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## HYDROLYSIS OF CL-20

Julius Pavlov  
Muhammad Sidhoun  
Chris Christodoulatos  
Stevens Institute of Technology  
Center for Environmental Technology  
Castle Point on the Hudson  
Hoboken, NJ 07030

Wendy Balas  
Steven Nicolich  
Project Engineers  
ARDEC

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The Energetics and Warheads Division of the U.S. Army Armament Research, Development and Engineering Center has been involved in the development of CL-20. An aqueous hydrolysis study was performed to better understand the fate and transport of CL-20 through environmental systems.

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## SUMMARY

CL-20, also known as HNIW (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane), is a high energy, high density material. Concerns regarding the fate and transport of CL-20 are arising due to its potential introduction into soil and water matrices. The hydrolysis of  $\epsilon$ -CL-20 was investigated in buffered aqueous solutions over a pH range of 4 to 10 at 35°, 50°, and 65°C. The values of the kinetic parameters of the reaction were determined. A first-order kinetic rate was observed when the reaction was initiated with a saturated solution prepared from solid CL-20. However, a change in the hydrolysis mechanism was observed when CL-20 was introduced from a stock acetonitrile (ACN) solution. A change in the polymorph of CL-20, caused by its interaction with ACN, suggested by a double-exponential kinetics model, was verified by x-ray diffraction studies. X-ray diffraction studies indicate that the  $\epsilon$  polymorph of CL-20 was converted to an  $\alpha$ : $\beta$  polymorph mixture when it was re-crystallized from ACN.

## INTRODUCTION

The energetic properties of CL-20 were thoroughly studied; however, very little is known about its chemical behavior, particularly its fate in aqueous solutions. The fate of an organic compound in aquatic environment is determined by its water solubility, vapor pressure, and chemical and biological reactivity. For many organic compounds, hydrolysis is an important decomposition reaction. Some hydrolyses occur so rapidly that the greater concern is about the transformation products rather than for the parent substance (ref. 1). In other cases, compounds can be resistant to hydrolysis under typical environmental conditions. Lastly, a compound may have an intermediate stability 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.

The objective of this study was to investigate the hydrolysis kinetics of CL-20 over a wide range of pH and temperature, and to estimate the kinetic parameters of the reaction. In general, the kinetics of the hydrolysis of a substance follows pseudo-first-order kinetics

$$\frac{d[C_t]}{dt} = -k [C_t] \quad (1)$$

where  $k'$  is the pseudo-first-order rate constant. In aqueous solutions, three hydrolytic decomposition pathways are possible: (1) acid ( $H^+$ ) catalysis, (2) base or alkaline ( $OH^-$ ) catalysis, and (3) non-catalyzed nucleophilic attack of water on a bridging carbon atom (neutral). When all three pathways are operative,  $k'$  is given by

$$k' = k_H [H^+] + k_N + k_{OH} [OH^-] \quad (2)$$

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.

To determine  $k'$  as a function of pH at a fixed temperature  $T_j$ , it is necessary to obtain the values of  $k_H$ ,  $k_N$ , and  $k_{OH}$  according to equation 2. This is done by determining  $k'$  at three different pH levels for three fixed temperatures, and solving the resulting three equations for the unknowns'  $k_H$ ,  $k_N$ , and  $k_{OH}$  (ref. 2). The slope of a plot of  $k'$  versus pH can show the relative importance of the three hydrolytic mechanisms (ref. 3), which can in turn indicate the predominant hydrolytic pathway(s). The temperature-dependence of the hydrolytic constants ( $k_H$ ,  $k_N$ , and  $k_{OH}$ ) can be described, at least approximately, by the Arrhenius equation

$$\frac{d \ln k}{d\left(\frac{1}{T}\right)} = -\frac{E_a}{R} \quad (3)$$

where  $R$  is the gas constant and  $T$  the absolute temperature, and  $E_a$  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 (ref. 4).

## AQUEOUS HYDROLYSIS SETUP

Hydrolysis kinetic experiments were conducted with CL-20 below solubility limits. Since CL-20 is poorly soluble in water, two procedures (A and B) were used to prepare the starting reaction mixtures.

### Procedure A

Three saturated aqueous solutions of CL-20 procured from ATK Thiokol were prepared by shaking 100 mg of solid CL-20 in 500 mL Erlenmeyer flasks for 48 hrs at the three incubation temperatures. The saturated CL-20 solutions were vacuum-filtered through 2  $\mu$ m Whatman membrane filters at the corresponding temperatures to remove excess solids. Each saturated solution was diluted 1:1 with DI water to prepare CL-20 stock solutions. Next, after warming the CL-20 solutions to the required temperature, 100  $\mu$ L of the appropriate stock buffer were added to the 100-mL reaction flasks. The reaction flasks were incubated in the dark at three different temperatures (35°, 50°, and 65°C) in a G24 Environmental Incubator-Shaker, New Brunswick Scientific Company, Inc., Edison, New Jersey.

