PERIÓDICO TCHÊ QUÍMICA
ARTIGO ORIGINAL

CINÉTICA E MECANISMO DE OXIDAÇÃO DO TETRA-HIDROFURANO PELA CLORAMINA-T EM MEIOS ACIDICOS

KINETICS AND MECHANISM OF TETRAHYDROFURAN OXIDATION BY CHLORAMINE-T IN ACIDIC MEDIA

حركية وميكانيكية أكسدة تيترا-هيدروفوران بواسطة الكلورامين-T في المحيط الحامضي

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RESUMO

A cinética da oxidação do tetra-hidrofurano pelo N-cloro-p-tolueno sulfonamida de sódio no meio de ácido clorídrico foi estudada neste trabalho a temperatura de 308 K. A taxa de reação mostra uma dependência de primeira ordem em [CAT] e uma dependência em ordem fracionária, cada uma em [THF] e [H +]. A lei da taxa derivativa, adequada para resultados experimentais, é a Equação 24. A constante da taxa de primeira ordem foi avaliada a partir da relação entre o gráfico de Log [CAT] e o tempo. A variação da força iônica pela adição de perclorato de sódio ($NaClO_4$) e íon cloreto no meio não mostrou efeito significativo na reação. A taxa de reação aumentou com constante dielétrica decrescente (D), enquanto a adição de p-toluenosulfonamida retarda a taxa de reação. A reação de oxidação do tetra-hidrofurano foi estudada a uma temperatura diferente. Foram estimadas as constantes de equilíbrio para a formação de ácido hipocloroso, ácido hipocloroso protonado e o complexo ácido hipocloroso protonado-THF e sua constante de decomposição. Além disso, a taxa constante para a lenta (etapa de determinação da taxa) e o parâmetro de ativação foram calculados. Um mecanismo adequado para a reação de oxidação do tetra-hidrofurano foi proposto com base no achado experimental. O mecanismo inclui a reação de espécies ativas (H_2OCl) do agente oxidante com o tetra-hidrofurano em uma etapa rápida para dar o complexo (X). Este complexo será então transformado em complexo ($\bar{X}$) em passo lento e depois em γ-butirolactona em outro passo rápido.

Palavras-chave: *THF; Cinética; Oxidação; Mecanismo: Cloramina-T; Meio Ácido.*

ABSTRACT

The kinetics of tetrahydrofuran oxidation by sodium N-chloro-p-toluene sulfonamide in the hydrochloric acid medium was studied in this work at 308 K. The reaction rate shows a first-order dependence on [CAT] and fractional-order dependence each on [THF] and [H^+]. The derivative rate law, which suitable for experimental results, is Equation 24. The first-order rate constant has been evaluated from the relationship of the plot of Log [CAT] versus Time. The variation of the ionic strength by the addition of sodium perchlorate ($NaClO_4$) and chloride ion on the medium showed no significant effect on the reaction. The reaction rate raised with decreasing dielectric constant (D), while the addition of p-toluene sulfonamide retards the rate of reaction. The oxidation reaction of tetrahydrofuran have been studied at a different temperature, The equilibrium constants for the formation of hypochlorous acid, protonated hydrochlorous acid and protonated hydrochlorous acid–THF complex and its decomposition constant have been estimated. Also, the rate constant for the slow (rate-determining step) and the activation parameter have been calculated. A suitable mechanism for the oxidation reaction of tetrahydrofuran was proposed based on the experimental finding. The mechanism includes the reaction of active species (H_2OCl) of the oxidizing agent with the tetrahydrofuran in a fast step to give the complex(X). This complex will then transformed into complex ($\bar{X}$) in slow step then to γ-butyrolactone in another fast step.

Keywords: *THF; Kinetics; Oxidation; Mechanism; Chloramine-T; Acidic Medium.*

الملخص

تمت دراسة حركية أكسدة رباعي هيدروفيوران بواسطة N-chloro-p-toluene sulfonamide في وسط حامض الهيدروكلوريك وعند درجة حرارة 308 كلفن. بينت النتائج أن معدل سرعة التفاعل يعتمد على تركيز الكلورامين –T (الرتبة الأولى) ويعتمد على تركيز كل من تيتراهيدروفيوران وأيون

الهيدروجين (الرتبة كسرية)، وأن قانون سرعة التفاعل المشتق والذي يتلائم مع النتائج العملية موضح في المعادلة (24). تم حساب ثابت سرعة لتفاعل الرتبة الاولى من رسم العلاقة بين لوغارتيم [CAT] مقابل الزمن ووجد ان تغير الشدة الأيونية بأضافة بيركلورات الصوديوم ($NaClO_4$) وأختلاف أيون الكلوريد ليس له اي تاثير على ثابت سرعة التفاعل، بينما يرتفع معدل سرعة التفاعل مع تناقص ثابت العزل الكهربائي (D) وعند إضافة ناتج التفاعل p-toluene sulfonamide يؤدي ذلك ألى نقصان معدل سرعة التفاعل. تمت دراسة حركية اكسدة تيتراهيدروفيوران في درجات حرارية مختلفة وتم تقدير ثوابت التوازن لتكوين حامض الهيبوكلوروس، حامض الهيدروكلوريك البروتوني، معقد حامض الهيدروكلوريك البروتوني - THF وثابت تحلله وحساب ثابت سرعة تفاعل الخطوة البطيئة والمعاملات الثرموداينميكية، واخيرا اقترحت ميكانيكية ملائمة للتفاعل اعتماداعلى النتائج العملية والتي تتضمن تفاعل الجزء الفعال (H_2OCl) من المادة المؤكسدة [CAT] مع تيتراهيدروفيوران بسرعة ليعطي المعقد (X) والذي يتحول ببطىء الى المعقد ($\overline{X}$) والذي يعطي بدوره γ-بيوترلاكتون بخطوات سريعة أخرى لاحقة.

