Study on Kinetics of GD Hydrolysis in HCl aqueous

Shaoxiong Wu¹, Hongpeng Zhang¹, Ting Miao¹, Haiyan Zhu¹, Lianyuan Wang^{1, a*} and Liang Ge^{1, b*}

¹Institute of Chemical Defence, Army, Beijing, 102205, China

Abstract. Organophosphate neurotoxic agents like Sarin (GB) and Soman (GD) are lethal to person. Except various kinds of decontaminants, they can be also decomposed in natural environment through nucleophilic reaction, where acidic or alkaline substance was to accelerate their hydrolysis. Most of the papers were about GB hydrolysis. Information on GD hydrolysis was relatively small, especially about kinetics of GD in acidic solution. In view of possible effect of positive ion and negative ion on hydrolysis reaction, a relatively simple composes solution, HCl aqueous solutions, was selected to investigate the factors affecting GD hydrolysis rate. Results showed that GD hydrolysis was accorded with the first-order kinetics equation if pH value was kept constant. Its rate constant was independent of GD initial concentration when the amount of H⁺ was excess than its requested amount. The apparent hydrolysis rate constant (k_{obs}) in pH of 0.90 was about 0.202 min⁻¹ at 20°C, no matter what initial concentration of GD was. The concentration of H⁺ was the most important factor affecting its rate. The rate constant (k_{obs}) in HCl aqueous as a function of pH value (0.90~2.80) obeyed an equation in 25°C, that is $k_{obs} = 0.17 \times 10^{-0.82 \times \text{pH}}$. Reaction temperature had an obvious effect on hydrolysis rate of GD. Every 10°C increase in temperature, k_{obs} of GD hydrolysis was improved about 2.5 times. The activation energy value (E_a) of GD hydrolysis in HCl aqueous with a pH value of 0.90 was approximately 64.25 kJ/mol.

1 Introduction

Sarin (isopropyl methylphosphonofluoridate, GB) and Soman (pinacolyl methylphosphonofluoridate, GD) are highly toxic through dermal, oral, or inhalation routes [1]. Higher doses can result in excessive sweating, nausea and vomiting, difficulty breathing, convulsions and tremors, followed by death in minutes at sufficiently high doses.

Figure 1. Structure of Sarin (a) and Soman (b).

They can be decomposed through nucleophilic reaction, forming less harmful products. Except various kinds of decontaminants, such as hypochlorite [2], DF-200 [3], Decon Green [4], GDS2000 [5] and GD 6 [6], etc., they can also be degraded in natural environment, where acidic or alkaline substance was to accelerate their hydrolysis. Several workers have measured half-lives and rate constants for the GB hydrolysis at various pH values and temperatures [7-10]. The activation energy values (E_a) were 10.6 kcal mole⁻¹ [9] and 9.1 kcal mole⁻¹ [10] for base-promoted GB hydrolysis. It was reported that divalent cations are likely to catalyse the hydrolysis reaction [11,12]. Information on GD hydrolysis was relatively small, especially about kinetics of GD in acidic solution.

In view of the possible effect of positive ion and negative ion on hydrolysis, HCl aqueous, whose constitute was relatively simple, was as an acidic solution to study GD hydrolysis. Factors like GD concentration, pH value and reaction temperature on the hydrolysis rate were investigated. The activation energy (E_a) of GD hydrolysis in HCl aqueous solution was calculated according to hydrolysis rate at different temperatures.

2 Experimental

2.1 Materials

The toxic agent of GD has a purity >95%. Because of its high toxicity, it was handled only by well-trained personnel using appropriate safety procedures.

Hydrochloric acid (HCl, 36%, A. R.) was from Beijing Agents Inc. HCl aqueous with pH value ranging from 0.90 to 2.80 worked as decontaminant solutions were prepared by mixing HCl (36%) and deionized water at different ratios.

N-hexane (C. R., Meryer Reagent Company) was used as extractant of residual GD from hydrolysis samples as well as the solvent of GD standard solution.