Standard buffers were prepared as follows: the pH 4.00 buffer was prepared from 500 mL 0.1 M potassium hydrogenphthalate, 10 mL 0.1 M HCl, and DI water to 1.0 L. The pH 7.00 buffer was prepared from 500 mL 0.1 M  $\text{KH}_2\text{PO}_4$ , 291 mL 0.1 M NaOH, and DI water to 1.0 L. The pH 10.00 buffer was prepared from 500 mL 0.025 M sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), 183 mL 1.0 M NaOH, and DI water to 1.0 L. All stock buffers and glassware were autoclaved at 180°C for 1 hr before use.

## Procedure B

A 3500 mg/L stock was prepared by dissolving CL-20 in ACN. Reaction media were prepared by adding appropriate amounts of the ACN stock solution into 100 mL DI water and 100  $\mu$ L of the appropriate buffer. The amount of ACN added never exceeded 0.5% of the total solution volume, which is below the 1% external solvent limit set by the Environmental Protection Agency (EPA) protocol. The reaction flasks were incubated in the dark at three different temperatures (35°, 50°, and 65°) in a G24 Environmental Incubator-Shaker.

CL-20 disappearance was monitored by a high pressure liquid chromatography (HPLC) at room temperature. The HPLC method was based on the US EPA Standard Method 8330 (ref. 5). Measurements for CL-20 concentration were performed in a Varian high-performance liquid chromatograph with a 9065 Polychrom ultra violet detector, 9095 autosampler, and 9010 pump. A Symmetry Shield™ RP-18 (3.9 mm x 150 mm) 5  $\mu$ m column (Waters®, Milford, Massachusetts) was used. The mobile phase was an isocratic binary mixture water and ACN (40:60 v:v) pumped at a flow rate of 1.0 mL min<sup>-1</sup>. The analytical wavelength for spectrophotometric detection was 229 nm. Under these conditions, CL-20 elutes as a symmetrical peak with a retention time of 3.5 min.

Samples from the 35°C series were prepared by placing 1.0 mL of the corresponding buffered solutions in 2.0-mL screw-top glass vials [12 x 32 mm, with polypropylene/polytetrafluoroethylene (Teflon (PTFE)) septa, by Varian]. These samples were analyzed directly by HPLC. However, to avoid precipitation of CL-20, samples for analysis from the 50°C and 65°C series were prepared for analysis by diluting of 0.5 mL of the corresponding reaction solutions with 0.5 mL of ACN warmed to the corresponding reaction temperature.

Samples of  $\epsilon$ -CL-20 powder weighing 0.3 to 0.5 g were first dissolved in a pure solvent (ACN and acetone) and then re-crystallized at room temperature and the hydrolytic temperatures. X-ray diffraction (XRD) patterns of re-crystallized powdered samples were obtained with a Rigaku-TXR 3000 apparatus using CuK $\alpha$  radiation. The rate was 20/min over a range of 5 to 50 deg.

## RESULTS AND DISCUSSION

Figures 1 to 3 show the time-course disappearance of CL-20 due to hydrolysis at three reaction temperatures and pH levels, when experimental procedure A was used. The temperature-corrected pH values for each buffer were calculated using the pH-temperature relationships reported by Bates (ref. 6). For all buffers, the correction factors were found to be negligible, and no corrections were necessary.

Assuming, at first, that all three possible mechanisms of hydrolysis are operative [i.e., acid-catalyzed, base-catalyzed, and not catalyzed (neutral)], it is important to determine what species - H<sup>+</sup>, OH<sup>-</sup>, or H<sub>2</sub>O - has the greatest contribution to the rate of hydrolysis. Faster CL-20 disappearance was observed with increasing pH, suggesting that an important contribution to CL-20 hydrolysis is that of OH<sup>-</sup> ions. The plots of the logarithms of  $k'$  versus pH at 35°, 50°, and 65°C yield positive slopes of 0.0220, 0.0208, and 0.0213, respectively, implying (ref. 3) that the hydrolysis of CL-20 within the pH range investigated and under the given conditions was most strongly dependent on the concentration of OH<sup>-</sup>, that is, the OH<sup>-</sup> catalyzed hydrolysis is the dominant reaction pathway, and that the contributions of the other two pathways are relatively low.