الكلمات المفتاحية: *THF ، حركية ، أكسدة ، ميكانيكية ، كلورامين- T، وسط حامضي.*

1. INTRODUCTION

The chemistry of sodium N-chloro–p–toluenesulfonamide ($p\text{-}CH_3\text{-}C_6H_4SO_2\text{-}NCl\ Na.3H_2O$), well known as Chloramine-T (CAT or RNClNa), is a member of the aromatic sulphonyl haloamines. It is expected to behave as an oxidation agent in acidic and alkaline media and delivers a two-electron change in the reaction medium to form (p-TSA; RNH_2) and (NaCl). The oxidation potential of CAT/RNH_2 modify with the pH of the medium and increase with reducing the pH of the medium (Campbell and Johnson, 1978; Banerji *et al.,* 1987). Different reaction species were recorded depending on the medium acidity (pH), such as N-Chloro-p-Toluenesulfonamide, RNHCl, Dichloramine-T, $RNCl_2$, HOCl, H_2OCl and RNH_2Cl in acid medium, OCl and RNCl in alkaline medium. Chloramine-T has been vastly utilized as a volumetric reagent in the direct and indirect determination of several compounds (Kotthoff and Belcher, 1957; Jennings and Crit, 1974; Berka and Zvka, 1965).

Limited kinetic studies of these reactions are reported, such as oxidation of cyanide, thiocyanate, hexacyanoferrate, sulfoxide, α-hydroxy acid, primary and secondary alcohol, phenols, catecholamines, aldehyde, ketones, aldoses, formic acid, ether and substituted of amino acid (Mahadevappa and Gowda, 1979; Ahmed *et al.,* 1980; Mushran and Agrawal, 1971; Mahadevappa *et al.,* 1979; Mushran and Agrawal, 1971; Naidu *et al.,* 1988; Natarajan and Thiagarajan, 1975; Balasubramanian and Thiagarajan, 1975; Jagadeesh and Vaz, 2005; Agrawal and Mushran, 1973; Sanehi and Mushran, 1973; Agrawal and Mushran, 1972; Hassan and Al-Joraycee, 1989; Hassan and Saeed, 2012; Saeed, 2011). In addition, chlorination reactions of aniline, toluene, furan-2-carboxylic acid, and acetanilide have also been studied (Ramanujam and Trieff, 1977; Radhakrishnamurti *et al.,* 1982; Hassan and AL-Hatim, 1995; Hassan and Noor, 2010).

Tetrahydrofuran (THF) is usually utilized as a reaction medium and also as a chemical reactant. So it is interesting to explore the oxidation kinetics of the THF by CAT in the acidic medium as a solvent as well as, the oxidation of THF was studied by several oxidizing agents like chromium trioxide, lead tetraacetate, ruthenium tetraoxide to the corresponding γ-butyrolactone (Lee, 1969; Metsger and Bittner, 2000; Che *et al.*, 1991).

Little attention has been paid to the mechanism oxidation of these reactions. Also, these reactions are free of side reaction and usually give quantitative yields of pure product.

Also, the oxidation of THF by CAT has not been reported in the literature. Therefore, it is the benefit of studying the oxidation of THF by Chloramine-T in acidic medium.

2. MATERIALS AND METHODS

2.1. Materials

Tetrahydrofuran (Fluka™) of spectra grade (99.5%) used as received. Chloramines-T was purified by the method of Morris *et al.* (1948). CAT aqueous solution was standardized by the iodometric method. All other chemicals of analytical grade. The ionic strength was kept at high constant values utilizing concentrated $NaClO_4$ solution.

2.2. Kinetic measurements

In glass stoppered Pyrex™ tubs, the reaction was carried out beneath pseudo-first-order conditions by keeping with [CAT] in low compare with [THF], which kept in high concentration. In a typical kinetic experiment appropriate of THF, hydrochloric acid, methanol, sodium perchlorate, and water, which was placed in a thermostated – water bath for about 30 min at 308 K. The reaction was initiated by rapidly adding the desired amount of CAT solution to the mixture. CAT solution followed by drawing samples (5 mL) at different periods to the irrigating solution (2 M sulfuric acid, 5% KI, and water) in the volumetric flask. The absorption of the free iodine at 353 nm was recorded using the C-Cell spectrophotometer. Finally, the pseudo-first-order rate constant Ḱ was obtained from the slope of the straight line of Log [CAT] versus time.

2.3. Stoichiometry

Reaction solutions, including different proportions of CAT and THF, were equilibrated at 308 K in the existence of (0.2 M) for one day. Appreciation of the unreacted of chloramine-T showed that one mole of the (THF) expended two moles of (Chloramine-T), the suggested reaction can be seen in Equation 1.

The reaction product p-TSA was identified by chromatography, utilizing benzyl alcohol saturated with water with 0.5% vanillin in one percentage of HCl solution in ethanol as a spray reagent ($R_f = 0.905$). The oxidation product of THF is γ-butyrolactone was identified by infrared spectroscopy and characterized by reaction with hydrazine hydrate to form hydrazide derivative (Saleh and Ayoub, 2014). Pure γ-butyrolactone has a boiling point of 205 °C.

3. RESULTS AND DISCUSSION

3.1. Results

The kinetics of tetrahydrofuran oxidation by chloramine-T was inspected in different initial concentrations of reaction acid media.