Triethyl phosphate (C₆H₅PO₄) with a purity >98% (from Alfa Aesar) was as internal standard of GD analysed with GC-FPD. Its solution was prepared by 40 µl of triethyl phosphate in 10 ml n-hexane.

* Corresponding author: ^awangly09@sina.com

^b414945970@qq.com

2.2 Methods

2.2.1 Hydrolysis reaction

A three-neck flask with 300 ml HCl aqueous was placed in water bath (HH-2, a precision of 0.1°C) for 30 min in advance. Hydrolysis reaction was done when a certain dosage of GD (30 ~ 300 mg, 100~10000 mg/l) was added into 300 ml HCl aqueous (pH of 0.90 to 2.80) under a constant temperature ranging from 10°C to 40°C. Meanwhile, a digital (IKA RW20) worked at a speed of 1000 rpm to ensure the hydrolysis reaction undergoing in a homogenous solution, and a pH/ORP/temperature Meter (HI2221 HANNA) monitored pH value and temperature online.

2.2.2 Sampling and Analysis

2 ml solution in different reaction time was sampled from the three-neck flask and mixed with 5 ml of n-hexane in a 25 ml tube. Then it was immediately shaken for 20 s. After standing for 15 min, the upper n-hexane phase was removed for residual GD hydrolysis.

Residual GD was quantitatively analyzed by a gas flame photometric detector (GC-FPD) (Agilent 6890N) equipped with an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm), employing a temperature program (60 - 280°C at 15°C /min) and N₂ as carrier gas.

2.2.3 Calculation of GD hydrolysis rate

The residual ratio of GD (R , %) could be calculated as formula (1), where C_0 and C_t are the concentration of GD in reaction time of 0 and t , respectively, $A_{i,0}$ and $A_{s,0}$ are areas of GD and internal standard in initial GD sample respectively, while $A_{i,t}$ and $A_{s,t}$ are areas of GD and internal standard in GD hydrolysis sample of reaction time t respectively. The hydrolysis ratio of GD (D , %) could be calculated as formula (2).

$$R(\%) = \frac{C_t}{C_0} \times 100\% = \frac{A_{i,t} / A_{s,t}}{A_{i,0} / A_{s,0}} \times 100\% \quad (1)$$

$$D(\%) = 100\% - R(\%) \quad (2)$$

Since the concentration of H⁺ in HCl solution was 2.3 to 228.9 times larger than that of GD, and pH value as well as temperature were almost constant during GD hydrolysis, the hydrolysis reaction of GD was consequently considered to follow first order kinetics, and the first order kinetic rate constant (k_{obs} , min⁻¹) could be calculated through formula (3) and (4).

$$v = k_{obs} \cdot C_t \quad (3)$$

$$\ln\left(\frac{C_0}{C_t}\right) = \ln\left(\frac{100}{R(\%)}\right) = k_{obs} \cdot t \quad (4)$$

Half-life of GD hydrolysis ($t_{1/2}$, min) could be obtained from formula (5)

$$t_{1/2} = \frac{\ln 2}{k_{obs}} \quad (5)$$

The activation energy (E_a) and pre-exponential factor (A) are obtained according to Arrhenius equation as formula (6).

$$\ln k_{obs} = -\frac{E_a}{RT} + \ln A \quad (6)$$

3 Results and discussion

Theoretically, GD Hydrolysis in HCl solution could be affected by factors such as GD concentration, pH value and temperature, thus their effects on GD hydrolysis rate were investigated in experiments.

3.1 Effect of GD concentration

GD hydrolysis of different initial concentrations (100 ~ 10000 mg/l) in HCl solution at pH 0.90 were conducted, and the temperature was fixed at 20°C. Their related molar ratios of H⁺ and GD were from 228.9:1 to 2.3:1. The hydrolysis ratios of GD with reaction time in HCl solution were obtained according to formula (1) and (2), and the results were showed in Figure 2.

Figure 2. GD hydrolysis ratio (D %) with reaction time.

