

## Kinetics and Mechanism of Chlorination of N-Acetylglycin by Chloramine-T In Acidic Medium

Noor H. M. Saeed

Department of Chemistry / College of Education  
University of Mosul

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### الخلاصة

تمت دراسة حركية ومي كانيكية كلورة N-اسيتايل كلايسين بالكلورامين - T بوجود حامض الهيدروكلوريك عند درجة 318<sup>0</sup> مطلقة. وتبين ان التفاعل يتبع الرتبة الاولى في كل من المادة المؤكسدة وايون الهيدروجين ولا يعتمد على تركيز N-اسيتايل كلايسين . وجد ان تغير الشدة الايونية وإضافة ايون الكلوراي لا يؤثر على سرعة التفاعل . اما إضافة ناتج التفاعل (بارا-تلوين سلفونمايد) فانه يؤثر قليلا على معدل سرعة التفاعل . كما يزداد معدل سرعة التفاعل عند تقليل ثابت العزل الكهربائي لمحيط التفاعل . ووجد ان مول واحد من N-اسيتايل كلايسين يحتاج الى مول واحد من الكلورامي ن - T . وتم حساب معاملات التنشيط الترموداينميكية وأخيرا فان الميكانيكية المقترحة وقانون سرعة التفاعل المشتق مطابق للنتائج الحركية التي حصلنا عليها .

### ABSTRACT

The kinetics of chlorination of N-acetylglycin (AG) with sodium N-chloro -p- toluene sulphonamide (CAT) in presence of HCL has been studied at 318 °K. The reaction rate shows a first-order dependence each on [CAT] and [H<sup>+</sup>] and zero order dependence on [AG]. The Variation of ionic strength of the medium or chloride ion had no significant effect on the reaction rate. Addition of P-TSA is marginally affected the reaction rate. The rate increase with decreasing dielectric constant of the medium. The stiochiometry of the reaction was found 1:1 and the oxidation products were identified. The thermodynamic parameters were computed. The mechanism proposed and the derived rate law were in agreement with the observed kinetics.

### INTRODUCTION

Sodium N-chloro-4-methylbenzenesulphonamide,  $\text{P-CH}_3\text{-C}_6\text{H}_4\text{SO}_2\text{NCl}$ .  $\text{Na } 3\text{H}_2\text{O}$ , commonly called chloramine-T (CAT,  $\text{RNCINa}$ ), behaves as an oxidizing agent in both acidic and alkaline media, and undergoes a two electron change in its reactions forming p-toluenesulphonamide (p-TSA;  $\text{RNH}_2$ ) and sodium chloride<sup>(1-5)</sup>. The reduction potential of CAT/ $\text{RNH}_2$  varies with the pH of the medium and decrease with an increase in the pH<sup>(1)</sup>, having the values of 1.14V at pH 0.65 and 0.5V at (12)pH. A review<sup>(2)</sup> on the chemistry of chloramine-T records that a number of active species such as CAT,  $\text{RNHCl}$ , DCT (dichloramine-T) and HOCl in acid solution and  $\text{RNCl}$ ,  $\text{OCI}^-$  ions in alkaline medium, are possible. Although a large number of organic and inorganic compounds have been estimated by chloramine-T, very few kinetic investigations had been carried out with this reagent, such as decomposition of hydrogen peroxide<sup>(3)</sup> in the presence of HCl, oxidation of cyanid<sup>(4)</sup> thiocyanates<sup>(5)</sup> hexacyanoferrate  $\text{II}^{(6)}$ , sulphoxides<sup>(7)</sup>,  $\alpha$  hydroxyl acids<sup>(8)</sup>, hydroxylamine<sup>(9)</sup>, primary<sup>(10)</sup> and secondary alcohols<sup>(11)</sup>, p-cresols<sup>(12,13)</sup>, phenols<sup>(14)</sup>, catacholamines<sup>(15)</sup>, aliphatic aldehydes<sup>(16)</sup>, ketones<sup>(17)</sup>, aldoses<sup>(18)</sup>, and amino acids<sup>(19,20)</sup> by chloramines-T. In addition chlorination reactions of aniline<sup>(21)</sup>, toluene<sup>(22)</sup> furan-2 carboxylic acid<sup>(23)</sup> and acetanilide<sup>(24)</sup> had also been studied. The present work also an attempt to explore the mechanistic pathway involved in the chlorination of N-acetylglycine in acidic medium.

