

Article

Study of the Kinetics and Thermodynamic Parameters of Schiff Bases Derived from 4-Aminoantipyrine

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Abstract: The kinetic and thermodynamic properties of six well-known Schiff bases (A1, A3, A5, A6, A8, A12) derived from 4-aminoantipyrine and six different aromatic aldehydes were studied. The substituent on aldehydic ring of the compounds ranged from electron-withdrawing to electron-donating substituents, in addition to benzaldehyde itself. The hydrolysis kinetics of the Schiff bases revealed minimal disparity in their rate constant values. Faster rate of hydrolysis was observed in the case of (A5) comparing with the remaining compounds. The effect of an acidic pH on the hydrolysis process is in line with earlier research and studies, indicating that conducting the reaction in acidic or basic environments, as opposed to a neutral environment, speeds up the process. An investigation into the effect of temperature on the hydrolysis of the examined compounds revealed that the activation energy values for all compounds were quite low. This indicates that the reaction occurs readily and rapidly. The ΔG values indicated that the hydrolysis processes of the compounds under investigation did not proceed spontaneously, but were instead facilitated by the presence of a catalyst, specifically hydrogen and hydroxyl ions. The investigation verified the significance of the thermodynamic variables (ΔH and ΔS) in regulating reaction rates. Additionally, the calculated negative entropy value suggests a probable formation of the activated active complex.

Keywords: Schiff bases, Hydrolysis, Kinetics, 4-Aminoantipyrine, Thermodynamic parameters

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1. Introduction

The process of synthesizing Schiff bases from amines and carbonyl groups is typically characterized by reversible reactions. A number of crucial elements influence the hydrolysis process of Schiff bases, such as the acidity and polarity of the solvent, the substitution of the aryl ring, the presence of implicit hydrogen bonding associated with the azomethane group, and the temperature ^(1,2). Numerous investigations have indicated that Schiff bases synthesized from aniline or substituted aniline and isobutane show instability in inert solvents ⁽³⁾. Conversely, other studies have demonstrated that Schiff bases derived from isobutane and aliphatic amines are comparatively less stable than those derived from benzaldehyde, aniline, or their derivatives ^(3,4). The hydrolysis of Schiff bases involves their conversion into their conjugated acid in an acidic media ⁽⁵⁾. In the neutral

solution, water molecules serve as both the nucleophile and the acid, leading to the formation of the carbonium ion by attacking the isomethane group. The hydrolysis of benzylidene aniline ⁽⁶⁾ was investigated in an aqueous ethanol solution. It was observed that the rate of reaction is independent of the proton concentration in basic media within the pH range of 10-12. However, the rate of reaction does depend on the proton concentration within the pH range of 5-10, and the reaction rate accelerates when the pH exceeds 5 ⁽⁷⁾. In an investigation conducted on the hydrolysis of the salicylidene aniline compound ⁽⁸⁾, it was found that the ortho group slows down the hydrolysis rate at pH levels between 5.6 and 6.6. This result was attributed to the formation of hydrogen bonding between the nitrogen atom of the azomethane group and the hydroxy group in the ortho position of the aldehyde moiety ^(9,10). A study was conducted to investigate the effect of electron- withdrawing and electron-donating groups on the rate constant value of the hydrolysis of certain Schiff-bases and their complexes. The spectroscopic approaches were employed to analyze the data obtained ⁽⁹⁻¹¹⁾.

In our work, stability of Schiff bases synthesized from 4-aminoantipyrine and several aromatic aldehydes in 10% ethanolic aqueous solution was studied. The stability was investigated under acidic, neutral, and basic conditions, and the corresponding thermodynamic characteristics were recorded.

2. Materials and Methods

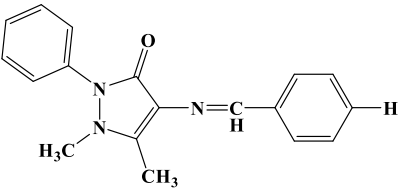
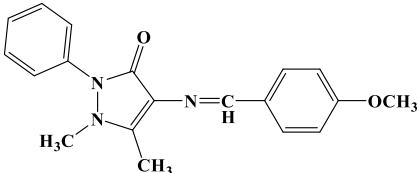
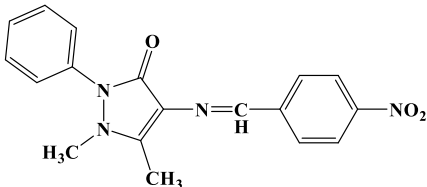
2.1. Used Devices:

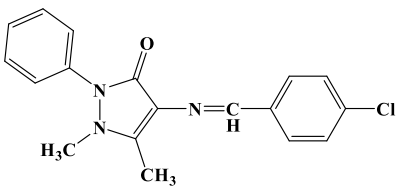
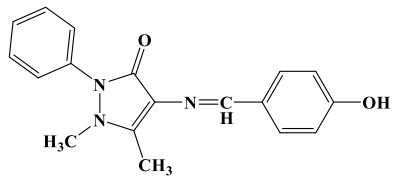
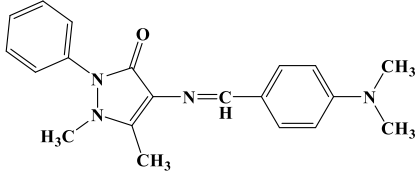
Thermostat to control temperatures from MINI Dry Bath, model Guanai. A pH meter model (PEAK - INSTRUMENTS) was also used to measure the pH.

2.2. The Schiff bases

(A1, A3, A5, A6, A8, and A12) shown in (table 1) were resynthesized according to the previously outlined process ⁽¹¹⁾.

Table 1. The structural formula and nomenclature of the resynthesized Schiff bases

Comp. No.	Structural formula	Nomenclature
A1		4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one
A3		4-((4-methoxybenzylidene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one
A5		1,5-dimethyl-4-((4-nitrobenzylidene)amino)-2-phenyl-1,2-dihydro-3H-pyrazol-3-one

A6		4-((4-chlorobenzylidene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one
A8		4-((4-hydroxybenzylidene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one
A12		4-((4-(dimethylamino)benzylidene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one

2.3. Chemical Kinetics Measurements

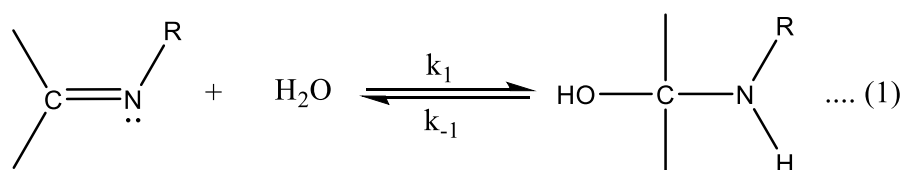
A solution containing Schiff bases at a concentration of (10^{-4} M) was prepared using a mixture of 10% ethanol and 90% distilled water. This solution was then utilized in all of the experiments. The pH of each sample was determined using calculated amount of HCl and NaOH, followed by measurement with a pH meter ⁽¹²⁾.