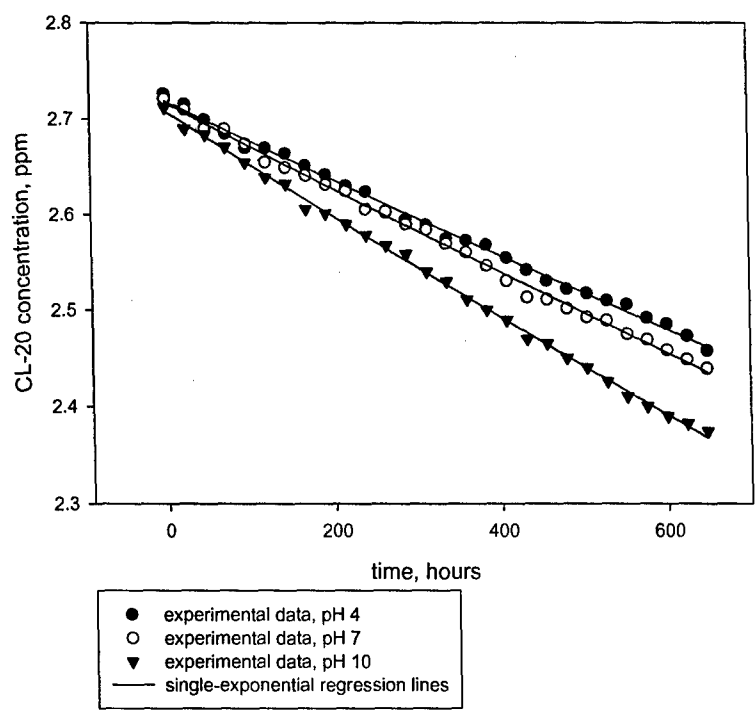


Figure 1  
Hydrolysis of  $\epsilon$ -CL-20 at 35°C

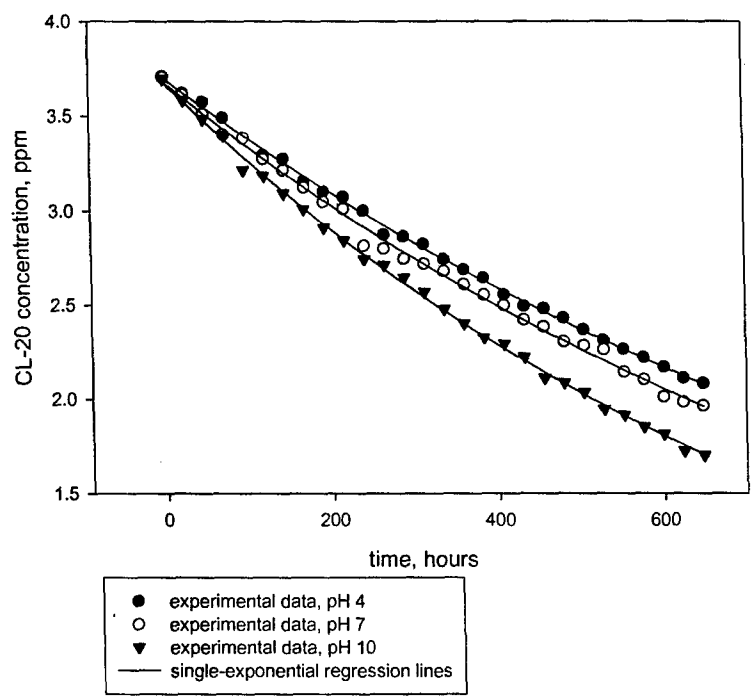


Figure 2  
Hydrolysis of  $\epsilon$ -CL-20 at 50°C

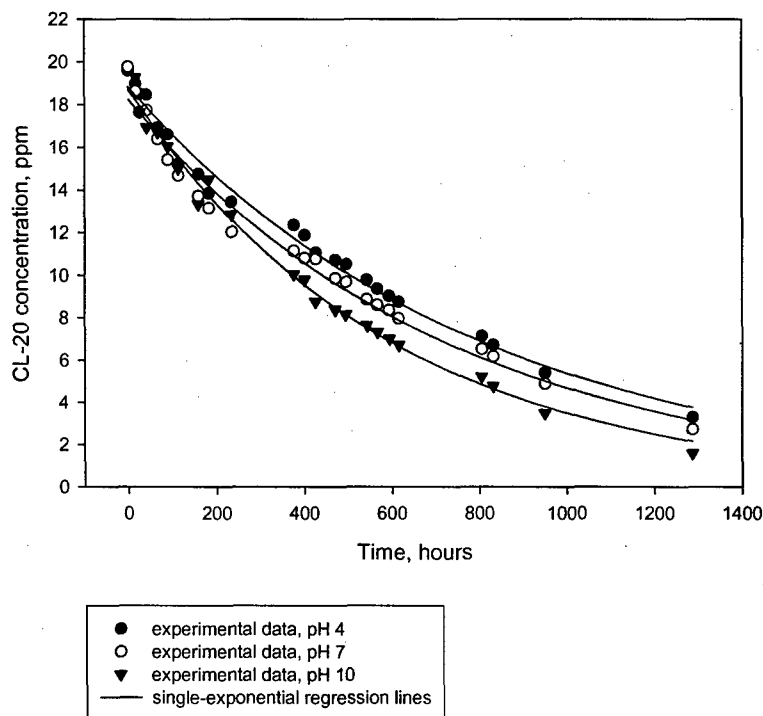


Figure 3  
Hydrolysis of  $\epsilon$ -CL-20 at 65°C

To test for the possibility that the neutral ( $k_N$ ) and the acidic ( $k_H$ ) pathways could also be contributing to the CL-20 hydrolysis, we plotted the observed  $k'$  at the different pHs and temperatures against the  $[OH^-]$  concentration. If the neutral and acidic pathways do not contribute to the overall hydrolysis, the plots should extrapolate to zero. The intercepts for the 35°, 50°, and 65°C extrapolate to  $0.0002 \pm 0.00003$ ,  $0.0009 \pm 0.00004$ , and  $0.0013 \pm 0.0001$  (95% confidence level), respectively, none of which is significantly different from zero. However, there is a trend in these numbers that could indicate that the low contribution of the neutral pathway may increase with temperature. A similar observation was made by Steinberg and Lena (ref. 3) in ester hydrolysis. Therefore, the contribution of the acid-catalyzed pathway was negligible, and  $k_{OH}$  was computed from the pH-10 hydrolysis data using

$$k_{OH} = \frac{k'_{(pH=10)}}{[OH^-]} \quad (4)$$

