Soman hydrolysis catalysed by hypochlorite ions

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Abstract. Sarin (GB) and soman (GD) are severely toxic nerve agents that react slowly in water, resulting in long-term poisoning of the water and a serious threat to personnel. Some ions can catalyse GB and GD hydrolysis in water; the relevant research for GB is detailed, whereas that for GD is relatively less so. In this paper, GD hydrolysis catalysed by hypochlorite (ClO^-) ions was studied via kinetic experiments. A fluoride-ion-specific electrode was used to monitor F^- ions produced, allowing the rate constant and half-life of the GD hydrolysis to be calculated. The results showed that ClO^- ions promote GD hydrolysis well; the higher the concentration of ClO^- , the faster the GD was hydrolysed. In NaClO solution at pH 8.0 with $3.22 \times 10^{-3} \text{ M}$ ClO^- ions, the half-life of GD hydrolysis was 82.5 s, about 875 times shorter than that in water at pH 8.0. The rate constant for catalysis of GD hydrolysis by ClO^- ions (k_{ClO^-}) was $2.6 \text{ M}^{-1} \text{ s}^{-1}$, about one quarter the value of k_{OH^-} but over 1500 times greater than k_{B} and $k_{\text{PO}_4^{3-}}$, with B representing *N*-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid present as a free base; this result indicated that ClO^- ions catalyse GD hydrolysis well.

1 Introduction

Sarin (GB) and soman (GD) are soluble in water, but they react slowly in water with a mid-range pH value, causing long-term poisoning [1]. The spontaneous hydrolysis rate constant of GB determined in water at pH 7 is $2 \times 10^{-4} \text{ min}^{-1}$ [2], and the half-life ($t_{1/2}$) is 3465.7 min. Hydroxide (OH^-) ions can catalyse the hydrolysis of GB through a nucleophilic reaction. The GB hydrolysis rate constants in water at pH 8 and pH 9 are approximately $2 \times 10^{-3} \text{ min}^{-1}$ and $2 \times 10^{-2} \text{ min}^{-1}$, respectively [2]. Therefore, alkaline decontamination has been widely used to detoxify GB [3][4]. Detailed studies showed that other ions can catalyse hydrolysis of GB as well, and the speed of GB hydrolyses catalysed by hypochlorite ions [2], amines [5], metal ions [6], catechols [7] and phenols [8] were obviously faster than that in water at a similar pH value.

The rate of reaction for GD is slower than that for GB. For instance, the $t_{1/2}$ of GD hydrolysis in water at pH 8 is 1200 min, about four times longer than that of GB hydrolysis. This is probably because of the greater steric hindrance of the pinacolyl group on GD relative to that of the isopropyl group on GB [9].

Studies on GD hydrolysis catalysed by ions are less available than those for GB. Albizo and Ward studied GD hydrolysis catalysed by *N*-2-hydroxyethylpiperazine-*N'*-

2-ethanesulfonic acid (HEPES) and determined that the rate of hydrolysis of GD was linearly related to the concentration of HEPES present as free base (B) in the solution [10]. Creasy found that the reactivity of GB and GD increased in phosphate buffer at pH 7 relative to those in distilled water or acetate buffer [9]. Other than this, there have been few related studies in the past two decades. However, GD is more acutely toxic than GB and there is no specific medicine for poisoning caused by it, so it is necessary to study the rapid decontamination of GD.

In this paper, kinetic experiments were performed to research GD hydrolysis rates in reaction solutions with different concentrations of ClO^- ions, with a fluoride-ion-specific electrode being used to monitor the F^- ions produced from GD hydrolysis. The impacts of ClO^- ions and other factors on GD hydrolysis were studied, the rate constants and half-lives of GD hydrolysis in different reaction solutions were calculated and the catalysing effect of ClO^- ions on GD hydrolysis was compared with those of other ions.

2 Experimental section

2.1 Chemicals

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

NaClO solution was supplied by Beijing Agents Inc. The available chlorine ($[\text{Cl}]$) was determined to be about 28000 mg L^{-1} by an available chlorine rapid determination instrument (Q-CL501C), and the pH value was measured to be 12.6 with a commercial laboratory

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pH/ORP/temperature tester (HI2221 HANNA). NaH_2PO_4 and Na_2HPO_4 were obtained from Beijing Agents Inc.