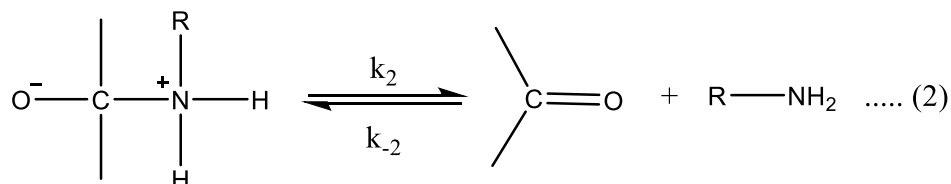
2.4. Experiments conducted to investigate the effect of temperature on the kinetics of hydrolysis of Schiff bases.

Solutions containing Schiff bases at a concentration of (10^{-4} M) were prepared using 10% ethanolic aqueous solutions, with pH values of 5, 7, and 9. The spectrophotometric monitoring of each solution's absorbance was conducted at regular intervals of 20 seconds, under various controlled temperatures (298, 308, 318, and 328) ⁽¹³⁾.

3. Results and Discussion

This study examined the stability of six well-known Schiff bases (A1, A3, A5, A6, A8, A12) toward hydrolysis in (10%) ethanolic aqueous solution at pH levels of 5, 7, and 9. The hydrolysis process occurs as described by equations (1,2)⁽¹³⁾. The selected compounds were chosen based on their diverse electron-withdrawing or donating substitutions on the benzene ring of the aldehyde moiety of Schiff bases. In both neutral and basic conditions, the first step (equation 1) is identified as the step that determines the rate of the reaction. However, in acidic situations, the second step (equation 2) becomes the rate determining one ^(13,14). The effect of hydrogen and hydroxyl ions on the formation and decomposition of imines was also studied ^(13,15).





The spectrophotometric measurement of the hydrolysis rate of Schiff base was conducted at several wavelengths according to the λ_{max} of each chemical under investigation. Buffered solutions were made and employed in accordance with the methodology outlined in a previous research work ^(13,16). The variation in the absorbance measurements of the Schiff bases were detected in a quartz cell within time intervals of 20 seconds, in comparison to a reference solution held in a separate quartz cell of the instrument, and the concentration of imine was consistently maintained at a molarity of 1.0×10^{-4} .

The order of the reactions was determined using the graphical method. The calculated rate constants and reaction orders were confirmed by plotting $\ln (A_0 - A_\infty / A_t - A_\infty)$ against time (t), as shown in Figures (1-3). The straight line passing through the origin indicates that the reaction follows a pseudo-first order. The rate constants for each reaction were obtained from the slopes of the lines. These figures also display the slopes of the lines and stability constants for the compounds studied at a neutral pH of 7.

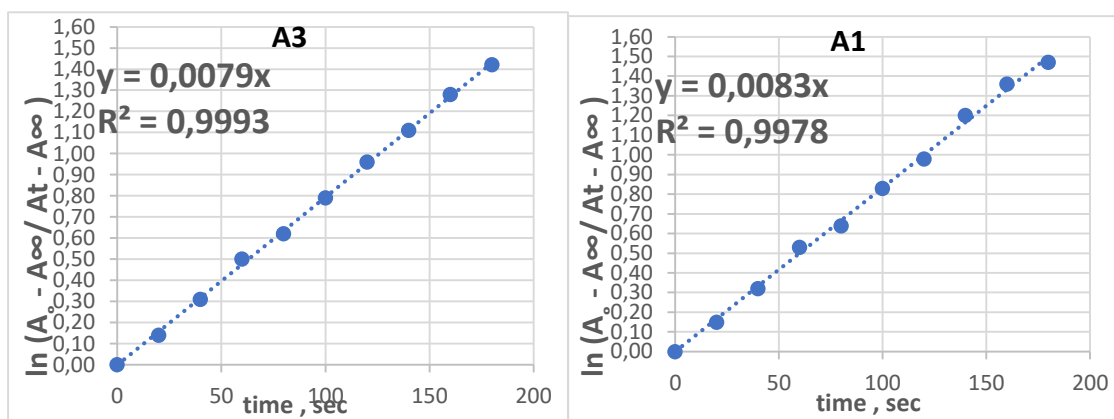


Figure 1. Plot of $\ln (A_0 - A_\infty / A_t - A_\infty)$ versus time for hydrolysis of compounds (A1 and A3) at pH = 7 and Temp. 298 °K

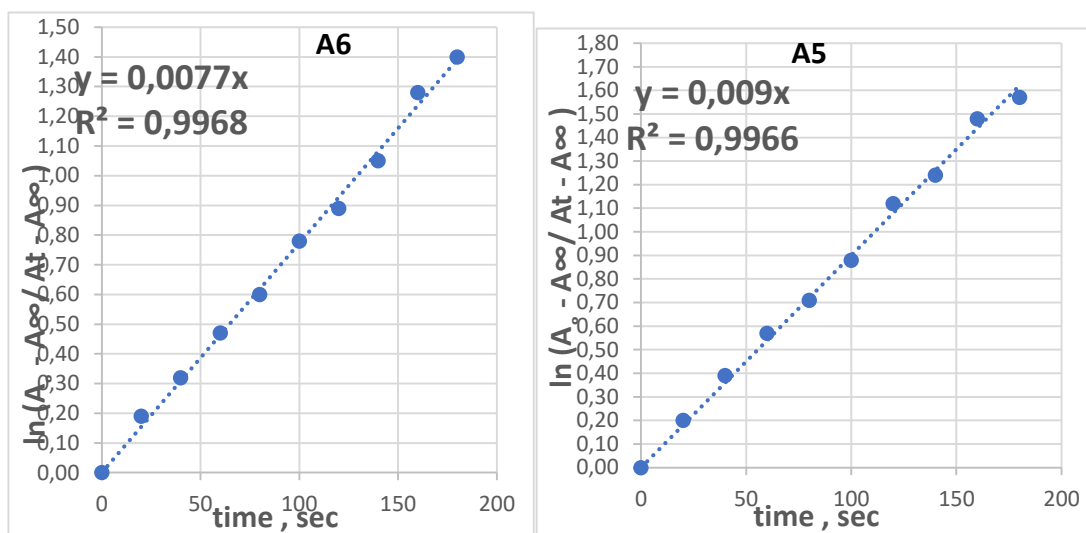


Figure 3. Plot of $\ln (A_o - A_\infty / A_t - A_\infty)$ versus time for hydrolysis of compounds (A5 and A6) at pH = 7 and Temp. 298 °K

