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Research Article

Photochemical Stability, Chemical Kinetics, and Electrical Characterization Studies as well as Some Theoretical Studies of Some Cyclic Hydrazones

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ABSTRACT

The kinetic and thermodynamic properties of six Schiff bases (M1-M4) derived from 4-Pyridinecarboxylic acid hydrazide, and various aromatic aldehydes were studied. The aldehyde rings contained both electron-withdrawing and electron-donating substituents, as well as benzaldehyde itself. Hydrolysis kinetics showed minimal variation in rate constant values, with M2 exhibiting the fastest hydrolysis. The effect of pH indicated that acidic and basic environments accelerated the reaction compared to neutral conditions. Temperature dependence revealed low activation energy values for all compounds, indicating rapid reactions. Thermodynamic analysis showed that the hydrolysis processes were non-spontaneous ($\Delta G > 0$), facilitated by hydrogen and hydroxyl ions. The significance of enthalpy (ΔH) and entropy (ΔS) in controlling reaction rates was also observed, with a negative entropy value suggesting the formation of an activated complex. A Density Functional Theory (DFT) study using ORCA software examined the electronic structures of para-substituted benzaldehyde derivatives, highlighting the impact of substituents on hydrazone formation. Imines, key intermediates in organic synthesis, were produced through the acid-catalyzed condensation of the Schiff bases (M1-M4) and aromatic aldehyde derivatives.

Keywords: Photochemical, Chemical Kinetics, Cyclic Hydrazones

1. INTRODUCTION

Isoniazid is a pro-drug with well-established therapeutic applications and has been used for almost half a century as a first-line drug for the prophylaxis and treatment of tuberculosis [1,2]. It is a nicotinamide analog consisting of a pyridine ring and a hydrazide group [3]. The free –NH2 group in the hydrazine moiety can react with various carbonyl compounds (aldehydes and ketones) to form Schiff bases, which contain the characteristic HC=N-NH- group. Schiff bases derived from isoniazid have traditionally been synthesized by refluxing aldehydes and ketones with isoniazid in organic solvents, often in the presence of a catalytic amount of acetic acid [4,5]. Greener and more cost-effective synthetic methods have also been explored, including the synthesis of hydrazones using fruit-derived organic acids as catalysts [6]. The synthesis of Schiff bases from amines and carbonyl groups is typically a reversible process. Several factors influence the hydrolysis of Schiff bases, such as the acidity and polarity of the solvent, the substitution on the aromatic ring, the presence of hydrogen bonding associated with the azomethane group, and temperature [7,8]. Several studies have shown that Schiff bases synthesized from aniline or substituted aniline and isobutane are unstable in inert solvents [9]. In contrast, Schiff bases derived from isobutane and aliphatic amines tend to be less stable than those derived from benzaldehyde, aniline, or their derivatives [10]. The hydrolysis of Schiff bases involves their conversion into conjugated acids under acidic conditions [11]. In neutral solutions, water molecules act both as nucleophiles and acids, leading to the formation of carbonium ions by attacking the azomethane group. The hydrolysis of benzylidene aniline in an aqueous ethanol solution showed that the reaction rate is independent of proton concentration in basic media (pH 10-12). However, the reaction rate does depend on proton concentration in acidic media (pH 5-10), and the reaction accelerates when the pH exceeds 5 [13]. In a study on the hydrolysis of salicylate aniline, it was found that the ortho group slows the hydrolysis rate between pH 5.6 and 6.6, likely due to hydrogen bonding between the nitrogen atom of the azomethane group and the hydroxy group in the ortho position of the aldehyde [14,15]. A study also investigated the effect of electron-withdrawing and electron-donating groups on the hydrolysis rate constant of certain Schiff bases and their complexes, using spectroscopic methods [16]. In our study, the stability of Schiff bases synthesized from 4-aminoantipyrine and several aromatic aldehydes in a 10% ethanolic aqueous solution was studied. The stability was assessed under acidic, neutral, and basic conditions, and the corresponding thermodynamic characteristics were recorded.