## EXPERIMENTAL

### Apparatus

Absorbance measurements are performed using CECEIL CE 1011, 1000 SERIES with 1- cm quartz cells,

### Materials

Chloramine-T was prepared<sup>(25A)</sup> and purified by method of Morris et al<sup>(26)</sup>. An aqueous solution of chloramine-T was standardized by the iodometric method<sup>(25B)</sup>. N-acetylglycine and all other chemicals were of analytical grade and supplied from (Fluka). The ionic strength of the reaction mixture was kept at high value by using a concentrated solution of sodium perchlorate.

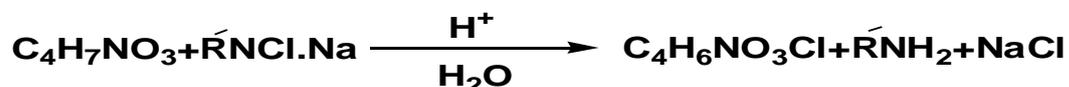
### Kinetic Measurements

The reaction were carried out under pseudo-first order conditions by keeping an excess of N-acetylglycine over CAT. Solution containing appropriate amounts of AG,  $\text{NaClO}_4$ , HCl, ethanol, and water (to keep the total volume constant for all runs) were taken in a glass-stoppered pyrex boiling tube, and thermostated at 313°K. A measured amount of CAT solution, also thermostated at the same temperature, was rapidly added to

the mixture. The progress of the reaction was followed by with drawing samples at various time intervals, to the quenched. Solution (5% potassium iodide solution, 2M sulphuric acid and water) in a fixed volumetric flask the liberated iodine was estimated. spectrophotometrically at 353 nm<sup>(27)</sup>. The course of the reaction was studied up to 75 to 80% completion by using a pseudo-first-order rate constant  $k_1'$  were obtained from the slope of the plot of log [CAT] versus time.

### Stoichiometry

Reaction mixture containing excess CAT over N-acetylglycin were kept at 318 °K, in the presence of 2M HCl, for 24 h. Estimation of unreacted CAT showed that one mole of [AG] consumed one moles of CAT



Were R'=(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)

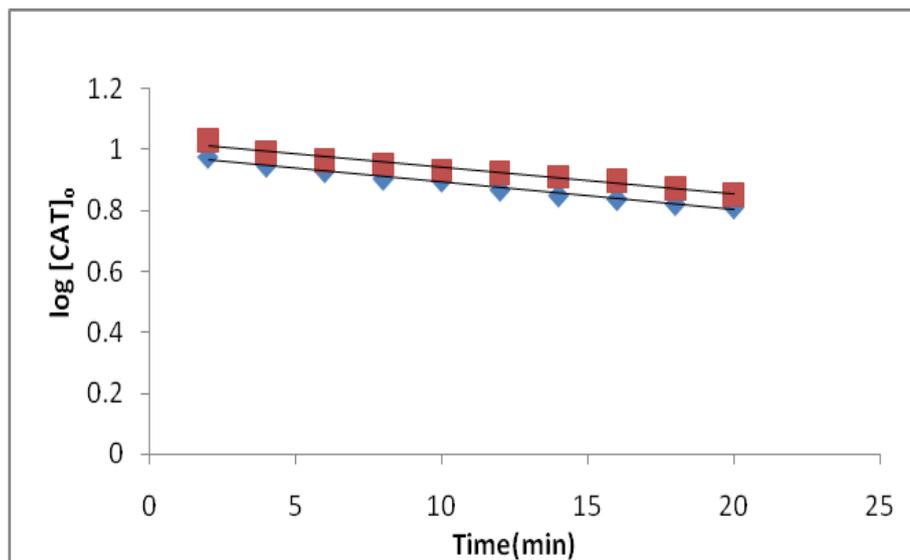
The reaction product P-Toluenesulphonamide (P-TSA) has been detected by paper chromatography<sup>(28,29)</sup>. Benzyl alcohol saturated with water was used as the solvent with 0.5% vaniline in 1% HCl solution in ethanol as spray reagent (R<sub>f</sub>=0.905). the N-chloroacetylglycine produced as awight crystal was identified by IR spectroscopy (816,1159,1350) cm<sup>-1</sup> for (N-Cl) bond<sup>(8,21)</sup> m.p( 167-169°C ) and from elemental analysis test for chlorine.

