reported for the alkaline hydrolyses of other nitramines and nitrocellulose [17]. On the other hand, the pre-exponential factors are 13–15 orders of magnitude lower than the one found for the homogeneous alkaline hydrolysis [17]. This is the key reason for the much slower rate of decomposition of CL-20 in water devoid of any strongly basic species, such as hydroxide.

There is no pH effect on the activation energy of CL-20 hydrolysis: the values are narrowly distributed around a mean value (Table 4). It is therefore justifiable for computational purposes to take the mean values of the activation energies when developing general predictive formulas for the hydrolytic behavior of CL-20. On the other hand, it is clear from Figure 3 that the hydrolytic pre-exponential factors are linearly dependent on pH. The trend is most pronounced with α-CL-20, less so with the β polymorph, and the least with the ε polymorph; this observation corresponds to the relative order of stability of the three polymorphs in the described hydrolytic conditions.

Accordingly, the general form of the Arrhenius equation for the hydrolysis of the three CL-20 polymorphs studied is:

$$k' = A\exp\left(-\frac{E_a}{RT}\right) = (\sigma \times pH + \tau)\exp\left(-\frac{E_a}{RT}\right) \qquad (4)$$

where σ is the slope of the A vs. pH line, and τ is the y-intercept.

Specifically for each polymorph, the observed pseudo-first-order hydrolytic rate constants at any pH and temperature in sub-solubility regions are as follows:

$$k'_\alpha = (9.439 \times 10^5 pH + 6.905 \times 10^6)\exp\left(-\frac{55748}{8.314 \times T}\right) \qquad (5)$$

$$k'_\beta = (5.085 \times 10^5 pH + 2.332 \times 10^5)\exp\left(-\frac{61530}{8.314 \times T}\right) \qquad (6)$$

$$k'_\varepsilon = (6.662 \times 10^4 pH + 4.875 \times 10^5)\exp\left(-\frac{56276}{8.314 \times T}\right) \qquad (7)$$

Table 4

Activation energies and pre-exponential factors for the hydrolysis of α, β, and ε-CL-20

	α			β			ε		
pH	E_a, kJ/mol	A, h^{-1}	R^2	E_a, kJ/mol	A, h^{-1}	R^2	E_a, kJ/mol	A, h^{-1}	R^2
4	55.794	$1.0407 \cdot 10^7$	0.9898	60.749	$2.5357 \cdot 10^6$	0.9977	56.171	$7.7685 \cdot 10^5$	0.9849
5.5	55.301	$1.2043 \cdot 10^7$	0.9799	61.226	$2.8907 \cdot 10^6$	0.9963	55.963	$8.1017 \cdot 10^5$	0.9925
7	55.988	$1.4119 \cdot 10^7$	0.9956	62.232	$3.5697 \cdot 10^6$	0.9911	56.383	$9.4979 \cdot 10^5$	0.9769
8	56.131	$1.4519 \cdot 10^7$	0.9875	61.594	$4.1226 \cdot 10^6$	0.9897	56.51	$1.0645 \cdot 10^6$	0.9982
9	55.636	$1.5340 \cdot 10^7$	0.9726	60.588	$4.8525 \cdot 10^6$	0.9863	56.294	$1.0709 \cdot 10^6$	0.9843
10	55.636	$1.6060 \cdot 10^7$	0.9942	62.793	$5.5483 \cdot 10^6$	0.9952	56.334	$1.1508 \cdot 10^6$	0.9976
Mean E_a, kJ/mol	55.748 ± 0.294			61.530 ± 0.858			56.276 ± 0.189		

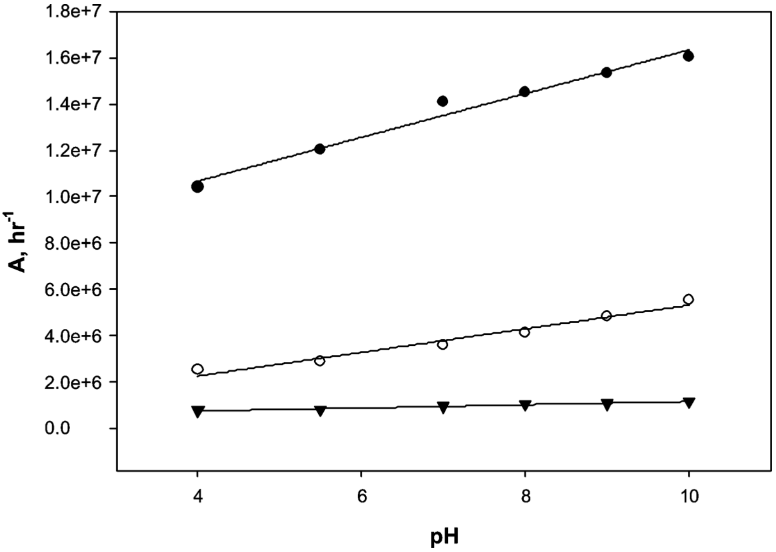

Figure 3. Dependence of the Arrhenius pre-exponential factor A on pH for the three CL-20 polymorphs. (●: α -CL-20; ○: β-CL-20; ▼ : ε-CL-20;—: linear models). For α-CL-20, slope $\sigma = 9.4390{\cdot}10^5$, intercept $\tau = 6.9050{\cdot}10^6$ ($R^2 = 0.9766$). For β-CL-20, slope $\sigma = 5.0850{\cdot}10^5$, intercept $\tau = 0.2332{\cdot}10^6$ ($R^2 = 0.9658$). For ε-CL-20, slope $\sigma = 0.6662{\cdot}10^5$, intercept $\tau = 0.4875{\cdot}10^6$ ($R^2 = 0.9595$).

Conclusions

In this study, we have established the kinetics of CL-20 hydrolysis, in view of its being a degradation reaction in the environment. Experiments were performed at five temperatures and six pH levels. Since three of the CL-20 polymorphs—ε, α, and β—are easily interconvertible through molecular conformational changes induced by organic solvents, we have investigated the hydrolysis kinetics of these three polymorphs in parallel. Pseudo-first-order kinetic behavior was observed in all cases; however, under identical conditions, the stability of the three CL-20 polymorphs decreases in the order $\varepsilon > \beta > \alpha$. With water as the predominant nucleophilic attacking species, the activation energies of the hydrolytic processes are about 40% lower than those of the alkaline hydrolyses of nitramines and nitrocellulose. It was determined that pH has no significant effect on the activation energy of the reactions. The pre-exponential factors, however, were much lower—in the range of 13–15 orders of magnitude—than those of the corresponding alkaline hydrolyses, which explains the overall slow rate of CL-20 hydrolysis. Furthermore, we found that the pre-exponential factors for the hydrolyses of the three polymorphs increase linearly with increasing pH. Based on our findings, it is evident that, in the absence of any strong bases, CL-20 will persist for days to months in aquatic environments, depending on the type of polymorph and temperature.

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Appendix

List of Symbols

A	Arrhenius pre-exponential factor
C_t	Concentration of test substance
$k^{'}$	Pseudo-first-order rate constant
k_H	Rate constant under acidic conditions
k_N	Rate constant under neutral conditions
k_{OH}	Rate constant under basic conditions
R	Universal gas constant, 8.314 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$
R^2	Statistical correlation coefficient
T	Absolute temperature
σ	Slope of the A vs. pH line
τ	Y-intercept of the A vs. pH line