It can be found in Figure 2 that GD hydrolysis ratios at same reaction time were almost equal no matter which initial GD concentrations they were. Their hydrolysis ratios of GD increased with reaction time. Especially within 30 min, almost half of GD was degraded. Then the speed of GD hydrolysis slowed down gradually. After 180 min, a high hydrolysis ratio of 99% could be obtained. It suggested the residual GD could reach to a less toxic level in HCl solution at pH 0.90 after several hours.

When the initial GD concentration (C_{GD}) was 10000 mg/l, there was a well linearity (see Figure 3) between $\ln(1/R)$ and reaction time t , suggesting GD hydrolysis in HCl solution (pH of 0.90) conformed to the characteristics of the first-order reaction. Its k_{obs} was 0.0204 min⁻¹ according to Formula (4). Similar results could be found in other reactions with different initial C_{GD} (Table 1). Their rate constants (k_{obs}) and half-time ($t_{1/2}$) were almost equal as about 0.02 min⁻¹ and 34 min, where the pH of HCl solution was at 0.90. It inferred that reaction rate constant was not mainly related to initial GD concentration. Thus,

the initial C_{GD} was fixed at 100 mg/l in subsequent experiments.

Figure 3. Semilog kinetic plot of the reaction of 10000 mg/l GD hydrolysis in HCl aqueous at pH 0.90.

Table 1. k_{obs} of various initial GD concentrations in HCl aqueous

Initial C_{GD} / (mg/l)	$nH^+ : n_{GD}$	$k_{obs} / \text{min}^{-1}$	Fitting (R^2)	$t_{1/2} / \text{min}$
100	228.9 : 1	2.04×10^{-2}	0.9967	34.0
200	114.4 : 1	2.03×10^{-2}	0.9957	34.1
500	45.8 : 1	2.01×10^{-2}	0.9991	34.5
1000	22.9 : 1	2.02×10^{-2}	0.9932	34.3
10000	2.3 : 1	2.01×10^{-2}	0.9995	34.5

*20 °C; pH value 0.90; Stirring 1000 rpm.

3.2 Effect of pH value

In order to keep GD hydrolysis carried out in a constant pH value, molar content of H^+ should be larger than GD. Thus, pH values of HCl aqueous were changed from 0.90 to 2.80 (Table 2), to investigate effect of H^+ concentration on GD hydrolysis. k_{obs} and $t_{1/2}$ of GD (initial C_{GD} of 100 mg/l) hydrolysis in different HCl aqueous at 25°C were calculated through formula (4) and (5). Results were shown in Table 2.

It could be found from Table 2 that rate constants (k_{obs}) in HCl aqueous were related to H^+ concentration (pH value), the higher H^+ concentration was, the higher k_{obs} was, and the shorter half-time was. k_{obs} in solution at pH 0.90 was 32 times larger than that in solution at pH 2.80. It revealed that H^+ accelerated GD hydrolysis. Electropositive of P atom was enhanced through H^+ combining with F (P-F) in GD, forming an activated intermediate (see Formula 7). High H^+ concentration was favourable in this activation process. Therefore, higher k_{obs} was obtained in solutions at relatively lower pH.

Table 2. k_{obs} and $t_{1/2}$ of GD hydrolysis in HCl aqueous at different pH values.

pH	$nH^+ : n_{GD}$	$k_{obs} / \text{min}^{-1}$	$t_{1/2} / \text{min}$
0.90	228.9 : 1	3.20×10^{-2}	21.7

1.23	107.1 : 1	1.72×10^{-2}	40.3
1.78	30.2 : 1	5.60×10^{-3}	123.8
2.30	9.1 : 1	1.80×10^{-3}	385.1
2.80	2.9 : 1	1.00×10^{-3}	693.1

*25 °C; Initial C_{GD} 100 mg/l; Stirring 1000 rpm.

The effect of H^+ concentration on GD hydrolysis was further studied. There was a good linear relationship between $\lg k_{obs}$ and pH value (Figure 4). k_{obs} of GD hydrolysis in HCl aqueous as a function of pH value (0.90~2.80) obeyed the following equation: $k_{obs} = 0.17 \times 10^{-0.82 \times \text{pH}}$ ($T=25^\circ\text{C}$).

Figure 4. The plot of logarithmic k_{obs} with different pH values of HCl aqueous.