3.1.1. Reactant Concentration Effect

At a high concentration of the reactant with a fixed acid concentration, plots of Log[CAT] or $Log[CAT]_o/[CAT]_t$ with time were linear ($r>0.9975$) pointing first – order reliance of [CAT] rate. Table 1 included the rate constants of pseudo-first-orderer. The values of ḱ raise with reactant concentration. Plots of Log ḱ with Log $[THF]_o$ is linear ($r = 0.99$) with a slope of (0.42). Figure 1 illustrated the reactant concentration in fractional-order.

3.1.2. Hydrogen ion Concentration Effect

The rate constant of reaction increased with increasing the concentration of hydrogen ion. The rate constant of fractional-order was obtained from the straight-line slope ($r = 0.9939$) of log k^{-}_1 versus log$[H^+]$, which dependence on hydrogen ion concentration. No detectable reaction observed between THF and CAT under varying conditions at 308 to 335 K in sulfuric acid rang (0.2-0.5 M) and perchloric acid medium in the range (0.2-0.6 M). The amount of unreacted CAT remained unchanged after 3 hours of the reaction mixture, which contained 0.01 M CAT, 1.4 M THF, and $\mu = 0.125$ M.

3.1.3. The chloride ion, ionic strength, and p-TSA concentration-effect

Extension of chloride ion from (NaCl) (0.25–0.45 M) at constant $[H^+]$ has no effect on the rate (Table 2). At a different concentration of the ionic strength (0.125–0.625 M of $[NaClO_4]$, no significant effect was seen on the rate (Table 2). Extension of the reaction product of p-toluene sulfonamide (0.025–0.125 M) to the reaction mixture retards the reaction rate significantly. The plot of Log ḱ versus Log [p-TSA] was linear ($r = 0.9963$) with a slope of nearly inverse unity (Table 2).

3.1.4. The solvent compositions effect

At different compositions of aqueous methanol, the reaction rate has been studied. The rate of the reaction raises with an increase a methanol content (Table 2). Linear plots ($r = 0.9948$) with a positive slope of log k_1 versus 1/D was seen (where D is the dielectric constant of the medium) (Jouyban *et al.,* 2004). The negligible effect of methanol oxidation was seen in the control experiments with methanol (Table 3).

3.1.5. Temperature effect

At different temperatures (298 K – 318 K), the reaction has been studied. The pseudo-first-order rate constants and the activation parameters of oxidation of THF by CAT are given in Table 4.

3.2 Discussion

The dependence of rate on acidity (Table 1) could be a consequence of protonation of either chloramine-T or tetrahydrofuran. The oxonium ions formed by protonation of THF would not readily undergo an electrophilic attack, and hence extensive protonation of the ether would decrease the rate of reaction. However, the enhancement of rate by H^+ ion indicates that the unprotonated ether is the reacting species, and consequently, the decrease in substrate concentration through the formation of oxonium ions can be neglected.

Chloramine-T behaves like a strong electrolyte, in aqueous solution and dissociates as Equation 2 (Bishop and Jennings, 1958).

In an acid medium, mono Chloramine-T (RNHCl). N-Chloro-p-Toluenesulfonamide has been formed, when the anion contracts a proton (Equation 3).

Due to the disproportionation of free acid, it has given rise to p-toluenesulfonamide ($\acute{R}NH_2$) and Dichloramine-T ($\acute{R}NCl_2$) (Equation 4).

Hypochlorous acid HOCl has been formed from the free acid hydrolyze and Dichloramine-T (Equations 5 and 6). Hypochlorous acid produced can be ionized as Equation 7. Protonation of the free acid in pH < 3 has also been reported Abdulsalam *et al.* (2018), to give (Equation 8). The protonated monochloramine-T (RN^+H_2Cl) hydrolyzed to give protonated hydrochlorous acid and $\acute{R}NH_2$ as Equation 9. In acid solution, free chlorine (Cl_2) has been found in the existence of chloride ion as Equations 10 and 11.

The possible reactive species in acidified CAT solution are $\acute{R}NHCl$, $\acute{R}NCl_2$, HOCl, Cl_2, and probably (H_2OCl and $\acute{R}N^+H_2Cl$) as a result of k_a values of chlorine which equal to 4.66×10^{-4}. A variation of experimental conditions will often favor one reactive species rather than others. No significant effect on the rate constant was seen when varying ionic strength adds to the reaction mixture by the addition of a concentrated solution of ($NaClO_4$). The reaction rate enhances significantly by decrease the dielectric constants of the medium (by adding methanol). For all aspects mentioned above, the reaction proposed takes place between a neutral molecule and a positive ion. In the opinion of this, either H_2O^+Cl or RN^+H_2Cl are likely to be the important probable reactive species. Since the reaction rate shows an enhancement by H^+ ion and retardation by the addition of reaction product p-TSA (Table 2), RN^+H_2Cl can be excluded as the oxidizing species. Under the supposition, H_2O^+Cl is the reactive species.

The reaction mechanism can be proposed in schemes 1 and 2. The reaction intermediates X and $\overline{X}$ involved in schemes 1, 2, and 3 are oxo – chloro derivative of the substrate. Rao *et al.* (1970) have reported the formation of such oxo-halo derivative during the oxidation of THF by sodium bromate. If $[CAT]_t$ is the overall efficient concentration of CAT, as Equations 12, 13, 14 and 15. Reparation for [HOCl] and $[H_2O^+Cl]$ from Equations 14 and 15 respectively in to Equation 13 one obtains Equation 16.