The value of  $k_N$  is then estimated by subtracting the contribution of the base-catalyzed pathway from the pH-7 hydrolysis data using

$$k_N = k'_{(pH=7)} - k_{OH} [OH^-] \quad (5)$$

The obtained values for  $k_{OH}$  and  $k_N$  are shown in table 1.

Table 1  
Rate constants of hydrolysis of  $\epsilon$ -CL-20

Temperature, °C	$k_{OH}$ , hr <sup>-1</sup>	$k_N$ , hr <sup>-1</sup>
35	2.077	$1.690 \times 10^{-4}$
50	11.87	$9.719 \times 10^{-4}$
65	16.77	$1.357 \times 10^{-3}$

A regression analysis of the data given in table 1 yields the activation energies and Arrhenius constants for the base and neutral hydrolyses which are presented in table 2.

Table 2  
Activation energies and pre-exponential factors for hydrolysis of  $\epsilon$ -CL-20

Pathway	$E_a$ , kJ/mol	$A$ , hr <sup>-1</sup>
Basic	60.896	$5.370 \times 10^{10}$
Neutral	60.745	$4.131 \times 10^6$

Figures 4 to 6 show the disappearance of CL-20 with time due to hydrolysis in water at three reaction temperatures and three pH levels, when experimental procedure B was used. An attempt to fit a first-order (single-exponential) kinetic model to the data produced unsatisfactory results. Next, the data were fitted using the following double-exponential model

$$C = C_{1,0}e^{-k_1t} + C_{2,0}e^{-k_2t} \quad (7)$$

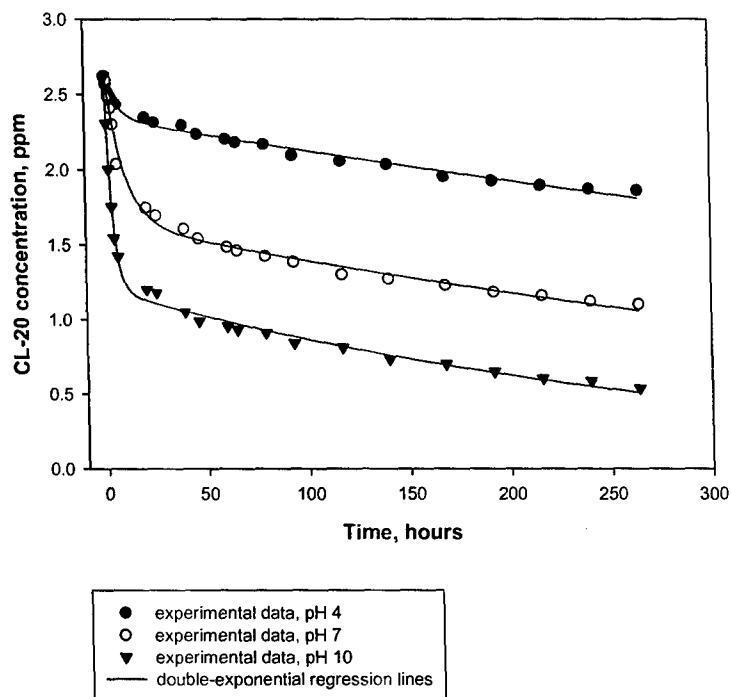


Figure 4  
Hydrolysis of CL-20 at 35°C (CL-20 introduced from ACN)