A phosphate buffer solution with a composition of 0.2 M PO_4^{3-} was prepared from a mixture of 0.2 M NaH_2PO_4 (5.3 mL) and 0.2 M Na_2HPO_4 (94.7 mL), and the pH value was measured to be 8.0. Phosphate buffer solutions containing ClO^- ions in different concentrations were prepared by adding different volumes of NaClO solution. The ClO^- concentration (C_{ClO^-} or $[\text{ClO}^-]$) could be

calculated from equation (1), in which $[\text{H}^+]$ is the H^+ concentration and K_a is the acid dissociation constant of hypochlorous acid (HClO) at 25 °C, which is 4.0×10^{-8} ($pK_a=7.4$) [11]. The C_{ClO^-} and pH values of the different phosphate buffer solutions are displayed in Table 1.

$$[\text{ClO}^-] = \frac{K_a [\text{Cl}]}{[\text{H}^+] + K_a} \quad (1)$$

Table 1. ClO^- concentration (C_{ClO^-}) and pH values of phosphate buffer solutions

V_{phos} (mL)	V_{NaClO} (mL)	$[\text{Cl}]$ (mg L^{-1})	C_{ClO^-} (M)	pH value
	0	0	0	8.0
30	0.04	30	3.22×10^{-4}	8.0
	0.36	300	3.22×10^{-3}	8.0

V_{phos} and V_{NaClO} were the volume of phosphate buffer and NaClO solution, respectively.

Solid NH_4Cl (supplied by Beijing Agents Inc.) was added to NaClO solution with a ratio of 1:100 (wt:vol) to decrease the pH value of the NaClO solution from 12 to approximately 8. The reaction was as follows:

This showed that the reaction did not produce new ions in NaClO solution and resulted in a C_{ClO^-} decrease. A series of NaClO solutions with different C_{ClO^-} values were prepared by mixing the pH 8 NaClO solution and water at different volume ratios. It was found that the pH values of these NaClO solutions were all about 8 (Table 2).

Table 2. ClO^- concentration (C_{ClO^-}) and pH value of NaClO solutions

Solution	$[\text{Cl}]$ (mg L^{-1})	C_{ClO^-} (M)	pH value
	300	3.22×10^{-3}	8.0
	1500	1.61×10^{-2}	8.1
NaClO solutions with different C_{ClO^-} values	3600	3.86×10^{-2}	8.1
	6600	7.08×10^{-2}	8.2
	10000	1.07×10^{-1}	8.2

2.2 Methods

A fluoride-ion-specific electrode purchased from METTLER TOLEDO was used for real-time monitoring of the concentration of F^- produced by GD hydrolysis in solution. The GD hydrolysis ratio (R_{GD} , %) could then be calculated and the hydrolysis kinetic curve could be drawn. Kinetic experiments were carried in a thermostatic environment (25 ± 1 °C).

GD (23 μL , about 23 mg) was added to phosphate buffer solutions or NaClO solutions with different C_{ClO^-} values (30 ml), resulting in a GD concentration of about 4.21×10^{-3} M. Magnetic stirring was used to maintain a stable mass-transfer process. Changes in pH value and temperature were monitored inline with a commercial laboratory pH/ORP/temperature tester (HI2221 HANNA). GD was thought to have been completely hydrolysed when the F^- concentration changed by less than 0.1 mg L^{-1} within 15 min.