Then substitute for $[H_2O^+Cl]$ from Equation 15 into equation 14 it is obtained Equation 17. Substituting for $[H_2O^+Cl]$, $[\acute{R}NHCl]$ and [HOCl] from Equations 15–17 respectively in to Equation 12 and solution of [X], it is obtainedt Equation 18 (from the slow step of scheme 1). $[\acute{R}NH_2]$ is negligible compared with other terms in the denominator, then Equation 19 becomes Equation 20. Since the rate = $\acute{k}_1[CAT]_t$, Equation 20 can be converted into Equations 21, 22 and 23. The constant k_4, K_2 and K_3 were computed from these equations while the equilibrium constant K_1 can be evaluated using scheme 2 derived law.

The concentration of the total effective of CAT is $[CAT]_t = [\acute{R}NHCl] + [H_2O^+Cl] + [X]$ and the reaction rate of the slow step = $k_8[X]$. Substitute $[\acute{R}NHCl]$ and $[H_2O^+Cl]$ obtained from step (i) and (ii) leads to rate law Equation 24. By negligee, the term $[\acute{R}NH_2]$, the rate = $\acute{k}_1[CAT]$, Equation 24 can be transformed into Equations 25 and 26. Equations 18 and 24 indicate first-order reliance of $[CAT]_t$ rate, and fractional-order reliance of each $[H^+]$ and [S] rate. Comparing the constants in both schemes 1 and 2, we get that $k_4 = k_8$, $K_3 = K_7$ and $K_1K_2 = K_6$, So Equations 25 and 26 can be written as Equations 27 and 28.

According to Equations 22 and 23, Figure 1 and Figure 2 show the plots of $1/\acute{k}_1$ versus 1/[S] (r = 0.9949) and $1/[H^+]$ (r = 0.9939) respectively were linear. Form the intercept of $1/\acute{k}_1$ versus 1/[S]. The value of k_4 was obtained as 1.4×10^{-3} sec^{-1}. Substituted this value in the value of intercept of the plot of $1/\acute{k}_1$ versus $1/[H^+]$ (Equation 23) K_3 was obtained as (7.1). The value of k_4 and K_3 were substituted in the slope of plot $1/k_1$ versus $1/[H^+]$. K_2 value was obtained as (0.546). Then, substitute the value of K_4 and K_3 in the slope of the plot $1/k_1$ versus 1/[S] (Equation 26). The value of $K_6/\acute{K}_1$ was obtained as 0.43, and the value of $\acute{k}_1$ is obtained as (0.765) (were $K_1 = \acute{K}_1/[H_2O] = (1.38 \times 10^2)$. Finally, the constants K_1, K_2, K_3, and k_4 were utilized to calculate the rate constant under different conditions using Equations 21 and 28, respectively. The calculated rate constants were listed in (Table 5). As can be seen, there is an excellent agreement between the rate values indicating the correctness of the suggested scheme and the derived rate laws. Since the reaction preset a fractional-order relay on [S], Michaelis–Menten kinetics was used to calculating the rate constant k_4 from the slop step. The activation parameters reaction rates were calculated by the use of Arrhenius plots of log κ_1 with 1/T (Table 4).

Scheme 3 shows the THF oxidation by CAT, The intermediate of complex (X) establishment by the electrophilic. The attack of protonated hydrochlorous acid H_2O^+Cl on the oxygen of the THF gives oxo–chloro derivative of THF (X^-). Elimination of H^+ and then hydrolysis with the elimination of H^+ Cl^- to give α–THF alcohol. The last will then interact with the second active H_2O^+Cl molecule in the fast step to give the product γ – butyrolactone.

The derived rate law and the suggested mechanism are confirmed by the following experimental finding. The solvent composition has been changed in different methanol content in the methanol-water mixture. The effect of the solvent on bimolecular reaction has been discussed by Geng and Wei (2007), Laidler and Landskroener (1956), and Amis (1955). Also, this topic and other theories have been illustrated by Entelis and tiger (1976). Equation 29 has been developed for the limiting case of the head-on approach of an ion to the dipolar molecule.

A linear relationship between log k_1 and 1/D was suggested for the addition Equation 29 with a positive slope for the relationship of negative ion and dipole or between two dipoles. Further, the rate constant of the first order slightly rose with increasing the initial concentration of Chloramine-T (Table 1). This reaction deactivation may result from the formation of small amounts of $NaClO_4$ inside reaction, as Equations 30 and 31.

Finally, the suggested mechanism was supported by activation energy and parameter values. The high positive value of enthalpy $\Delta H^{\neq}$ and activation free energy $\Delta G^{\neq}$ refer to the slight solvation of the transition state while the negative values of entropy $\Delta S^{\neq}$ propose the figuration of the activated complex with some reduction in the freedom molecule's degree.

4. CONCLUSIONS

THF is an inert solvent, and it can be easily oxidized under certain conditions. The kinetics of the THF oxidation process is carried out by the formation of HOCl in the hydrochloric acid medium at 308 K. HOCl has acquired the hydrogen ion to form H_2OCl, which interacts with THF to gives the intermediate compound which in turn gives the final product (γ-butyrolactone). The reaction rate was first-order dependence on [CAT], fractional-order dependence each on [THF] and [H^+]. No significant effect of the medium ionic strength was seen on the reaction. The inverse relationship was seen between the reaction rate and the dielectric constant (D). The equilibrium constants have been suggested for the formation of hypochlorous acid, protonated hydrochlorous acid, and protonated hydrochlorous acid-THF complex. The reaction mechanism was proposed and found consistent with the observed kinetics.