### RESULTES

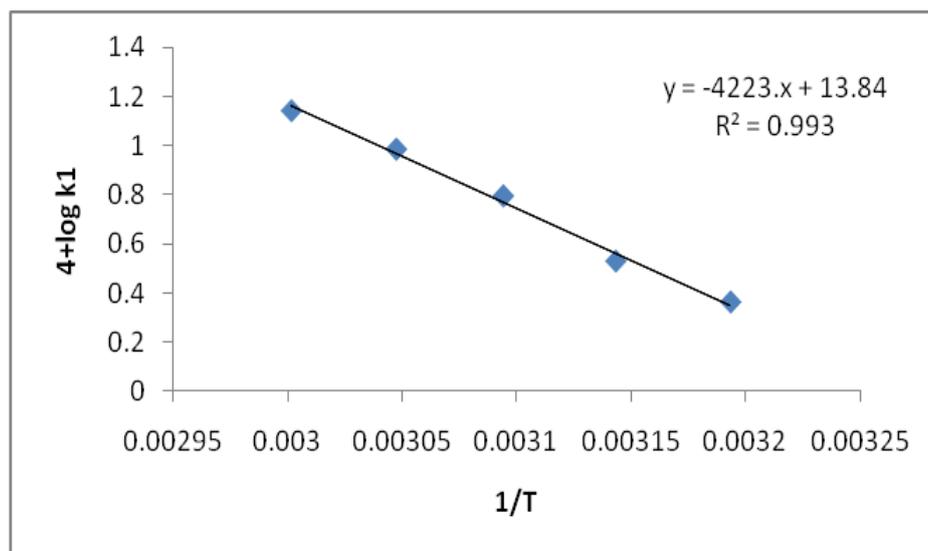
The kinetics of chlorination of N-acetylglycine by chloramine-T was investigated at several initial concentration of the reactant in acid media. At constant acid concentration with the substrate in large excess plots of log [CAT] versus time were linear (r>0.9987) figure(1), indicating a first-order dependence of rate on [CAT] the pseudo first order constants,  $k_1$  are given in Table 1, the values of  $k_1$  were unaffected with the increase in [AG]<sub>0</sub> indicating that the rate is independent on [AG] concentration (Table 1). The reaction was studied with different concentrations of HCl The rate increase with the increase in [H<sup>+</sup>], (Table 2) and a plot of Log  $k_1$  versus log [H<sup>+</sup>] at constant [Cl<sup>-</sup>] gave straight line (r > 0.9984) with a unit slope.

The reaction was also studied in aqueous ethanol of varying composition. An increase in ethanol content enhanced the rate (Table3). A plot of log  $k_1$  aginst 1/D (where D is the dielectric constant of the medium), taken from the literature<sup>(30)</sup>, gave a straight line with positive slope, indicating a positave ion –dipole, Variation of ionic strenght of the medium (0.125 – 0.625)M using sodium perchlorate (Table 4), or

addition of chloride ion in the form of NaCl (Table 2) had no effect on the reaction rate. Addition of the reaction product p-tolunesulphonamide [p-TSA] (up to 0.00125M) to the reaction mixture has no significant effect on the rate reaction ( $k_1$  is marginally affected) (Table 4). The reaction was also studied at different temperature(313-333)K<sup>0</sup> from the Arrhenius plot (log  $k_1$  versus  $1/T$ ) figure(2). the pseudo- first-order rate constants and the activation parameters of oxidation of N-acetyl glycin by CAT are given in (Table 5).



**Figure 1. plot of  $\log [CAT]_0$  versus Time; [N-Acg]=0.02 M; [HCl]=0.4 M;  $\mu=0.125$  M; Temp.318°K**



**Figure2. plot of  $4+\log K_1$  versus  $1/T$ ; [N-Acg]= 0.02 M; [CAT]<sub>0</sub>= 0.001M; [HCl]= 0.4 ; Temp.318°K**

**Table 1:** Effect of varying reactant concentration on rate of oxidation of N-Acetylglycine by chloramine – T in acid media at 45°C, [HCl]=0.4 M,  $\mu=0.125$  M, 1:1 (V/V) ethanol: water.