The R_{GD} value could be calculated from equation (2), in which C_{GD} (mg L^{-1}) was the GD concentration when time was t (s) and $C_{\text{GD},0}$ (mg L^{-1}) was the total GD concentration added into the reaction solution.

$$R_{\text{GD}} = \left(1 - \frac{C_{\text{GD}}}{C_{\text{GD},0}} \right) \times 100\% \quad (2)$$

Because the pH value in the reaction solutions and the temperature were controlled during the experiments, GD hydrolysis was considered to follow first-order kinetics. The first-order kinetic rate constant of GD hydrolysis (k_1 , s^{-1}) could be calculated from equation (3).

$$C_{\text{GD}} = C_{\text{GD},0} e^{-k_1 t} \quad (3)$$

The F^- concentration at the time that GD was hydrolysed completely was recorded as C_{F}^- , the F^- concentration during GD hydrolysis was $C_{\text{F}^-,t}$, and the F^- concentration at the moment that GD was added into the reaction solution was $C_{\text{F}^-,0}$, which is regarded as the background F^- concentration. This led to equations (4) and (5).

$$R_{\text{GD}} = \frac{C_{\text{F}^-,t} - C_{\text{F}^-,0}}{C_{\text{F}^-,t} - C_{\text{F}^-,0}} \times 100\% \quad (4)$$

$$k_1 t = -\ln \left(1 - \frac{C_{\text{F}^-,t} - C_{\text{F}^-,0}}{C_{\text{F}^-,t} - C_{\text{F}^-,0}} \right) \quad (5)$$

The half-life of GD hydrolysis ($t_{1/2}$, s) could be calculated according to equation (6).

$$t_{1/2} = \frac{\ln 2}{k_1} \quad (6)$$

3 Results and discussion

Initially, experiments were performed to study GD hydrolysis in phosphate buffer solutions with different

C_{ClO^-} values, and the results are shown in Table 3. Compared with that of GD hydrolysis in NaOH solution at pH 8.0, the k_1 of GD was relatively higher in phosphate buffer solution at a similar pH value. When ClO^- was introduced into the phosphate buffer solution, the speed of GD hydrolysis was further accelerated with the increase in C_{ClO^-} . Therefore, it could be concluded that ClO^- at a relatively low concentration could promote GD hydrolysis to some extent.

Table 3. GD hydrolysis in NaOH solution and phosphate buffer solutions with different ClO^- concentrations ($25 \pm 1^\circ\text{C}$)

Reaction solution	pH	Major ion in reaction solution and its concentration (M)	$C_{\text{GD},0}$ (M)	k_1 (s^{-1})	$t_{1/2}$ (s)
NaOH	8.0	OH^- , 1.00×10^{-6}		9.6×10^{-6}	72000.0
phosphate buffer	8.0	PO_4^{3-} , 2.00×10^{-1}		6.0×10^{-4}	1155.3
phosphate buffer + NaClO	8.0	PO_4^{3-} , 2.00×10^{-1} ; ClO^- , 3.22×10^{-4}	4.21×10^{-3}	1.3×10^{-3}	553.2
	8.0	PO_4^{3-} , 2.00×10^{-1} ; ClO^- , 3.22×10^{-3}		1.0×10^{-2}	69.3

Changes in the pH value during GD hydrolysis in the reaction solutions were monitored and corresponded to the GD hydrolysis rate (Figure 1). The results showed that the pH value hardly decreased during GD hydrolysis in each reaction solution and the final pH values of the solutions were very similar. Consequently, it could be concluded that the ClO^- ions did not accelerate GD hydrolysis by affecting the pH value of the reaction solution.

Temperature fluctuations during GD hydrolysis in different solutions were also monitored. It was found that the change in the temperature of the reaction solutions was within 0.1°C , so temperature fluctuation was not a factor in promoting GD hydrolysis in our experiments. In conclusion, it should be the presence of the ClO^- ions that is a critical factor for accelerating GD hydrolysis.

Figure 1 Change in pH value and hydrolysis rate of GD (R_{GD}) in phosphate buffer solutions with different C_{ClO^-} values ($C_{\text{GD},0}$ was 4.21×10^{-3} M)

GD hydrolysis in NaClO solutions with ClO^- ions at different concentrations was then studied through the kinetic experiments mentioned in the Experimental Section, and the results were compared with those for NaOH solutions. Changes in pH value were monitored (Figure 2), hydrolysis ratios of GD were calculated (Figure 3), and the first-order kinetic rate constants (k_1) and half-lives ($t_{1/2}$) of GD hydrolysis were calculated and are shown in Table 4.