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Equations

$$\mathrm{C_4H_8O\ +\ 2\acute{R}NCl.Na\ +\ H_2O\ \xrightarrow{H^+}\ C_4H_8O_2\ +\ 2\acute{R}NH_2 + 2NaCl} \qquad \text{(Eq. 1)}$$

where $\acute{R} = \mathrm{CH_3\,.\,C_6H_4SO^{2-}}$

$$\mathrm{\acute{R}NClNa\ \leftrightarrow\ \acute{R}NCl^- +\ Na^+} \qquad \text{(Eq. 2)}$$

$$\mathrm{\acute{R}NCl^- +\ H^+\ \overset{K_a}{\leftrightarrow}\ \acute{R}NHCl} \qquad \text{(Eq. 3)}$$

$\mathrm{K_a} = 2.82 \text{ x } 10^{-5}$ at 298 K

$$\mathrm{2\acute{R}NHCl^-\ \overset{K_d}{\leftrightarrow}\ \acute{R}NCl_2 +\ \acute{R}NH_2} \qquad \text{(Eq. 4)}$$

$\mathrm{K_d} = 6.10 \text{ x } 10^{-2}$ at 298 K

$$\mathrm{\acute{R}NCl_2 +\ H_2O\ \overset{K_h}{\leftrightarrow}\ \acute{R}NHCl +\ HOCl} \qquad \text{(Eq. 5)}$$

$\mathrm{K_h} = 8.00 \text{ x } 10^{-7}$ at 298 K

$$\mathrm{\acute{R}NHCl\ +\ H_2O\ \overset{K_h}{\leftrightarrow}\ \acute{R}NH_2 +\ HOCl} \qquad \text{(Eq. 6)}$$

$\mathrm{K_h} = 4.88 \text{ x } 10^{-8}$ at 298 K

$$\mathrm{HOCl\ \overset{K_i}{\leftrightarrow}\ H^+ +\ OCl^-} \qquad \text{(Eq. 7)}$$

$\mathrm{K_i} = 3.30 \text{ x } 10^{-8}$ at 298 K

$$\mathrm{\acute{R}NHCl\ +\ H^+\ \overset{K_p}{\leftrightarrow}\ \acute{R}N^+H_2Cl} \qquad \text{(Eq. 8)}$$

$\mathrm{K_p} = 1.03 \text{ x } 10^{2}$ at 298 K

$$\mathrm{\acute{R}N^+H_2Cl\ +\ H_2O\ \leftrightarrow\ \acute{R}NH_2\ +\ H_2O^+Cl} \qquad \text{(Eq. 9)}$$

$$\mathrm{\acute{R}N^+H_2Cl\ +\ Cl^- \leftrightarrow\ Cl_2\ +\ \acute{R}NH_2} \qquad \text{(Eq. 10)}$$

$$\mathrm{HOCl + H^+ + Cl^- \overset{K}{\leftrightarrow} H_2O + Cl_2} \qquad \text{(Eq. 11)}$$

$\mathrm{K} = 2.15 \times 10^3$ at 298 K

$$[\mathrm{CAT}]_t = [\acute{R}\mathrm{NHCl}] + [\mathrm{HOCl}] + [\mathrm{H_2O^+Cl}] + [\mathrm{X}] \qquad \text{(Eq. 12)}$$

From step (i) $\mathrm{K_1} = \dfrac{[\acute{R}\mathrm{NH_2}][\mathrm{HOCl}]}{[\acute{R}\mathrm{NHCl}][\mathrm{H_2O}]}$

$$\text{or } [\acute{R}\mathrm{NHCl}] = \frac{[\acute{R}\mathrm{NH_2}][\mathrm{HOCl}]}{\mathrm{K_1}[\mathrm{H_2O}]} = \frac{[\acute{R}\mathrm{NH_2}][\mathrm{HOCl}]}{\acute{K}_1} \qquad \text{(Eq. 13)}$$

where $\acute{K}1 = \mathrm{K_1}[\mathrm{H_2O}]$

From step (ii) $\mathrm{K_2} = \dfrac{[\mathrm{H_2O^+Cl}]}{[\mathrm{HOCl}][\mathrm{H^+}]}$

$$\text{or } [\mathrm{HOCl}] = \frac{[\mathrm{H_2O^+Cl}]}{\mathrm{K_2}[\mathrm{H^+}]} \qquad \text{(Eq. 14)}$$

From step (iii) $\mathrm{K_3} = \dfrac{[\mathrm{X}]}{[\mathrm{H_2O^+Cl}][\mathrm{S}]}$

$$\text{or } [\mathrm{H_2O^+Cl}] = \frac{[\mathrm{X}]}{\mathrm{K_3}[\mathrm{S}]} \qquad \text{(Eq. 15)}$$

$$[\acute{R}\mathrm{NHCl}] = \frac{[\acute{R}\mathrm{NH_2}][\mathrm{X}]}{\acute{K}_1\mathrm{K_2K_3}[\mathrm{H^+}][\mathrm{S}]} \qquad \text{(Eq. 16)}$$

$$[\mathrm{HOCl}] = \frac{[\mathrm{X}]}{\mathrm{K_2K_3}[\mathrm{H^+}][\mathrm{S}]} \qquad \text{(Eq. 17)}$$

$$[\mathrm{CAT}]_t = \frac{[\acute{R}\mathrm{NH_2}][\mathrm{X}]}{\acute{K}_1\mathrm{K_2K_3}[\mathrm{H^+}][\mathrm{S}]} + \frac{[\mathrm{X}]}{\mathrm{K_2K_3}[\mathrm{H^+}][\mathrm{S}]} + \frac{[\mathrm{X}]}{\mathrm{K_3}[\mathrm{S}]} + [\mathrm{X}]$$

$$[\mathrm{CAT}]_t = [\mathrm{X}] \left\{ \frac{[\acute{R}\mathrm{NH_2}]}{\acute{K}_1\mathrm{K_2K_3}[\mathrm{H^+}][\mathrm{S}]} + \frac{1}{\mathrm{K_2K_3}[\mathrm{H^+}][\mathrm{S}]} + \frac{1}{\mathrm{K_3}[\mathrm{S}]} + 1 \right\}$$