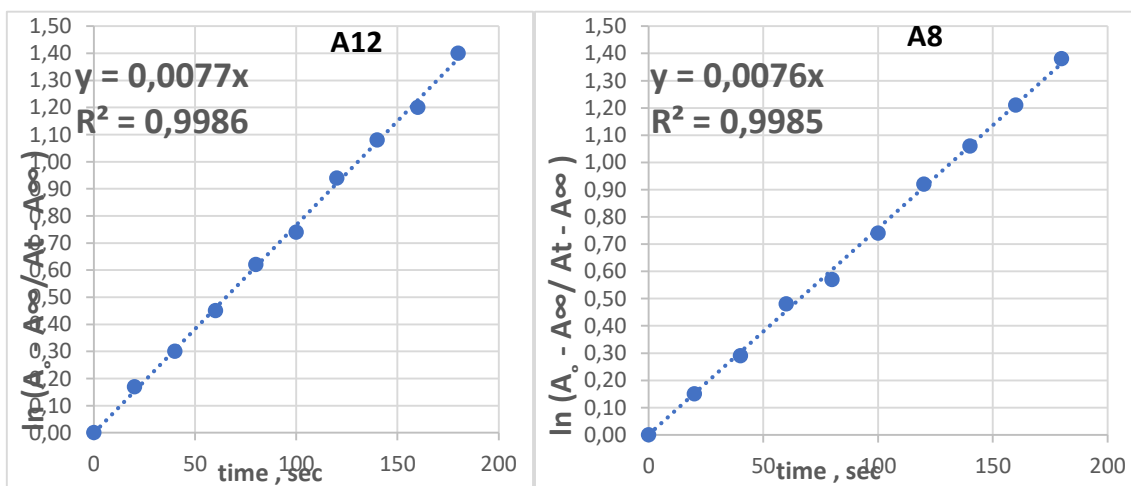


Figure 3. Plot of $\ln (A_o - A_\infty / A_t - A_\infty)$ versus time for hydrolysis of compounds (A8 and A12) at pH = 7 and Temp. 298 °K

The investigation into the effect of the pH on the stability constant value was carried out by preparing solutions of the compounds being examined in three distinct environments: alkaline (pH = 9), neutral (pH = 7), and acidic (pH = 5), at a temperature of 25°C. It was observed that conducting hydrolysis experiments in a neutral media resulted in lower rate constant values (k) of the compounds compared to acidic (pH= 5) and basic media (pH = 9), indicating enhanced stability in a neutral pH and confirming the role of acidity on the rate of the reactions ^(13,17). The results were documented in (Table 2), displaying the rate constants for the six compounds (A1, A3, A5, A6, A8, A12) in at pH levels of 5, 7, and 9.

Table 2. Rate constants (k , s^{-1}) for hydrolysis of the compounds (A1, A3, A5, A6, A8, A12) at pH3, pH5, pH9 at Temp 298

pH	A1	A3	A5	A6	A8	A12
pH=5	8.45×10^{-3}	8.1×10^{-3}	9.15×10^{-3}	7.78×10^{-3}	7.7×10^{-3}	7.8×10^{-3}
pH=7	8.3×10^{-3}	7.9×10^{-3}	9.0×10^{-3}	7.7×10^{-3}	7.6×10^{-3}	7.7×10^{-3}
pH=9	8.50×10^{-3}	8.23×10^{-3}	9.4×10^{-3}	7.9×10^{-3}	7.85×10^{-3}	8.0×10^{-3}

The findings derived from our ongoing investigation as displayed in the aforementioned table reveals that: First, the disparity in the rate constant values is rather small between resonance-donating substituent groups of compounds (A3, A6, A8, and A12) and the resonance-withdrawing ones of compound (A5) when compared to the unsubstituted compound (A1) in general. Second, the high value of rate of the hydrolysis reaction, specifically the heightened values of the rate constant (indicating reduced stability) observed in the case of compound (A5), can be attributed to the role of the substituent (4-NO₂) in withdrawing of electrons through negative induction (-I) and negative resonance (-M). This process intensifies and consolidates the positive charge that is generated on the intermediate state of the imine. It also lowers its stability and diminishes its lifetime following protonation. Inductive electron removal is the primary factor in this context ^(11, 18). Third, the decrease in the rate constant (indicating increased stability of the intermediate state) during the hydrolysis process of compounds (A3, A6, A8, A12) is linked to the presence of substituents (-OH, -Cl, -N, N-(CH₃)₂). The positive resonance effect (+M) reduces the charge on the intermediate state by distributing it throughout the whole molecule in a new resonant state, which prolongs the life of the positively charged intermediate state ^(11, 19) by counteracting the negative induction (-I). Four, the impact of the acidic strength aligns with prior research and investigations, indicating that carrying out the reaction under acidic or basic conditions, as opposed to neutral conditions, hastened the hydrolysis process ^(11, 13, 20).

3.1. The Suggested Mechanism Of Hydrolysis

Within the pH range of 3, 5, and 9, it is hypothesized that the Schiff base (HA) undergoes decomposition through four rate-limiting steps ⁽¹³⁾.

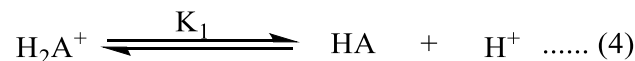
- The first step involves the acid-catalyzed addition of a water molecule to the imine bond of the protonated Schiff base, H₂A⁺ (k_1).
- The Second step, the spontaneous process involves the addition of water to the specific bond on the neutral Schiff base, H₂A (k_2).
- The third step involves the introduction of water to the imine anion, A⁻ (k_3).
- Fourth - The hydroxyl ion is added to the imine alanion, A⁻(k_4). The fourth stage, characterized by the prevalence of the hydroxyl ion, can be excluded when the rate

constant's value is not significantly influenced by the concentration of the hydroxyl ion at pH = 9 as shown in (Table 2).