Fig 2 shows that the pH values decreased slightly except in the NaClO solution with 3.22×10^{-3} M C_{ClO^-} , which might because there is not sufficient capacity to neutralise the acid produced by GD hydrolysis. However,

other solutions with higher C_{ClO^-} values had sufficient neutralising capacity, so the pH values of these solutions remained almost unchanged during GD hydrolysis.

It can be seen from Fig. 3 and Table 4 that the speed of GD hydrolysis was obviously promoted by ClO^- ions in NaClO solutions relative to that in NaOH solution at a similar pH value. In NaClO solution at pH 8.0 with 3.22×10^{-3} M C_{ClO^-} , the first-order rate constant k_1 of GD hydrolysis was $8.4 \times 10^{-3} \text{ s}^{-1}$, about 4230 times larger than that in NaOH solution at pH 8.0. The higher the C_{ClO^-} , the faster the speed of GD hydrolysis (Figure 3, Table 4), but the promoting effect of ClO^- ions on GD hydrolysis tended to be gradual (Figure 4).

Figure 2 Change in pH value during GD hydrolysis in NaClO solutions with different C_{ClO^-} values ($C_{\text{GD},0}$ was 4.21×10^{-3} M)

Figure 3 Hydrolysis ratio of GD (R_{GD}) in NaClO solutions with different C_{ClO^-} values ($C_{\text{GD},0}$ was 4.21×10^{-3} M)

Table 4. pH value, C_{ClO^-} , C_{OH^-} , and the first-order rate constant of GD hydrolysis in different reaction solutions

Reaction solution	pH	C_{ClO^-} (M)	C_{OH^-} (M)	k_1 (s^{-1})	$t_{1/2}$ (s)
NaOH	8.0	0	1.00×10^{-6}	9.6×10^{-6}	72000.0
	11.0		9.12×10^{-4}	6.1×10^{-3}	113.6
phosphate buffer + NaClO	8.0	3.22×10^{-3}	3.02×10^{-6}	8.4×10^{-3}	82.5
	8.1	1.61×10^{-2}	2.09×10^{-6}	3.0×10^{-2}	23.3
	8.1	3.86×10^{-2}	1.66×10^{-6}	4.1×10^{-2}	16.8
	8.2	7.08×10^{-2}	2.69×10^{-6}	4.7×10^{-2}	15.7
	8.2	1.07×10^{-1}	1.62×10^{-6}	5.0×10^{-2}	13.8

25 ± 1 °C; $C_{\text{GD},0} = 4.21 \times 10^{-3}$ M.

Figure 4 First-order rate constant (k_1) of GD hydrolysis in NaClO solutions with different C_{ClO^-} values

After the GD hydrolysis reached completion in NaClO solution at pH 8.0 with $3.22 \times 10^{-3} \text{ M}$ ClO^- ions, the C_{ClO^-} value of the remaining NaClO solution was determined to be $3.00 \times 10^{-3} \text{ M}$; the decrease in concentration of ClO^- ions was about $2.2 \times 10^{-4} \text{ M}$, which is less than 6% of $C_{\text{GD},0}$ ($4.21 \times 10^{-3} \text{ M}$). This indicates that few ClO^- ions were lost during GD hydrolysis. Consequently, it is reasonable to consider that the ClO^- ions accelerate GD hydrolysis via a

catalysing effect, and the mechanism proposed is as follows. Nucleophilic attack of ClO^- ions on the P atom in GD produces an intermediate product, which would transform into GD acid, with concomitant HClO formation. Dissociation of HClO would produce H^+ and ClO^- . HClO is unstable in solutions at pH 8, which is a possible reason for the slight decrease in pH value and the low loss of ClO^- ions.

The rate constant for catalysis of GD hydrolysis by ClO^- ions (k_{ClO^-} , $\text{M}^{-1} \text{ s}^{-1}$) in NaClO solution at pH 8.0 with a $3.22 \times 10^{-3} \text{ M}$ concentration of ClO^- could be calculated from equation (7) [9], in which k_1 was the first-order rate constant of GD hydrolysis in s^{-1} ; k_{OH^-} was the rate constant for the catalysis of GD hydrolysis by OH^- in $\text{M}^{-1} \text{ s}^{-1}$ (which could be obtained from equation (8) [4] and $[\text{OH}^-]$ or $[\text{ClO}^-]$ was the concentration of OH^- or ClO^- in M.