$$[\mathrm{X}] = \frac{\acute{K}_1\mathrm{K_2K_3}[\mathrm{CAT}]_t[\mathrm{H^+}][\mathrm{S}]}{[\acute{R}\mathrm{NH_2}] + \acute{K}_1 + \acute{K}_1\mathrm{K_2}[\mathrm{H^+}] + \mathrm{K_1K_2K_3}[\mathrm{H^+}][\mathrm{S}]}$$

$$\text{rate} = -\frac{d[\mathrm{CAT}]_t}{dt} = \mathrm{k_4}[\mathrm{X}] \qquad \text{(Eq. 18)}$$

$$\text{rate} = \frac{\mathrm{k_4K_1K_2K_3}[\mathrm{CAT}]_t[\mathrm{H}][\mathrm{S}]}{[\acute{R}\mathrm{NH_2}] + \acute{K}_1 + \acute{K}_1\mathrm{K_2}[\mathrm{H^+}] + \acute{K}_1\mathrm{K_2K_3}[\mathrm{H^+}][\mathrm{S}]} \qquad \text{(Eq. 19)}$$

$$\mathrm{rate} = \frac{\mathrm{K_2K_3k_4[CAT]_t[H][S]}}{1 + \mathrm{K_2[H^+]} + \mathrm{K_2K_3[H^+][S]}} \qquad \text{(Eq. 20)}$$

$$\acute{\mathrm{K}}_1 = \frac{\mathrm{K_2K_3k_4[H][S]}}{1 + \mathrm{K_2[H^+]} + \mathrm{K_2K_3[H][S]}} \qquad \text{(Eq. 21)}$$

$$\frac{1}{\acute{\mathrm{K}}_1} = \frac{1}{\mathrm{K_3k_4[S]}}\left(\frac{1}{\mathrm{K_2[H^+]}} + 1\right) + \frac{1}{\mathrm{k_4}} \qquad \text{(Eq. 22)}$$

$$\frac{1}{\acute{\mathrm{K}}_1} = \frac{1}{\mathrm{K_2K_3k_4[H^+][S]}} + \frac{1}{\mathrm{K_3k_4[S]}} + \frac{1}{\mathrm{k_4}} \qquad \text{(Eq. 23)}$$

$$\mathrm{rate} = \frac{\mathrm{K_6K_7k_8[CAT]_t[H^+][S]}}{\left[\acute{\mathrm{R}}\mathrm{NH_2}\right] + \mathrm{K_6[H^+]} + \mathrm{K_6K_7[H^+][S]}} \qquad \text{(Eq. 24)}$$

$$\frac{1}{\acute{\mathrm{K}}_1} = \frac{1}{\mathrm{K_7k_8[S]}}\left\{\frac{1}{\mathrm{K_6[H^+]}} + 1\right\} + \frac{1}{\mathrm{k_8}} \qquad \text{(Eq. 25)}$$

$$\frac{1}{\acute{\mathrm{K}}_1} = \frac{1}{\mathrm{K_6K_7k_8[H^+][S]}} + \frac{1}{\mathrm{K_7k_8[S]}} + \frac{1}{\mathrm{k_8}} \qquad \text{(Eq. 26)}$$

$$\frac{1}{\acute{\mathrm{K}}_1} = \frac{1}{\mathrm{K_3k_4[S]}}\left\{\frac{1}{\frac{\mathrm{K_6}}{\mathrm{K_1}}\,\mathrm{[H^+]}} + 1\right\} + \frac{1}{\mathrm{k_4}} \qquad \text{(Eq. 27)}$$

$$\frac{1}{\acute{\mathrm{K}}_1} = \frac{\acute{\mathrm{k}}_1}{\mathrm{K_6K_3k_4[H^+][S]}} + \frac{1}{\mathrm{K_3k_4[S]}} + \frac{1}{\mathrm{k_4}} \qquad \text{(Eq. 28)}$$

$$\ln \mathrm{k_D} = \ln \mathrm{k_\infty} + \frac{\mathrm{Ze_{\mu 0}}}{\mathrm{DKTr^2}} \qquad \text{(Eq. 29)}$$

where,
$\mathrm{K_\infty}$ = rate constant of dielectric constant
Ze = charge on ion
μ_0 = permanent moment of the dipole
r = radius of the ion
K = Boltzmann constant
T = absolute temperature

$$\mathrm{HOCl + Na^+ \leftrightarrow NaOCl + H^+} \qquad \text{(Eq. 30)}$$

$$\mathrm{3NaOCl \leftrightarrow NaClO_3 + 2NaCl} \qquad \text{(Eq. 31)}$$

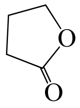
Scheme 1

$\acute{R}NHCl + H_2O \overset{K_1}{\leftrightarrow} HOCl + \acute{R}NH_2$ (i) fast

$HOCl + H^+ \overset{K_2}{\leftrightarrow} H_2OCl^+$ (ii) fast

$H_2OCl^+ + S \overset{K_3}{\leftrightarrow} X$ (iii) fast

$X \overset{K_4}{\leftrightarrow} \overline{X} + H_2O$ (iv) slow (r. d. s)

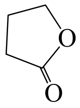
$\overline{X} + H_2OCl^+ \overset{k_5}{\rightarrow}$  $+ H_2O + H^+Cl^-$ (v) fast

Scheme 2

$\acute{R}NHCl + H^+ + H_2O \overset{K_6}{\leftrightarrow} H_2O^+Cl + \acute{R}NH_2$ (i) fast