Thus, the overall rate of hydrolysis will be as it displayed by (equation 3).

$$\text{Rate} = k_1 (\text{H}_2\text{A}^+) + k_2 (\text{HA}) + k_3 \text{A}^- \dots\dots\dots (3)$$

The equilibria of deprotonation and protonation of the Schiff base (HA) maybe outlined by



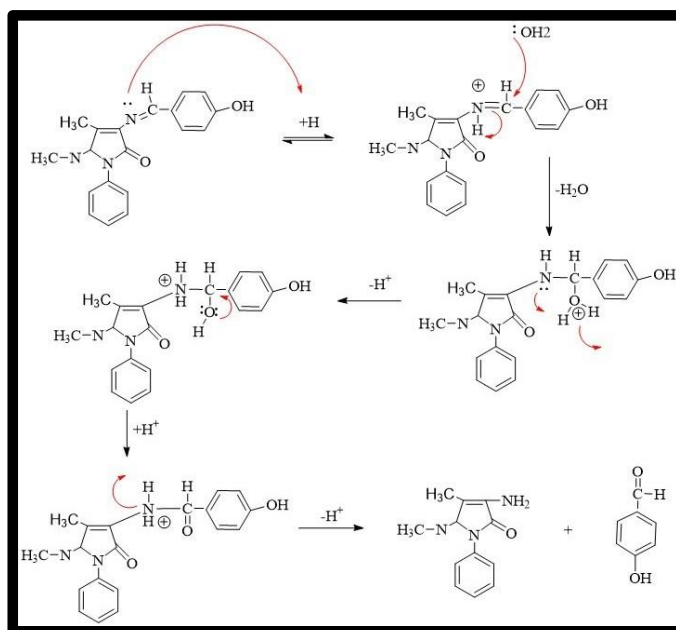
3.2. Hydrolysis Of Schiff Bases In Neutral, Acidic And Basic Environments

The rate constant varies linearly with the hydrogen ion concentration in the acidic pH range ⁽¹³⁾, and in the case of our study (pH=5) (Table 2), since at this acidic exponent, equation (3) is reduced to equation (7), as is it mentioned below:

$$\text{Rate} = k_1 (\text{H}_2\text{A}^+) + k_2 (\text{HA}) \dots\dots\dots (6)$$

$$K = (k_1/K_1) [\text{H}^+] + k_2 \dots\dots\dots (7)$$

Therefore, it is proposed that at this acidic pH, the primary factor causing decomposition (Scheme 1) is the water-assisted proton attack on the active imine (HA) bond. Conversely, the slow rates observed at neutral pH (pH = 7) can be attributed to the minimal protonation of (HA), resulting in a significantly slower water attack on the protonated imine. Thus, the addition of a water molecule to the neutral may potentially act as the step that determines the rate. In Scheme 1, the process of hydrolysis of compounds is illustrated ^(13, 21).



Scheme 1. The proposed mechanisim for the hydrolysis of compound A8 at basic media

Within the alkaline pH range, specifically at pH 9, the rate constant exhibited an upward trend as the pH increased. This behavior is illustrated in (Table 2). The rate constant continued to rise until it hit a threshold where it becomes independent of pH. This threshold occurred when the concentration of hydroxyl ions exceeded a pH value greater than this number as it was mentioned earlier ^(13,22). Within this pH range, it can be inferred that the Schiff base exists in its anionic form (A^-) as a result of the neutralization of the phenolic proton from the para-hydroxy group of the molecule (A8) by the hydroxyl ion of the base ^(13, 23). Based on the aforementioned observations, we can infer that the produced complex is likely an Arrhenius complex. When there is an excess of catalyst present, the Arrhenius complex accelerates the reaction of the hydroxyl ion, namely compound A8, at a low concentration of the hydroxyl ion. The reaction rate reached a specific value at a higher concentration of the hydroxyl ion ⁽²⁴⁾. The aforementioned findings suggest that the rate-determining step is the slower reaction step involving the Schiff base anion and water ($A \cdot H_2O$) (k_4) ^(13, 25).

3.3. The Reaction Rate Changes with Temperature

The influence of temperature is a crucial factor on investigating the characteristics of hydrolysis and assessing the stability of the Schiff rules being examined. Calculating the thermodynamic parameters of the reaction products is essential in order to comprehend the forces that govern them and the characteristics of the reaction system. To investigate the impact of temperature on the rate constants for the hydrolysis reaction of the studied bases, the values of these constants were determined by conducting the reactions at various temperatures within the range of 288 to 318 °K. The reactions were carried out at a molar concentration of 1×10^{-4} and at a pH of 7.

The data depicted in figures (4-9) demonstrate that the rate constants of the examined compounds exhibit an upward trend with rising temperature. This indicates that the hydrolysis of these compounds becomes easier, leading to a decrease in their stability.

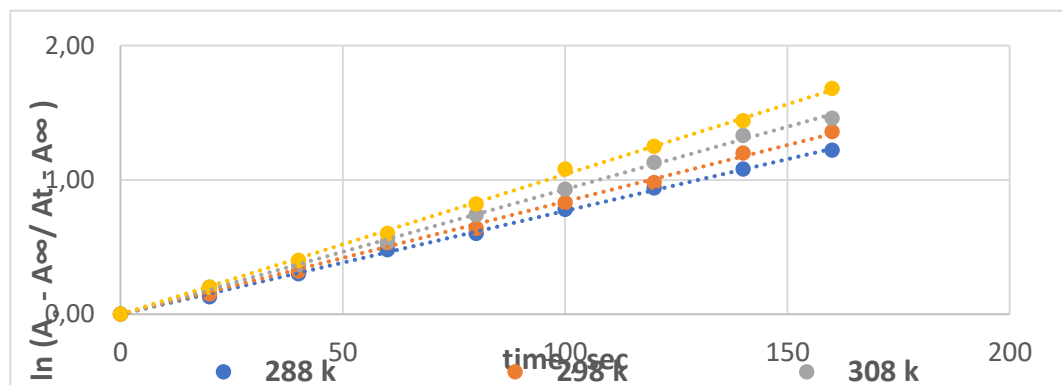


Figure 4. Plot of $\ln (A_o - A_\infty / A_t - A_\infty)$ versus time for hydrolysis of compound A1 at pH = 7 and Temperatures (298, 308, 318, 328°K)