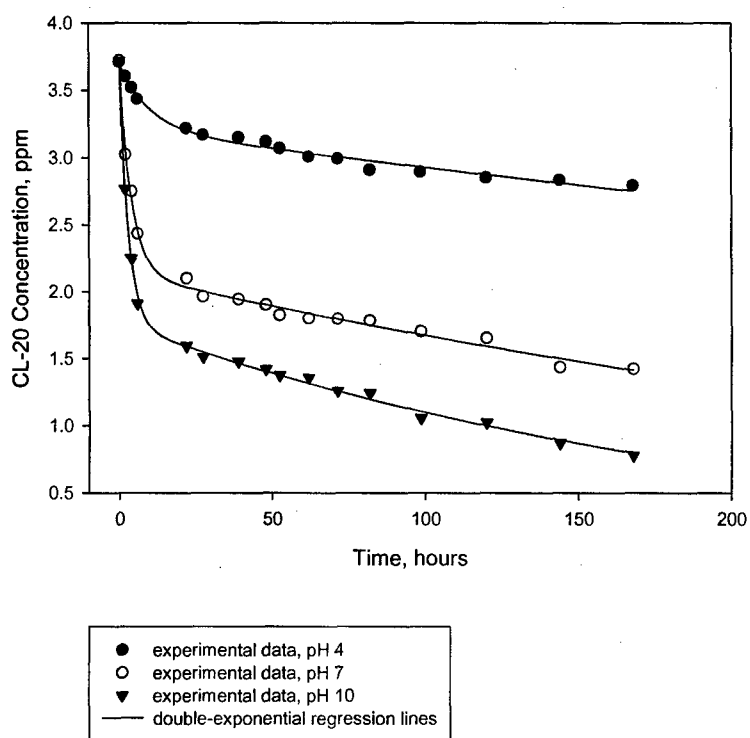


Figure 5  
Hydrolysis of CL-20 at 50°C (CL-20 introduced from ACN)

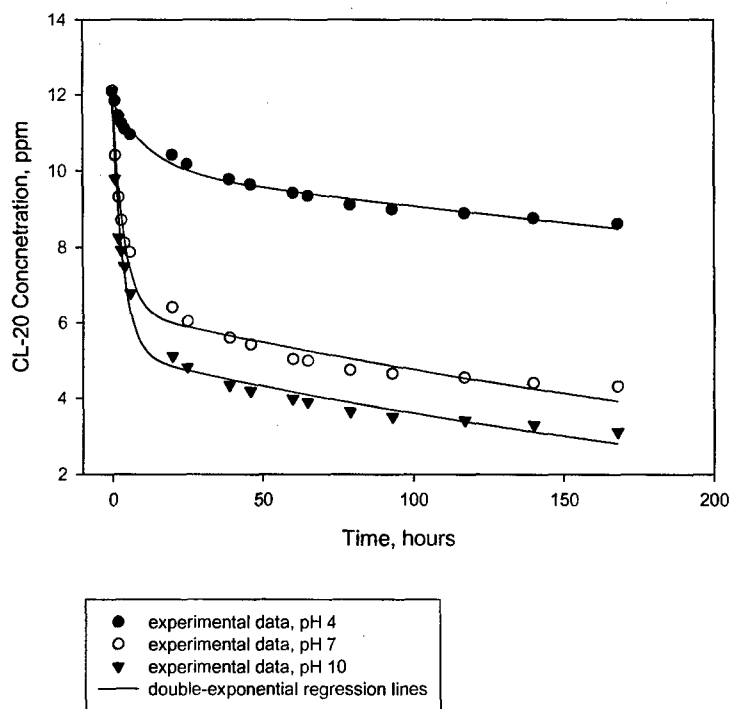


Figure 6  
Hydrolysis of CL-20 at 65°C (CL-20 introduced from ACN)

As shown in table 3, this model fits the data very well.

Table 3  
Kinetic parameters for CL-20 aqueous hydrolysis (with ACN)

Temperature, °C	pH	C <sub>1,0</sub> , mg/L	k' <sub>1</sub> , hr <sup>-1</sup>	C <sub>2,0</sub> , mg/L	k' <sub>2</sub> , hr <sup>-1</sup>	R <sup>2</sup>
35	4	0.2633	0.1623	2.3436	0.0010	0.9895
35	7	1.0098	0.1089	1.6491	0.0017	0.9937
35	10	1.4496	0.3097	1.1999	0.0033	0.9958
50	4	0.4849	0.0977	3.2105	0.0009	0.9882
50	7	1.5630	0.2512	2.1426	0.0025	0.9952
50	10	1.9640	0.3394	1.7620	0.0047	0.9983
65	4	1.8376	0.0797	10.0098	0.0010	0.9838
65	7	5.5416	0.2605	6.3172	0.0028	0.9878
65	10	6.5325	0.2820	5.1885	0.0036	0.9877

It was established that solvent polarity can exert powerful influence on molecular conformation (ref. 7). This led us to postulate the co-existence of two conformers of CL-20 (polymorphs  $\alpha$  and  $\beta$ ) in the aqueous solution, which are formed due to the interaction of the parent molecule with ACN (CH<sub>3</sub>CN) in the stock solution. Accordingly, it was suggested that the hydrolysis proceeds as shown in figure 7.