$H_2O^+Cl + S \overset{K_7}{\leftrightarrow} X$ (ii) fast

$X \overset{K_8}{\leftrightarrow} \overline{X} + H_2$ (iii) slow (r. d. s)

$\overline{X} + H_2O^+Cl \overset{k_9}{\rightarrow}$  $+ H_2O + H^+Cl^-$ (iv) fast

Scheme 3

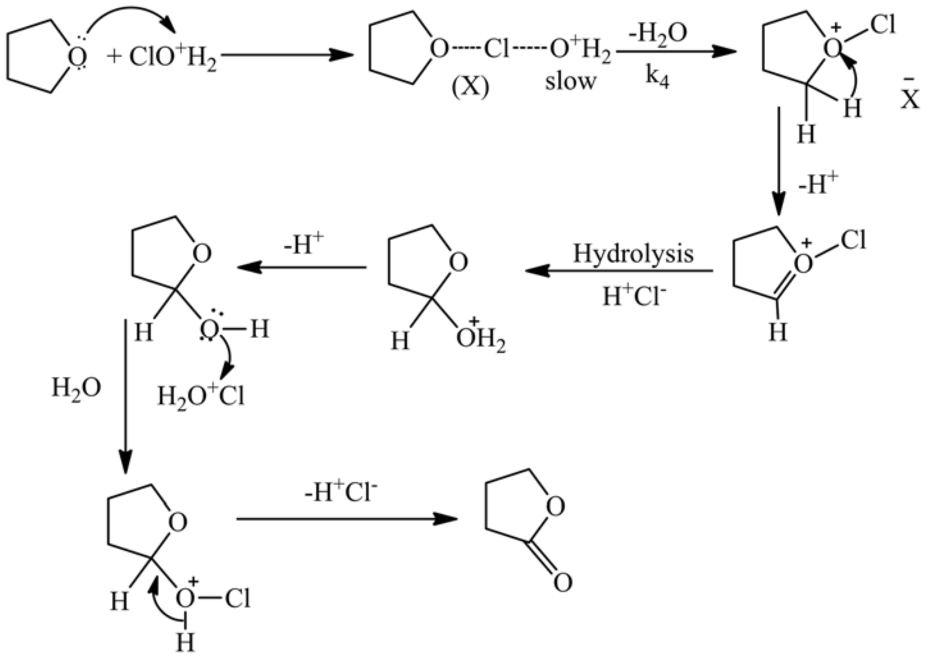


Table 1: Effect of different reactant, Chloramine-T, and hydrogen ion concentration on the rate constant at 308K, μ = 0.125 M.

10^2[CAT] M	**[THF] M**	**[H$^+$] M**	**$10^4 \acute{k}_1$ Sec^{-1}**	**$10^4 \acute{k}_1$ /[H$^+$or S]^n**
1.00	1.40	0.20	6.410	- -
1.25	1.40	0.20	5.140	- -
1.50	1.40	0.20	4.180	- -
1.75	1.40	0.20	3.610	- -
2.00	1.40	0.20	3.000	- -
1.00	1.40	0.20	6.410	5.570
1.00	2.11	0.20	7.800	5.560
1.00	2.80	0.20	8.910	5.620
1.00	3.50	0.20	9.520	5.620
1.00	4.20	0.20	10.00	5.500
1.00	1.40	0.10	4.980	15.75
1.00	1.40	0.15	6.000	15.50
1.00	1.40	0.20	6.410	14.83
1.00	1.40	0.25	7.640	15.30
1.00	1.40	0.30	8.330	15.21

(n) was obtained from the slope of log k^{-}_{1} with log [H or THF], and the unit of ^{a}k is L^{n}.mol^{-n}.sec^{-1}.

***Table 2**: Effect of different chloride ion, ionic strength and p-TSA concentration on the rate constant at 308 K; [CAT]$_o$ = 0.001 M; [THF]$_o$ = 1.4 M; [H$^+$] = 0.2 M; μ = 0.125 M.*

[Cl$^-$]$_t$ M	**$10^4 \acute{k}_1$ Sec^{-1}**	**[NaClO$_4$] M**	**$10^4 \acute{k}_1$ Sec^{-1}**	**[p-TSA] M**	**$10^4 \acute{k}_1$ Sec^{-1}**
0.25	6.63	0.125	6.41	0.025	5.18
0.30	6.53	0.250	6.46	0.050	2.57
0.35	6.64	0.375	6.50	0.075	1.32
0.40	6.83	0.500	6.45	0.100	1.27
0.45	6.53	0.625	6.45	0.125	1.08

***Table 3:** Effect of different dielectric constant (D) on the rate constant at 308 K; [CAT] = 0.001 M; [THF] = 1.4 M; [H$^+$] = 0.2 M and μ = 0.125 M.*

%CH$_3$OH	**D**	**$10^4 \acute{k}_1$**
0.00	74.93	6.41
10.0	70.64	6.83
20.0	65.81	7.22
30.0	61.12	7.67
40.0	58.44	8.94

Table 4: Effect of different temperature on the rate constant, [CAT] = 0.001 M, [THF] = 1.4 M, [H$^+$] = 0.2 M and μ = 0.125 M.