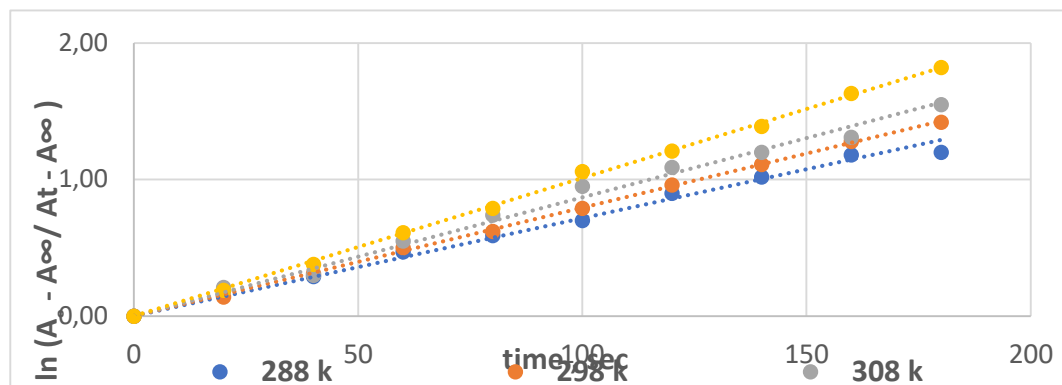


Figure 5. Plot of $\ln (A_o - A_\infty / A_t - A_\infty)$ versus time for hydrolysis of compound A3 at pH = 7 and Temperatures (298, 308, 318, 328°K)

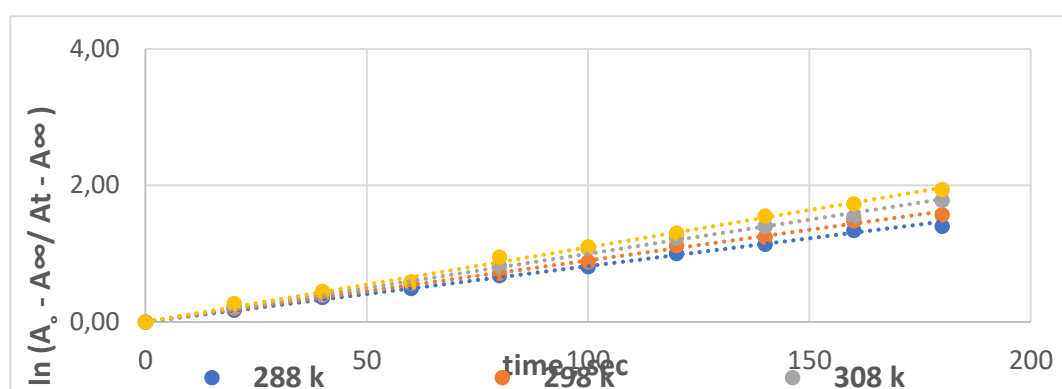


Figure 6. Plot of $\ln (A_o - A_\infty / A_t - A_\infty)$ versus time for hydrolysis of compound A5 at pH = 7 and Temperatures (298, 308, 318, 328°K)

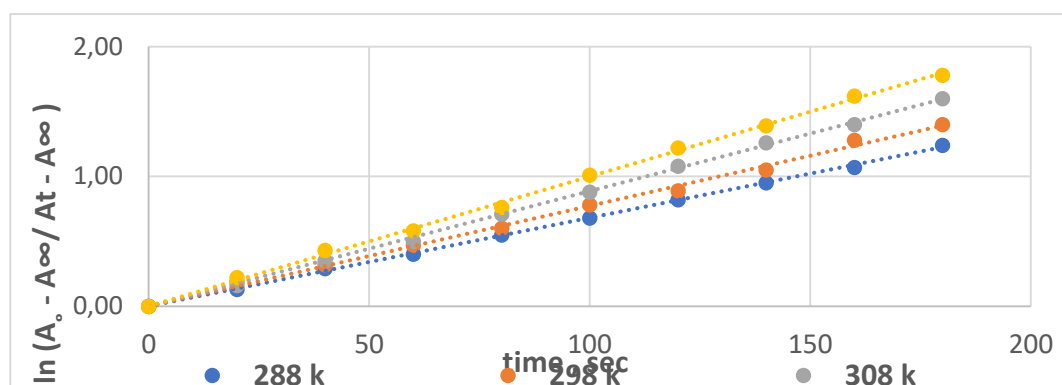


Figure 7. Plot of $\ln (A_o - A_\infty / A_t - A_\infty)$ versus time for hydrolysis of compound A6 at pH = 7 and Temperatures (298, 308, 318, 328°K)

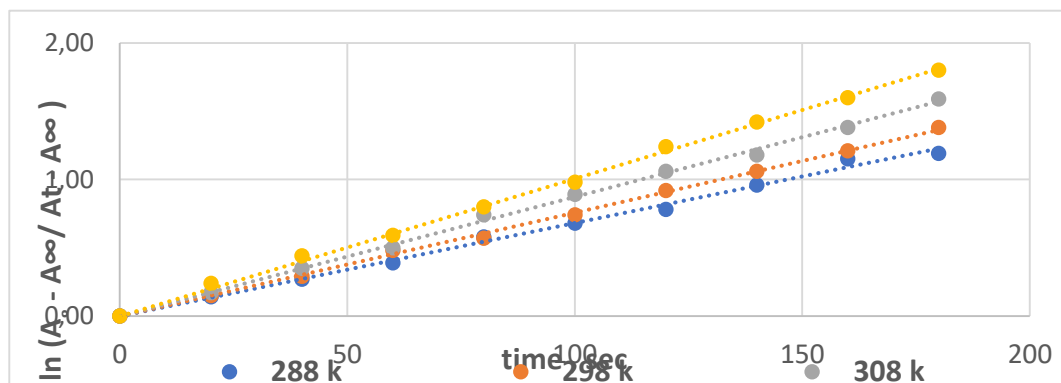


Figure 8. Plot of $\ln (A_o - A_\infty / A_t - A_\infty)$ versus time for hydrolysis of compound A8 at pH = 7 and Temperatures (298, 308, 318, 328°K)