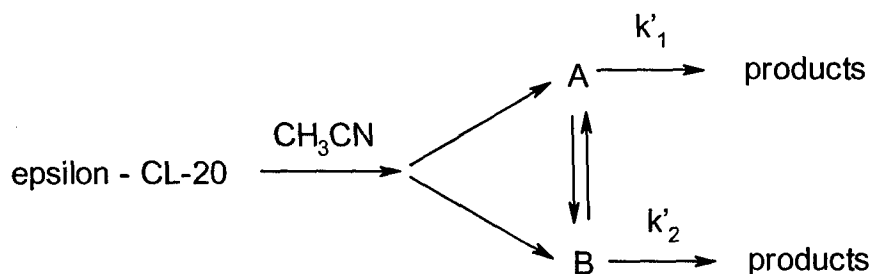


Figure 7  
Suggested reaction scheme for CL-20 hydrolysis when ACN stock solution is used

The slopes of  $\log k'$  and  $\log k'$  versus pH plots at 35°, 50°, and 65°C are shown in table 4. As in the case of the hydrolysis of  $\epsilon$ -CL-20 (procedure A), the slopes are positive. These slopes are much greater for each conformer than those obtained with  $\epsilon$ -CL-20, which indicates a stronger dependence on the [OH<sup>-</sup>]. As in the case with  $\epsilon$ -CL-20 hydrolysis, we observed that there was a trend in these numbers, which could indicate that the low contribution of the neutral pathway may increase with temperature.

Table 4  
Slopes of  $1nk'_1$  versus pH for the CL-20 hydrolysis from ACN stock solution

T, °C	Slope of $1nk'_1$ versus pH	R <sup>2</sup>	Slope of $1nk'_2$ versus pH	R <sup>2</sup>
35	0.1072	0.923	0.1990	0.996
50	0.2075	0.915	0.2755	0.988
65	0.2106	0.804	0.5973	0.826

We proceeded as with the  $\epsilon$ -CL-20 hydrolysis, to test for the possibility that the neutral ( $k_N$ ) and the acidic ( $k_H$ ) pathways could also be contributing to the CL-20 hydrolysis in both parallel reactions. The plots of observed  $k'_1$  and  $k'_2$  at the different pH's and temperatures versus the [OH<sup>-</sup>] concentration yield the slopes and intercepts shown in table 5.

Table 5  
Intercepts of the plots of  $k'_1$  and  $k'_2$  versus [OH<sup>-</sup>]

T, °C	$k'_1$ versus [OH <sup>-</sup> ]		$k'_2$ versus [OH <sup>-</sup> ]	
	Intercept	R <sup>2</sup>	Intercept	R <sup>2</sup>
35	0.1355 ± 0.0091	0.931	0.0090 ± 0.0015	0.852
50	0.1699 ± 0.0701	0.910	0.0017 ± 0.0004	0.824
65	0.1743 ± 0.0325	0.840	0.0145 ± 0.0025	0.833

As in the case of  $\epsilon$ -CL-20 hydrolysis, the contributions of the acid-catalyzed and neutral pathways were evaluated. The values of the intercepts of  $k'_1$  and  $k'_2$  versus [OH<sup>-</sup>] plots are again small, which indicates that the acid-catalyzed pathways for both conformers are negligible. However, since the  $k'_2$  intercepts are much smaller and closer to zero than those of the  $k'_1$  plots, the neutral pathway contribution was much lower in the second reaction proposed in figure 8 (B → Products) as compared to the first reaction (A → Products).

The values of  $k_{OH}$  and  $k_N$  and the Arrhenius parameters shown in tables 6 and 7, respectively, were computed using the same procedure as in the case of  $\epsilon$ -CL-20 hydrolysis.

Table 6  
Hydrolysis rate constants of CL-20 introduced from ACN stock solution

Temperature, °C	Case 1		Case 2	
	$k_{OH}$ , hr <sup>-1</sup>	$k_N$ , hr <sup>-1</sup>	$k_{OH}$ , hr <sup>-1</sup>	$k_N$ , hr <sup>-1</sup>
35	1464	0.0797	33	8.97 × 10 <sup>-4</sup>
50	2023	0.0977	47	2.495 × 10 <sup>-3</sup>
65	2417	0.1623	36	4.696 × 10 <sup>-3</sup>

Table 7  
 Activation energies and pre-exponential factors for hydrolysis of CL-20  
 introduced from ACN stock solution

Pathway	$E_a$ (1), kJ/mol	$A$ (1), hr <sup>-1</sup>	$E_a$ (2), kJ/mol	$A$ (2), hr <sup>-1</sup>
basic	9.6359	69,982.5	2.7852	126,374
neutral	20.386	215.81	47.944	108.1

To validate the proposed reaction scheme (fig 7), x-ray diffractometric analyses were performed on CL-20 re-crystallized from ACN. The results indicate that the re-crystallized material consists of a mixture of the  $\alpha$  and  $\beta$  polymorphs of CL-20 (fig. 8). No changes in the polymorph structure were observed when  $\epsilon$ -CL-20 was re-crystallized from acetone.