$10^3$ [CAT] M	$10^2$ [AG] M	$10k_1'.\text{Sec}^{-1}$
1.00	1.00	3.8767
1.00	1.50	3.7999
1.00	2.00	3.8383
1.00	2.50	3.8383
1.00	3.00	3.7999
1.00	2.00	3.8383
1.25	2.00	3.3393
1.50	2.00	2.9939
1.75	2.00	2.6868
2.00	2.00	2.5716

**Table 2:** Effect of hydrogen ion concentration and chloride ion concentration  $[\text{Cl}]_t$  on reaction rate at 45°C,  $[\text{CAT}]_o = 0.001$  M,  $[\text{N-Acg}] = 0.02$  M,  $[\text{NaClO}_4] = 0.125$  M, 1:1 (V/V) ethanol: water.

$[\text{H}^+]$ M	$[\text{Cl}]_t$ M	$10^4k_1'.\text{Sec}^{-1}$	$10 k_1'/[\text{H}^+]$
0.4	0.6	4.6060	1.1515
0.45	0.6	5.2201	1.1600
0.5	0.6	5.9878	1.1975
0.55	0.6	6.5635	1.1933
0.6	0.6	7.0625	1.1770
0.4	0.050	3.7615	
0.4	0.075	3.8383	
0.4	0.100	3.8075	
0.4	0.125	3.9918	
0.4	0.150	3.9151	

**Table 3:** effect of ionic strength and p-toluenesulphonamide [p-TSA] concentration on reaction rate at 45°C,  $[\text{CAT}]=0.001$  M,  $[\text{N-Acg}]=0.02$ M,  $[\text{H}^+] = 0.4$  M, 1:1 (V/V) ethanol: water varying [p-TSA] and  $\mu=0.125$ M.

$[\text{NaClO}_4]$ M	$10^4 k_1'.\text{Sec}^{-1}$	$10^4$ p-TSA	$10^4 k_1'.\text{Sec}^{-1}$
0.125	3.8383	2.5	3.5696
0.250	3.5241	5.0	3.4545
0.375	3.3393	7.5	3.4545
0.500	3.4125	10.0	3.2242
0.625	3.6152	12.5	3.0322

**Table 4:**Effect of varying dielectric constant(D) on the reaction rate at 45<sup>0</sup>C, [CAT]=0.001M, [N-acg]=0.02M, [H<sup>+</sup>]=0.4M, 1:1(V/V)ethanol: water and μ =0.125M.

%CH <sub>3</sub> OH	D	10 <sup>4</sup> k <sub>1</sub> <sup>-1</sup>
0.00	76.73	6.41
10.0	72.37	6.83
20.0	67.48	7.22
30.0	62.7	7.67
40.0	58.06	8.94

**Table 5:**Effect of varying temperature on reaction rate, [CAT]=0.001M, [N-acg]=0.02M, [H]=0.4M and μ=0.125M, 20%(v/v) ethanol: water

Temperature	313	318	323	328	333
10 <sup>4</sup> k <sub>1</sub> (sec) <sup>-1</sup>	2.303	3.3838	6.2564	9.7109	11.2079

Ea =76.0715 KJ/mole

log A = 1.1738

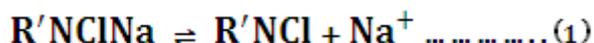
ΔH<sup>‡</sup> = 73.384 kJ/mole

ΔG<sup>‡</sup> = 99.331 kJ/mole

ΔS<sup>‡</sup> =-80.284 J/mole.deg.

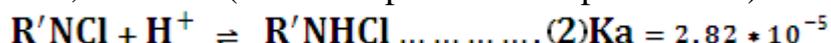
### Discussion

Chloramine-T (CAT) behaves like a strong electrolyte in aqueous solution and it dissociates as<sup>(23)</sup>:

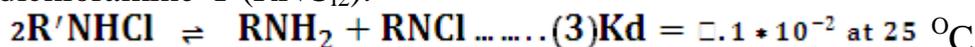


Where (R' =P-CH<sub>3</sub>-C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>)

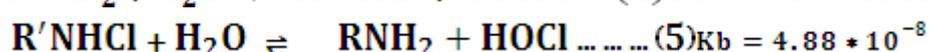
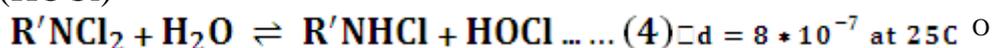
The anion picks up a proton in acid solution to give the free acid mono chloramine-T, RNHCl.(N-chloro-p-toluene sulphonamide)<sup>(24)</sup>.