Temperature K	298	303	308	313	318
$10^4 \acute{k}_1$ (sec^{-})	4.34	5.30	6.41	7.72	9.21

E$_a$ =29.80 KJ/mole
Log A = 6.8684
$\Delta H^{\neq}$ = 27.11 ± 0.07 KJ/mole
$\Delta G^{\neq}$ = 94.4 ± 2.18 KJ/mole
$\Delta S^{\neq}$ =21.8 ± 0.04 KJ/mole

Table 5: *The rate constant of the observed and the calculated first-order rate in different concentrations of [THF] and [H⁺] at 308 K [CAT] = 0.00 1M, μ = 0.125 M.*

[THF] M	**[H^+] M**	**$10^4\acute{k}$ Sec^{-1}**	**$10^4\acute{k}_1/[H^+orS]^n$**	**$10^4\acute{k}_{cal}$ Sec^{-1}**	**$10^4\acute{k}_{cal}/[h^+orS]^n$**
1.4	0.20	6.410	5.560	6.88	5.90
2.1	0.20	7.800	5.560	8.28	5.98
2.8	0.20	8.910	5.650	9.18	5.91
3.5	0.20	9.520	5.630	9.85	5.64
4.2	0.20	10.02	5.480	10.36	5.66
1.4	0.10	4.980	15.80	4.73	14.44
1.4	0.15	6.000	15.50	5.98	15.13
1.4	0.20	6.410	14.85	6.89	14.95
1.4	0.25	7.640	15.30	7.58	15.20
1.4	0.30	8.330	15.20	8.20	15.00

(n) was obtained from the slope of the plot log k^{-}_{1} with log [H or THF], and k^a is the unit of $L^n.mol^{-n}.sec^{-1}$.

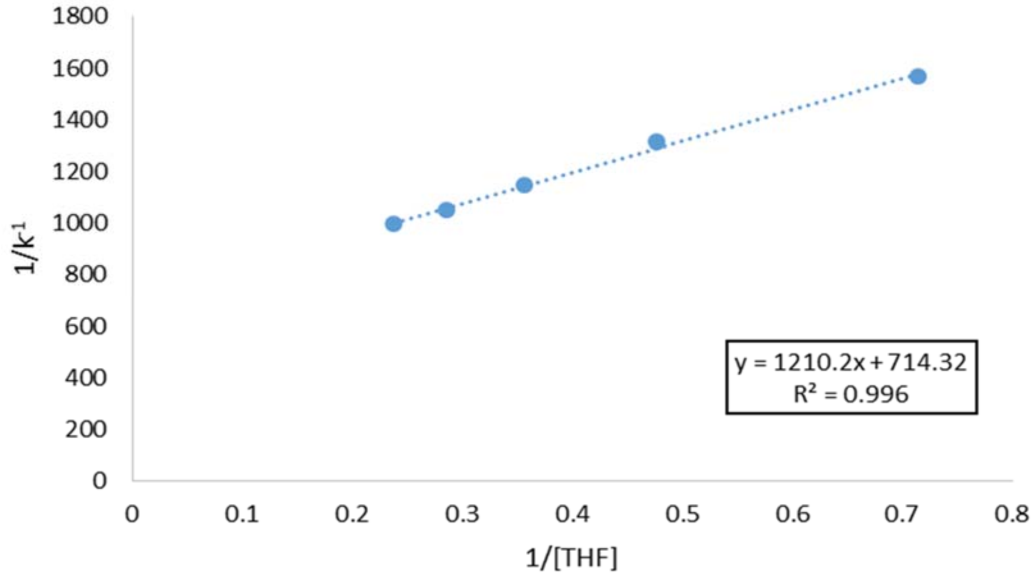


Figure 1: *Plot of $1/k_1$ versus 1/[THF]; [CAT] = 0.0015 M; [H] = 0.2 M; μ = 0.125 M; Temperature = 308 K.*

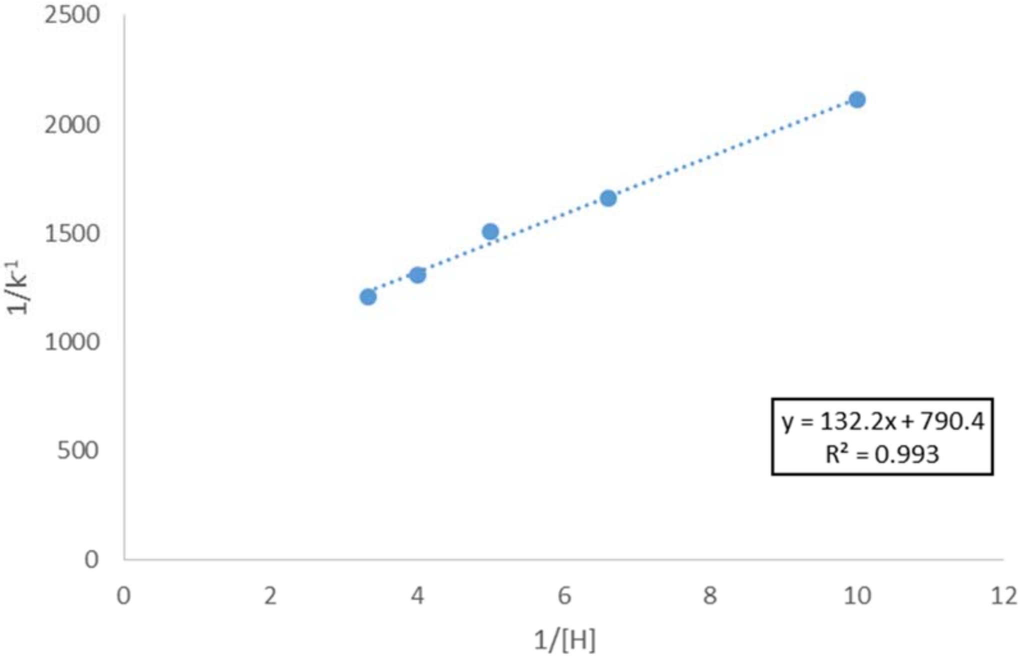


Figure 2: *Plot of $1/k_1$ versus 1/[H]; [CAT] = 0.0015 M; [THF] = 1.4 M; μ = 0.125 M; Temperature = 308 K.*