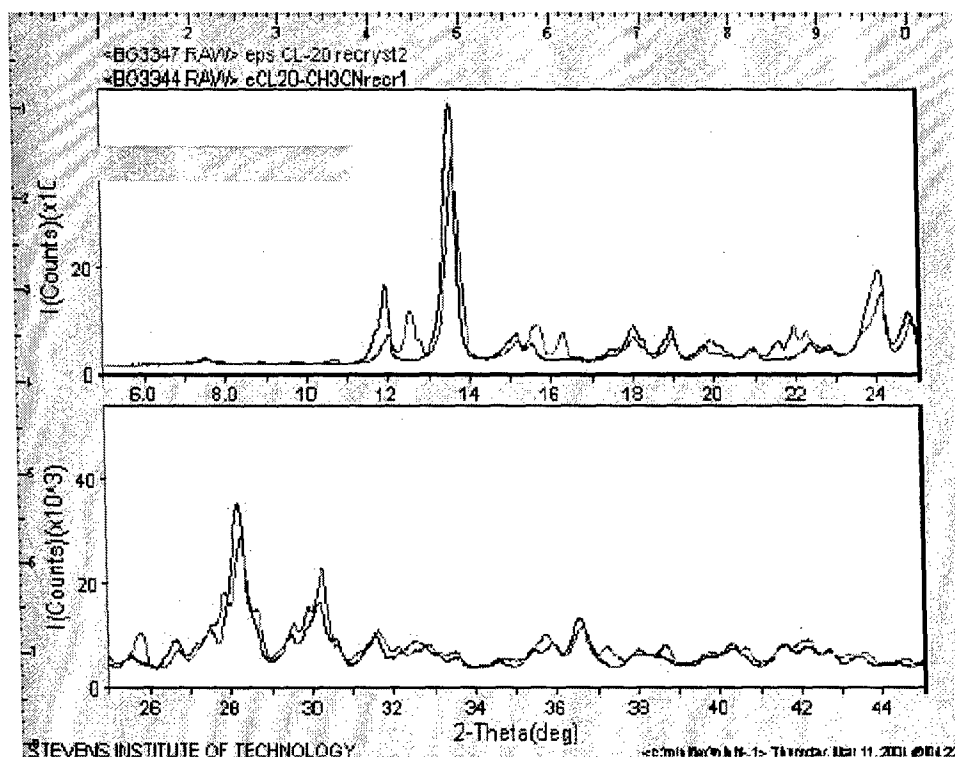
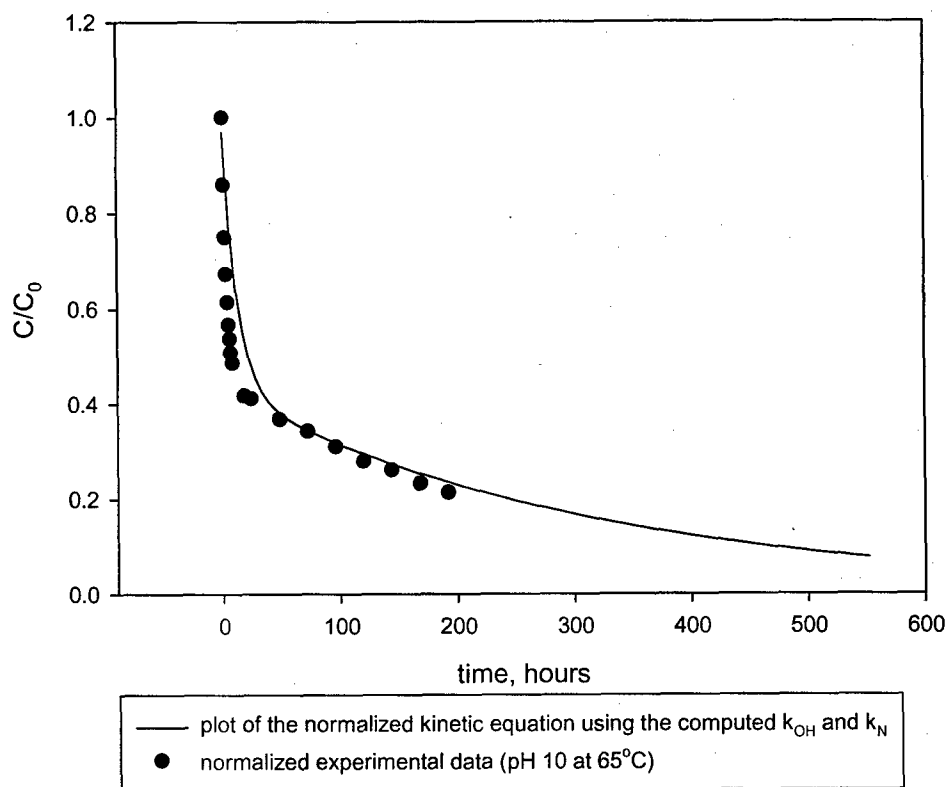


Figure 8  
 X-ray diffraction patterns of two regions of  $\epsilon$ -CL-20 sample re-crystallized from ACN