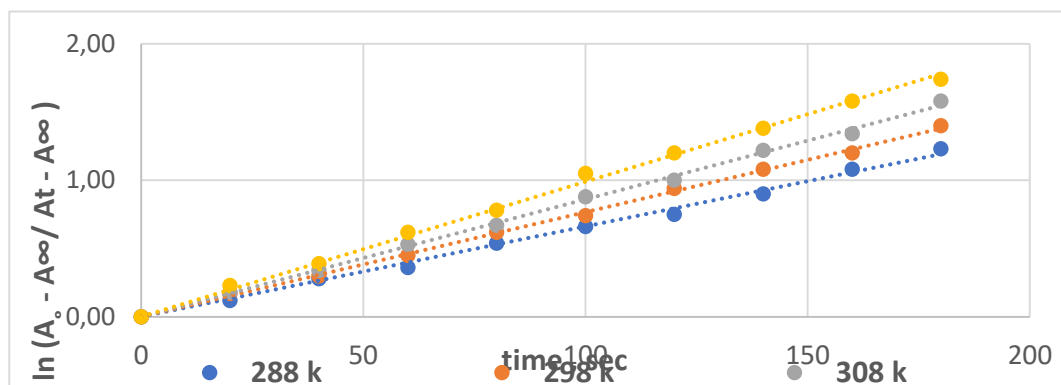


Figure 9. Plot of $\ln (A_o - A_\infty / A_t - A_\infty)$ versus time for hydrolysis of compound A12 at pH = 7 and Temperatures (298, 308, 318, 328°K)

A linear relationship was observed when the Arrhenius equation was used to determine the activation energy values for each compound. This was done by plotting the natural logarithm of the reaction rate constants (k) for each compound at four different temperatures (288, 298, 308, and 318°K) against the reciprocal of these values ($1/T$), and the activation energy value (E_a) for each compound were determined using the Arrhenius equation (8).

$$\ln k = \ln A - E_a/RT \dots \dots \dots (8)$$

The findings were displayed in Figures 10-15. The variables (ΔH , ΔG , ΔS) were calculated and are presented in (Table-3). The activation energy values were equated with the change in enthalpy (ΔH), and the value of the change in Gibbs free energy (ΔG) was determined for each value of k using (equation 9).

$$\Delta G = -nRT \ln k \dots \dots \dots (9)$$

The change in entropy (ΔS) was calculated using (equation 10). The objective of the thermodynamic study was to determine the characteristics of the reaction system being investigated, including the possibility of the chemical reaction to take place and if it can occur spontaneously. There was a need for specific external conditions to be available for the purpose

of starting the reaction. Furthermore, this study allowed for the determination of both the quality of the reaction and the underlying factors that cause it.