The free acid undergoes giving rise to p-toluene sulphonamide (R'NH<sub>2</sub>) and dichloramine-T (RNC<sub>l2</sub>):



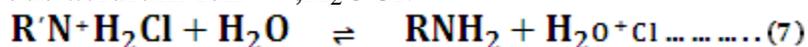
the dichloramine\_T and the free acid –hydrolyse to give hypochlorous acid (HOCl)<sup>(11,31)</sup>



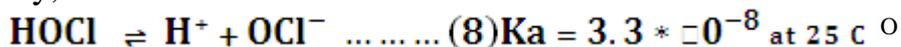
In addition,protonaion of the free acid in (pH less 2.8) give (R'N<sup>+</sup>H<sub>2</sub>Cl)



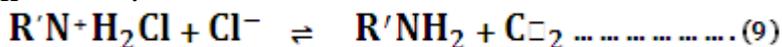
The protonated monochloramine -T (RNH<sub>2</sub>Cl) can also hydrolyzed to give hypochlorous acidium ion<sup>(32)</sup>,H<sub>2</sub>OCl:



Finally, HOCl ionizes to



Free chlorine has also been detected in acid medium in the presence of chlorine ion<sup>(33,34,35)</sup>.



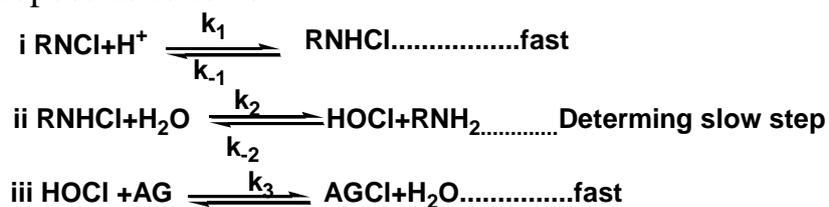
The hydrolysis constant of chlorine is  $4.66 \times 10^4$ , Thus, the probable oxidizing species in acidified chloramine\_T solution are  $\text{RNCl}_2$ ,  $\text{RNHCl}$ ,  $\text{HOCl}$  and  $\text{HO}_2\text{Cl}^+$ . if  $\text{RNCl}_2$  were to be the reactive species, then the rate law predicats a second –order dependence on chloramine\_T but experimentally clean first –order plots were obtained for disappearance of chloramine-T figure(1). approximation calculation by Bishop and Jennings on decinornial solutions of chloramine\_T have shown that concentration of  $\text{RNHCl}$  and  $\text{HOCl}$  are approximately  $10^{-2}$  and  $10^{-7}\text{M}$  respectively around PH 0-1. Although the concentration of former species is larger, Pryde and Soper<sup>(12)</sup> have shown that interaction of  $\text{RNHCl}$  with substrate could be slow while  $\text{HOCl}$  would attack at faster rate. from the earlier work of Soper<sup>(31)</sup> Higuehi and Hussain<sup>(13)</sup> and from the experimental observation.the rate determined by the formation of  $\text{HOCl}$  (Scheme I and II, step 2 in both schemes) which would interact with N-acetyl glycine in a fast step.protonation converts the later into a stronger electrophil ( $\text{H}_2\text{O}^+\text{Cl}$ ) than the precursor  $\text{HOCl}$ , Moreover as reported<sup>(36)</sup>, that  $\text{H}_2\text{OCl}^+$  is more reactive, than  $\text{HOCl}$  it will attack the N-acetyl glycine more rapidly. Absence of significant ionic strength effect on the rate rules out the involvement of ionic in a rate determing step. further a change in the solvent composition by varying the ethanol content in ethanol –water enhance the reaction rate.