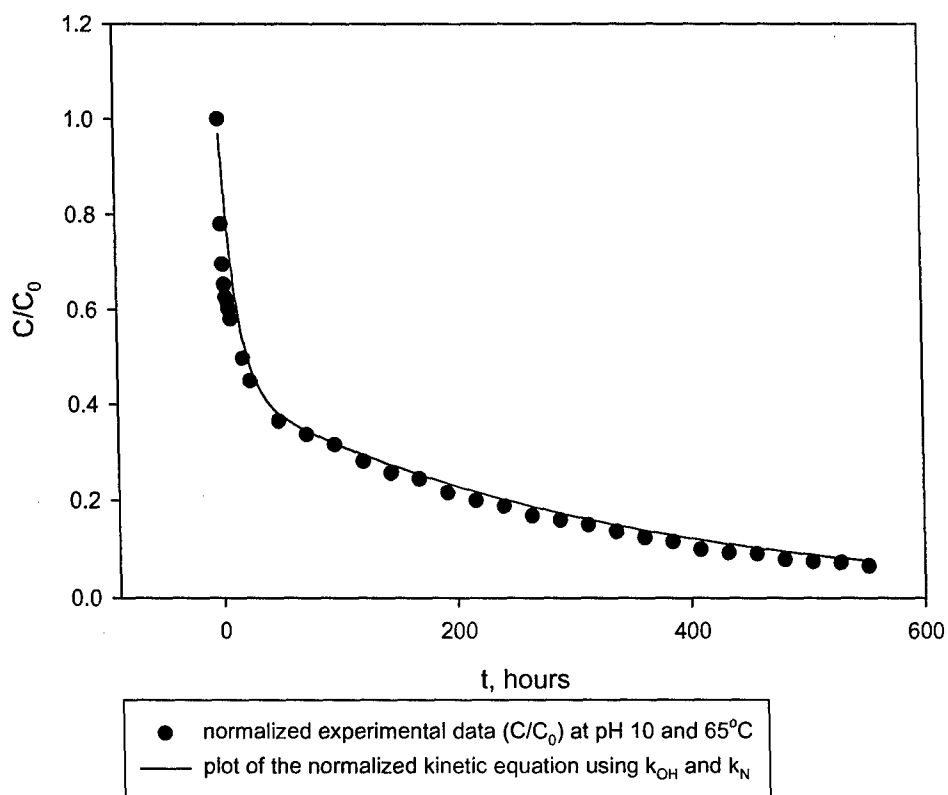
To test the predictive capability of the calculated kinetic parameters, two additional hydrolysis experiments were carried out. For the first one, the starting solution was prepared by dissolving in water CL-20 re-crystallized from ACN (as per procedure A). Figure 9 clearly illustrates that the proposed kinetic parameters predict the CL-20 time-concentration profile very well. In addition, the results confirm the existence of two conformers.



A good fit is obtained with the normalized kinetic equation  $C/C_0 = C_{1,0}/C_0 \cdot \exp(-k_{OH,1}[\text{OH}^-] - k_{N,2})t + C_{2,0}/C_0 \cdot \exp(-k_{OH,2}[\text{OH}^-] - k_{N,2})t$  for the corresponding hydrolytic run with CL-20 introduced from ACN stock solution.

Figure 9  
Hydrolysis of CL-20 re-crystallized from ACN (65°C, pH 10)

For the second additional experiment, the starting solution was prepared by introducing CL-20 from ACN stock solution (as per procedure B), but at higher initial concentration ( $\sim 30$  mg/L). Again, as shown in figure 10, the proposed kinetic parameters predict the experimental data very well.



A good fit is obtained with the normalized kinetic equation  $C/C_0 = C_{1,0}/C_0 \cdot \exp(-k_{OH,1}[\text{OH}^-] - k_{N,2})t + C_{2,0}/C_0 \cdot \exp(-k_{OH,2}[\text{OH}^-] - k_{N,2})t$  for the corresponding hydrolytic run with CL-20 introduced from ACN stock solution.

Figure 10

Hydrolysis of CL-20 (introduced from ACN) with higher initial concentration (65°C, pH 10)

## CONCLUSIONS

Our results in the pH range of 4 to 10 show that the hydrolysis of CL-20 is predominantly base-catalyzed, and that only this mechanistic pathway need be considered when estimating the effects of environmental pH on the stability of CL-20. The hydrolysis of  $\epsilon$ -CL-20 follows a first-order exponential decay pathway. However, CL-20 taken from acetonitrile (ACN) stock solution hydrolyzes much faster and follows a double exponential model. The latter reflects on the CL-20 crystalline structure when it is re-crystallized from ACN, which was confirmed by XRD analyses. It is therefore inadvisable for ACN to be used as a storage solvent for the propellant, and for experiments that involve subsequent re-crystallization of CL-20, such as sand coating and soil experiments, and for the preparation of CL-20 stock solutions. However, if acetone is used to dissolve and re-crystallize CL-20, the  $\epsilon$  polymorph structure is not altered. This, combined with the lower toxicity and higher volatility of that solvent next to those of ACN, suggests that acetone should be the solvent of choice in CL-20 research.

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