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots (10)$$

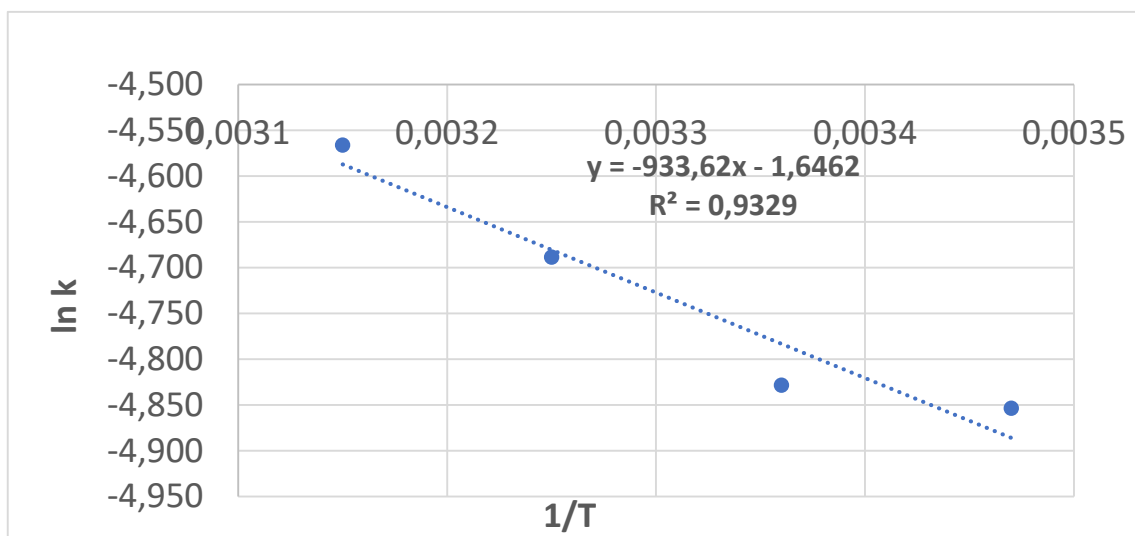


Figure 10. Plot of ln k against 1/T for compound A1 at pH=7

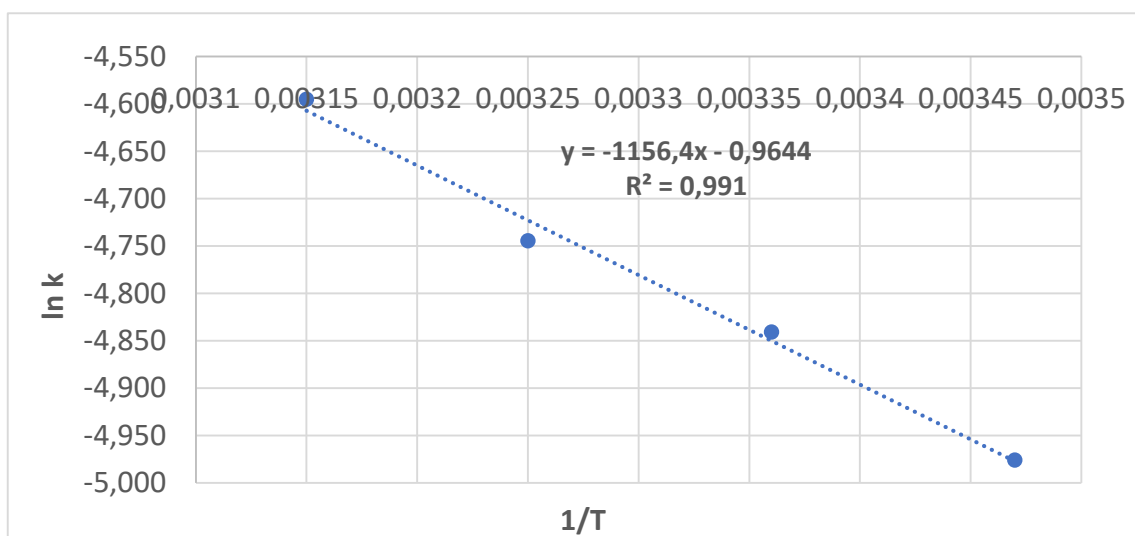


Figure 11. Plot of ln k against 1/T for compound A3 at pH=7

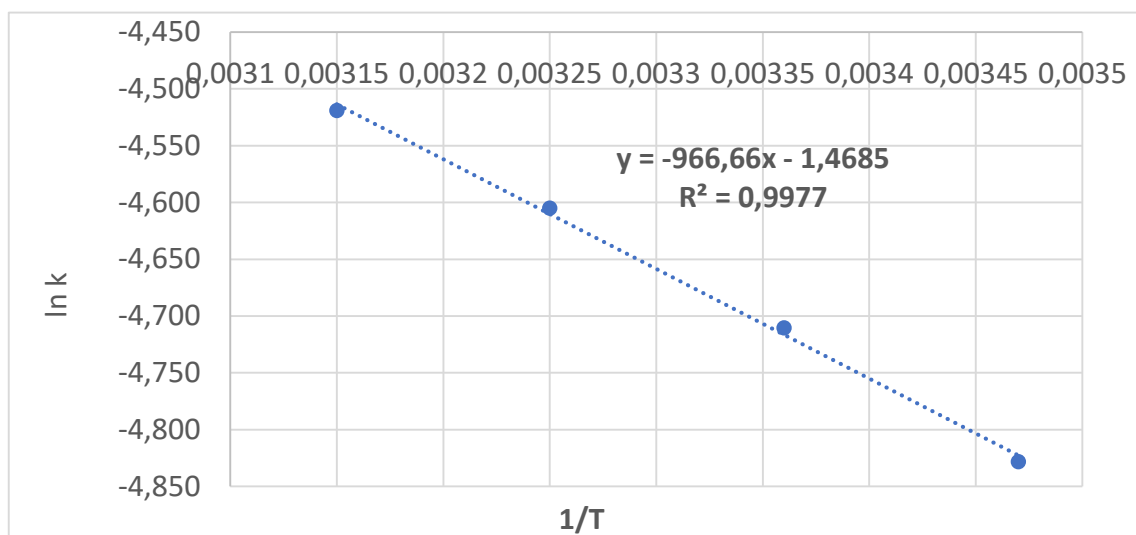


Figure 12. Plot of $\ln k$ against $1/T$ for compound A5 at pH=7

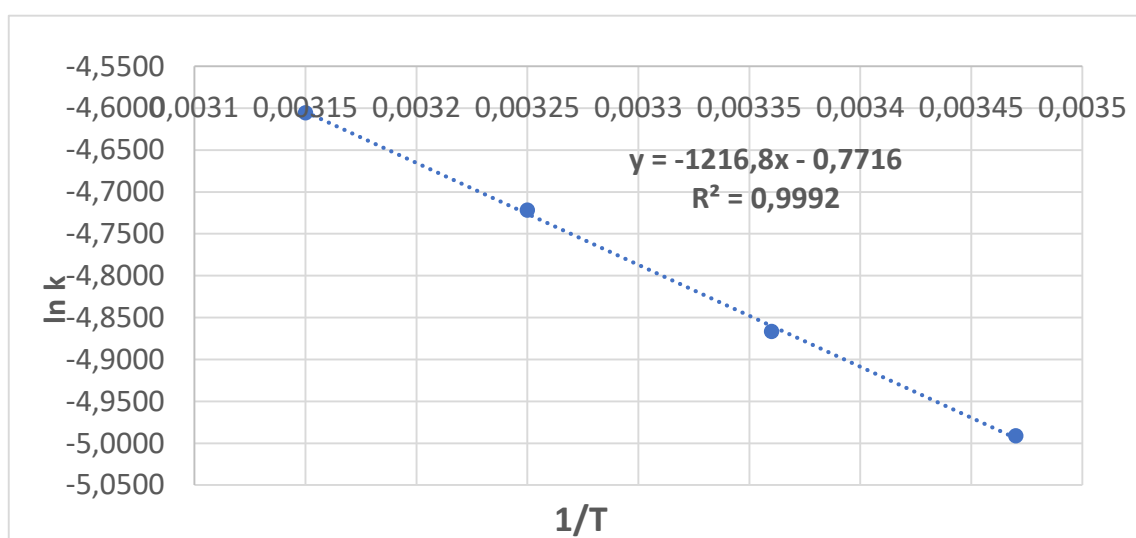


Figure 13. Plot of $\ln k$ against $1/T$ for compound A6 at pH=7

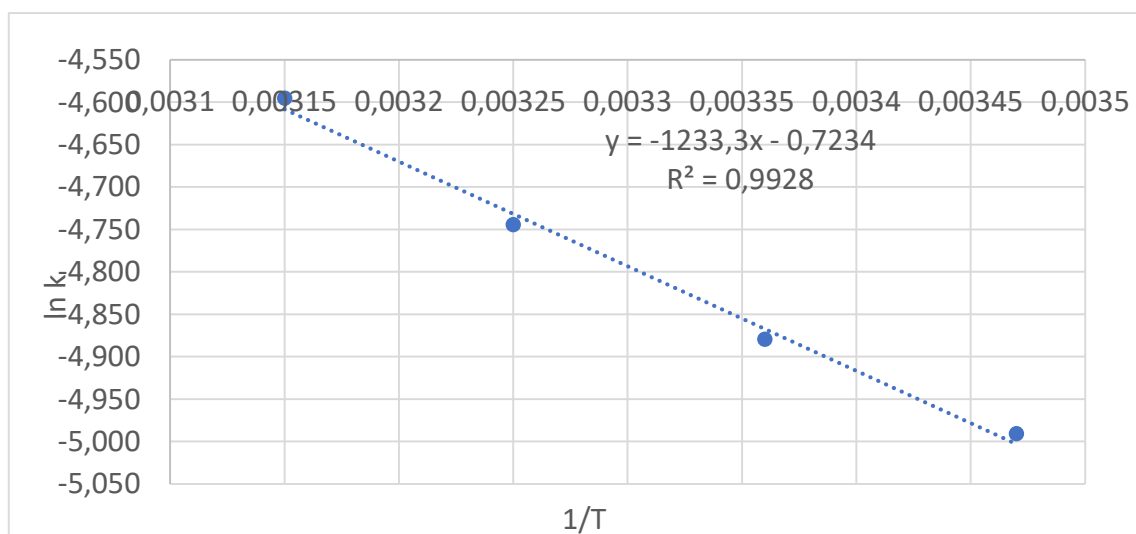


Figure 14. Plot of $\ln k$ against $1/T$ for compound A8 at pH=7

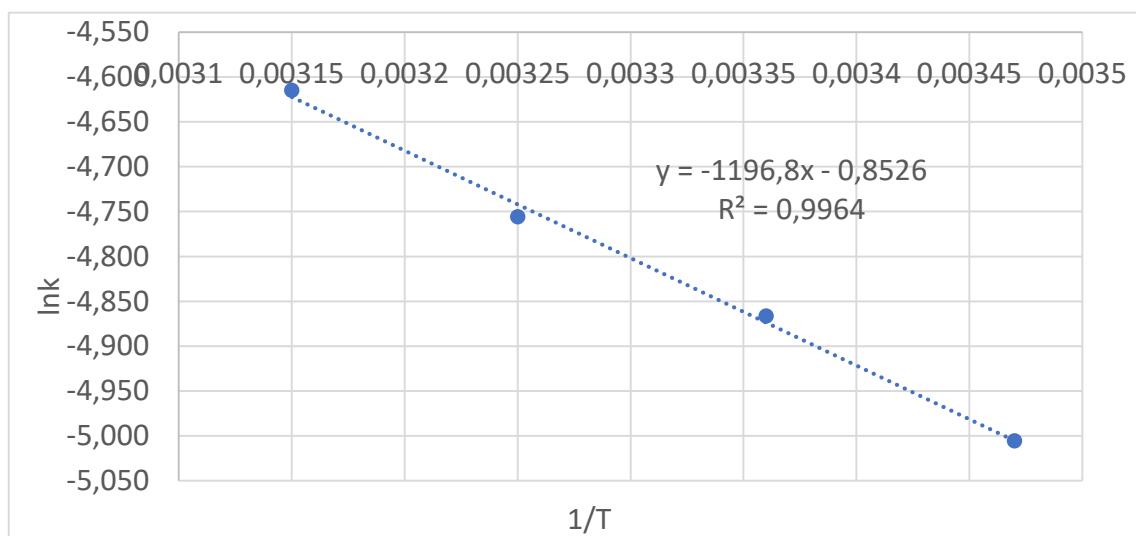


Figure 15. Plot of $\ln k$ against $1/T$ for compound A13 at pH=7

Table 3. Thermodynamic parameters of the compounds (A1, A3, A5, A6, A8, A12)

Comp.	T(K°)	1/T (K ⁻¹)	Ln k	t _{1/2}	ΔG (J.mol ⁻¹)	ΔH (J.mol ⁻¹)	ΔS (J.mol ⁻¹ . K ⁻¹)
A ₁	288	0.00347	-4.8536	88.8461538	11621.61516	7390.23146	-14.69230
	298	0.00336	-4.7795	82.5	11841.55537		-14.93733
	308	0.00325	-4.6886	75.326087	12006.15428		-14.98676
	318	0.00315	-4.5659	66.6346154	12071.56385		-14.72117
A ₃	288	0.00347	-4.97623	100.43478	11915.25361	9614.30960	-7.98939
	298	0.00336	-4.84089	87.72152	11993.65976		-7.98440
	308	0.00325	-4.74443	79.65517	12149.12460		-8.22992
	318	0.00315	-4.59522	68.61386	12149.08120		-7.97098
A ₅	288	0.00347	-4.82831	86.62500	11561.06892	8036.81124	-12.23701
	298	0.00336	-4.71053	77.00000	11670.67897		-12.19419
	308	0.00325	-4.60517	69.30000	11792.51456		-12.19384
	318	0.00315	-4.51899	63.57798	11947.54733		-12.29791
A ₆	288	0.00347	-4.99083	101.91176	11950.20944	10116.47520	-6.36713
	298	0.00336	-4.86653	90.00000	12057.19073		-6.51247
	308	0.00325	-4.72170	77.86517	12090.92410		-6.41055
	318	0.00315	-4.60517	69.30000	12175.38841		-6.47457
A ₈	288	0.00347	-4.99083	101.91176	11950.20944	10253.65620	-5.89081
	298	0.00336	-4.87961	91.18421	12089.57775		-6.16081
	308	0.00325	-4.74443	79.65517	12149.12460		-6.15412
	318	0.00315	-4.59522	68.61386	12149.08120		-5.96046
A ₁₂	4288	0.00347	-5.00565	103.43284	11985.68316	9950.19520	-7.06767
	298	0.00336	-4.86653	90.00000	12057.19073		-7.07045
	308	0.00325	-4.75599	80.58140	12178.72854		-7.23550
	318	0.00315	-4.61522	70.00000	12201.96001		-7.08102

Upon examining the thermodynamic parameters presented in (Table 3), the following conclusions can be drawn:

1. The compounds studied exhibited low activation energy values, indicating a high likelihood and rapidity of the reaction occurring. This result is consistent with the Arrhenius relationship ($k=Ae^{-(E_a/RT)}$), which establishes an inverse correlation between the reaction rate, represented by the rate constant (k), and the value of activation energy (E_a).
2. The hydrolysis processes of all the investigated compounds did not proceed spontaneously, but were solely accelerated by the presence of a catalyst, specifically hydrogen and hydroxyl ions. Positive values of the change in free energy (ΔG) support this findings.
3. Postive values of (ΔH) reveals that the studied chemicals undergownt an endothermic thermal breakdown reaction. Consequently, the produced compounds transition from a stable state is characterized by lower potential energy comparing to the products, which consist (the amine and aldehydes).
4. The thermodynamic parameters, specifically the change in enthalpy (ΔH) and the change in entropy (ΔS), play a crucial role in regulating the rate of reactions ⁽²⁶⁾.
5. The activation entropy's negative value suggests that the reaction likely involves the interaction of similarly charged ions or ions with neutral molecules, resulting in the formation of a solid intermediate transition state. This leads to a slow reaction rate ⁽²⁷⁾, indicating that the current reaction likely involves similar ions ⁽²⁸⁾. The presence of the protonated water molecule at the nitrogen atom of the imine bond suggests that the solvent molecules undergo significant reorientation due to the creation of the activated complex ^(13, 29, 30).

4. Conclusion

There is no discernible disparity in the rate constant values during investigating the hydrolysis kinetics of the compounds under study (A1, A3, A5, A6, A8, and A12). The results of the acid pH study align with earlier research and investigations, indicating that the hydrolysis process exhibits a faster reaction in both acidic and basic conditions compared to neutral conditions. All the chemicals tested had low activation energy values, indicating that their hydrolysis reaction can occur easily and rapidly. All tested substances exhibited positive values for ΔG and ΔH , and negative values for ΔS .

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