3.3 Effect of reaction temperature

GD hydrolysis in HCl aqueous (pH 0.90) under five different reaction temperature (10°C~40°C) were done to investigate the effect of temperature on GD hydrolysis. The first-order apparent rate constant (k_{obs}) and half-time ($t_{1/2}$) were calculated through formula (4) and (5), respectively. They were showed in Table 3.

Results suggested temperature was an essential factor for GD hydrolysis. High temperature could accelerate GD degradation in HCl solution. Table 3 showed that k_{obs} increased by 2.5 times for every 10°C of reaction temperature rose.

The relationship between reaction temperature and GD hydrolysis rate constants in HCl aqueous was fitted by formula (5), and the result was shown in Figure 5. The slope and intercept of the line (Figure 5) was the activation energy (E_a) and pre-exponential factor (A) of GD hydrolysis reaction. The value of E_a and $\ln A$ was about 64.25 kJ/mol and 22.5 min^{-1} , respectively. Such E_a of 64.25 kJ/mol suggested that reaction temperature was still an important factor, even if H^+ acted as a catalyst in this reaction. [1]

Table 3. k_{obs} and $t_{1/2}$ of GD hydrolysis in HCl aqueous at different reaction temperatures.

T/°C	$k_{obs} / \text{min}^{-1}$	$t_{1/2} / \text{min}$
10	8.90×10^{-3}	77.9
20	2.02×10^{-2}	34.3
25	3.50×10^{-2}	19.8
30	5.10×10^{-2}	13.6
40	1.20×10^{-1}	5.8

*Initial C_{GD} 100 mg/l; pH value 0.90; Stirring 1000 rpm.

Figure 5. Rate of GD hydrolysis in HCl aqueous (pH 0.90) at different temperatures.

4 Conclusions

GD with different initial concentrations hydrolysis in HCl aqueous at pH 0.90 and 20°C was conducted. It showed that GD hydrolysis could be regarded as a first-order reaction when H^+ content was more than 2.3 times of GD in HCl solution. Therefore, other data of GD hydrolysis could be calculated by first-order dynamics model to obtain first-order apparent hydrolysis rate constant.

From experiments of GD hydrolysis in HCl aqueous at different pH values (0.90~2.80), it was founded that GD hydrolysis rate was pH value dependent. The quantitative relationship between k_{obs} and pH value under 25°C was follow as $k_{obs} = 0.17 \times 10^{-0.82 \times \text{pH}}$.

The activation energy (E_a) of GD hydrolysis in HCl aqueous was about 64.25 kJ/mol. Consequently, temperature was a very important factor for GD hydrolysis in acidic solutions. Results showed that k_{obs} of GD hydrolysis increased by 2.5 times for per 10 °C of reaction temperature rise.

References

1. J. Harald, B. Frank, K. Kai, W. Franz, and T. Horst. **52**, 875-919. (2020)
2. R. Reiner and R. Rossmann. Monatshefte fuer Chemie, **113**, 223–231. (1983)
3. M. E. Tadros and M. D. Tucker. US Patent, **6,566-574**. (2003)

4. G. W. Wagner and Y.-C. Yang. Baking soda, hydrogen peroxide, alcohol the refreshing, universal
5. C. M. Boone, TNO report, TNO-DV A028, TNO Defense, Netherlands (2007).
6. GD-6 Decontamination Agent (2008) (http://www.owrgroup.net/index.php?article_id=107&clang=1)
7. Z. Rađl, F. Oplus̃til, and M. Skoumal. Stockholm, pp. 87–94. (1992)
8. J. Epstein. Journal American Water Works Association, **66**(1), 31–37. (1974)
9. R. L. Gustafson and A. E. Martell. Journal American Chemical Society, **84**(12), 2309–2316. (1962)
10. L. Larsson. Acta Chemica Scandanavica, **11**, 1131–1142. (1957)
11. J. Epstein. Science, **170**(3965), 1396–1398. (1970)
12. J. Epstein and D. H. Rosenblatt. Journal of the American Chemical Society, **80**(14), 3596–3598. (1958)