A general equation (11)<sup>(37)</sup> relate the rate with the dielectric constant is give by

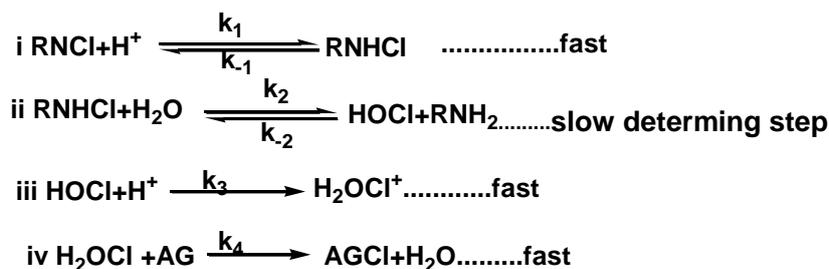
$$\text{Ln } k'_D = \text{Ln } k'_D - 2\mu_1\mu_2/DKTr^3 \dots\dots\dots (11)$$

Where  $k'_D$  is function of dielectric constant  $D$ ,  $\mu_1$  and  $\mu_2$  are the dipole moments of the reactants,  $r$  is the distance of approach for the two dipoles,  $k$  is the Boltzman constant and  $T$  is absolute temperature. Equation (10) predicates a linear relation between  $\log k_{(\text{obs})}$  and  $1/D$ . The slop of the line should be negative for a reaction between two dipolar molecules while a positive is obtained for ion-dipole reactions.

Scheme I and II for the oxidation of N-acetyl glycine by chloramine\_T; may be propose as follows:



Scheme I



Scheme II

The formation of HOCl takes place in a slow step in both scheme through the hydrolysis of RNHCl followed by a rapid reaction with N-acetyl glycin (Scheme I, step iii) or it may be protonated in (scheme II, step iii) to give H<sub>2</sub>OCl<sup>+</sup> which react rapidly with the substrate.

Applying steady state approximation with respect to CAT and HOCl and VIZ.  $k_4\{k_{-1} + k_2[\text{H}_2\text{O}]\}[\text{S}] \gg k_{-1}k_{-3}[\text{TSA}]$ ,

The following equation is obtained

$$\frac{-d}{dt} [\text{CAT}] = \frac{k_1 k_2 [\text{H}_2\text{O}]}{k_{-1} + k_2 [\text{H}_2\text{O}]} [\text{CAT}][\text{H}^+] \quad \dots\dots\dots (12)$$

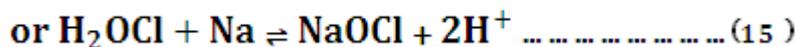
Thus, the equation becomes

$$\frac{-d}{dt} [\text{CAT}] = K[\text{CAT}][\text{H}^+] \quad \dots\dots\dots (13)$$

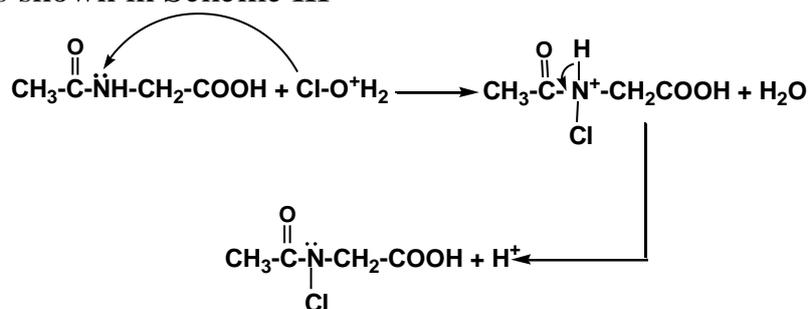
Where

$$K = \frac{k_1 k_2 [\text{H}_2\text{O}]}{k_{-1} + k_2 [\text{H}_2\text{O}]} = \text{constant}$$

The derive rate law –equation (13) is incomplete accordance with the the experimentally kinetic results. An increase in initial concentration of chloramine-T (table 1) results in a slight decrease in a first –order constant which may be due to deactivation caused by the formation of small quantities<sup>(8,38,39)</sup> of NaClO<sub>3</sub> in a side reactions which give another prove that HOCl or H<sub>2</sub>OCl is the reactive species



A detailed mechanism of oxidation of N-acetyl glycin by CAT in acid medium is shown in Scheme III



Scheme III

In scheme III an electrophilic attack by the partially positive chlorine of  $\text{H}_2\text{OCL}^+$  at the nitrogen atom of N-acetyl glycine followed by elimination of  $\text{H}^+$  to give N-chloro acetyl glycine (product).

Finally, the proposed mechanism is supported by the large negative value of entropy of activation which is an indication of rigid transition-state configuration also more-ordered activated complex than the reactant<sup>(40,41)</sup> with fairly high positive value of free energy of activation<sup>(23,40,42)</sup>.

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