The results are shown in Table 5, in comparison with those for GD hydrolysis in other solutions. The k_{ClO^-} value was about $2.6 \text{ M}^{-1} \text{ s}^{-1}$, which is about one quarter of the value of k_{OH^-} , whereas it is over 1700 times and 2000 times larger than k_{B} (the rate constant for catalysis of GD

hydrolysis by B, in which B represents HEPES present as a free base) and $k_{\text{PO}_4^{3-}}$ (the rate constant for catalysis of GD hydrolysis by PO_4^{3-}), respectively. The results showed that the catalysing effect of ClO^- on GD hydrolysis was relatively weaker than that with OH^- , but much stronger than those of some other ions. Consequently, GD hydrolysis could be well catalysed by ClO^- ions.

$$k_{\text{ClO}^-} = \frac{k_1 - k_{\text{OH}^-} [\text{OH}^-]}{[\text{ClO}^-]} \quad (7)$$

$$k_{\text{OH}^-} = \frac{k_1}{[\text{OH}^-]} \quad (8)$$

Table 5. Rate constant of GD hydrolysis in different reaction solutions ($25 \pm 1^\circ \text{C}$, $C_{\text{GD},0} = 4.21 \times 10^{-3} \text{ M}$)

Reaction solution	pH	Major ion in reaction solution and its concentration / M	k_1 / s^{-1}	$k_i / \text{M}^{-1} \text{ s}^{-1}$
NaOH	8.0	OH^- , 1.00×10^{-6}	9.6×10^{-6}	9.6 ($i=\text{OH}^-$)
NaClO	8.0	ClO^- , 3.22×10^{-3}	8.4×10^{-3}	2.6 ($i=\text{ClO}^-$)
phosphate buffer	7.0	PO_4^{3-} , $7.66 \times 10^{-2 \text{ a}}$	9.7×10^{-5}	1.3×10^{-3} ($i=\text{PO}_4^{3-}$) ^a
HEPES buffer	7.0	B, $8.80 \times 10^{-2 \text{ b}}$	$1.4 \times 10^{-4 \text{ b}}$	1.5×10^{-3} ($i=\text{B}$) ^b

a: [9]. b: [10]. k_1 is the first-order rate constant of GD hydrolysis. k_i is the rate constant for catalysis of GD hydrolysis by different ions.

4 Conclusions

In this study, the impact of hypochlorite (ClO^-) ions on GD hydrolysis was studied. Kinetic experiments were performed to research the GD hydrolysis rate in reaction solutions with different concentrations of ClO^- ions. Factors that might affect the speed of GD hydrolysis like the pH value, temperature and concentration of ClO^- ions have been discussed. The rate constants and half-lives of GD hydrolysis in different reaction solutions were calculated, and the catalysing effect of ClO^- ions on GD hydrolysis was compared with those of other ions.

The results showed that the pH value and temperature during our experiments were not main factors that affect GD hydrolysis, whereas the presence of ClO^- ions was a critical parameter for accelerating the speed of GD hydrolysis through a catalysing effect. The first-order rate constant (k_1) of GD hydrolysis in NaClO solution at pH 8.0 with $3.22 \times 10^{-3} \text{ M}$ ClO^- ions was $8.4 \times 10^{-3} \text{ s}^{-1}$, which is 875 times larger than that in NaOH solution at pH 8.0. The higher C_{ClO^-} was, the larger k_1 was, but the increase in k_1 tended to be gradual. The rate constant for catalysis of GD hydrolysis by ClO^- ions (k_{ClO^-}) was $2.6 \text{ M}^{-1} \text{ s}^{-1}$, about one quarter that of k_{OH^-} , but it was over 1700 times and 2000 times greater than k_{B} and $k_{\text{PO}_4^{3-}}$, respectively (B represents HEPES present as a free base). In conclusion, ClO^- ions can catalyse GD hydrolysis well.

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