2-Materials and Methods

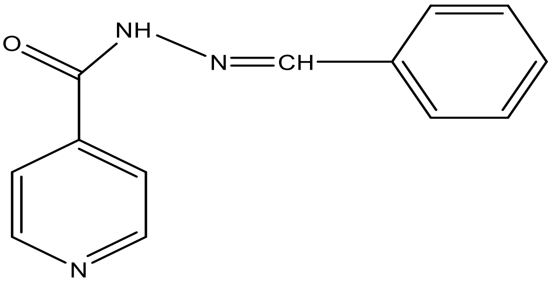
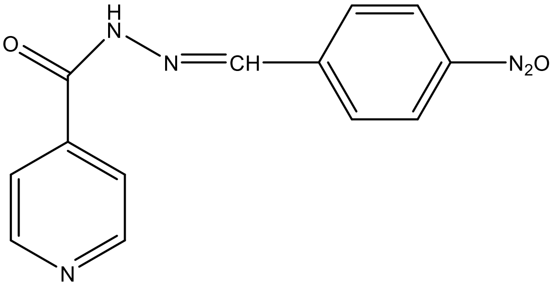
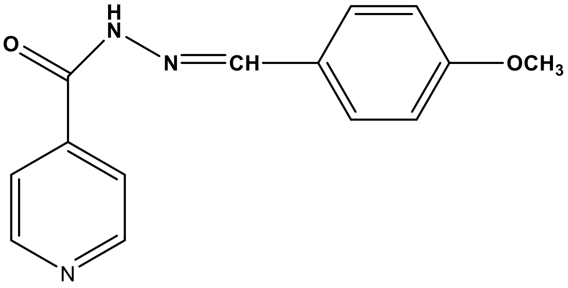
2.1. Used Devices

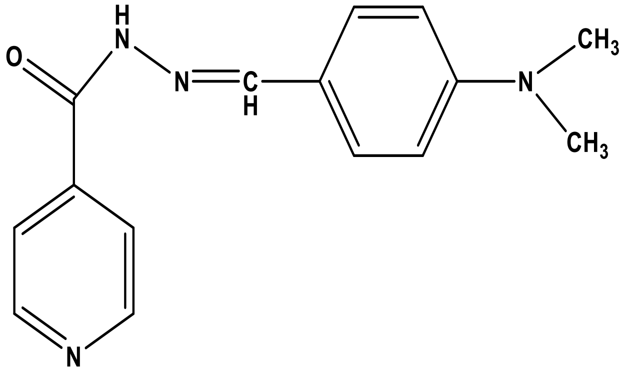
Thermostat to control temperatures from MINI Dry Bath, model Guanal. A pH meter model (PEAK - INSTRUMENTS) was also used to measure the pH.

2.2. The hydrazones

(M1-M4) shown in (table 1) were resynthesized according to the previously outlined process.

Table 1. The structural formula and nomenclature of the resynthesized hydrazines

Comp. No.	Structural formula
M1	 **N'-benzylidene isonicotinohydrazide**
M2	 **N'-(4-nitro benzylidene) isonicotinohydrazide**
M3	 **N'-(4-methoxybenzylidene) isonicotinohydrazide**

M4	 **N'-(4-(dimethylamino) benzylidene isonicotinohydrazide**

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 a calculated amount of HCl and NaOH, followed by measurement with a pH meter [17].

2.4. Experiments were 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) [18].

2.5. **Computational details**

All the calculations were carried out using the ORCA software package (version 4.2.1)[22-23] and Kohn–Sham DFT. We employed the geometry optimizations and vibrational frequency calculations were performed using the def2-SVP basis set [24] on all atoms.

3. Results and Discussion

This study examined the stability of six well-known Schiff bases (M1-M4) toward hydrolysis in (10%) ethanolic aqueous solution at pH levels of 5, 7, and 9. The hydrolysis process occurs as described by equations. 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. The effect of hydrogen and hydroxyl ions on the formation and decomposition of imines was also studied.

The spectrophotometric measurement of the hydrolysis rate of Schiff base was conducted at several wavelengths according to the λmax of each chemical under investigation. Buffered solutions were made and employed by the methodology outlined in previous research work [21]. The variation in the absorbance measurements of the Schiff bases was 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 x 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 (Ao - A∞ /At - A∞) against time (t), as shown in Figures (1-2). 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.

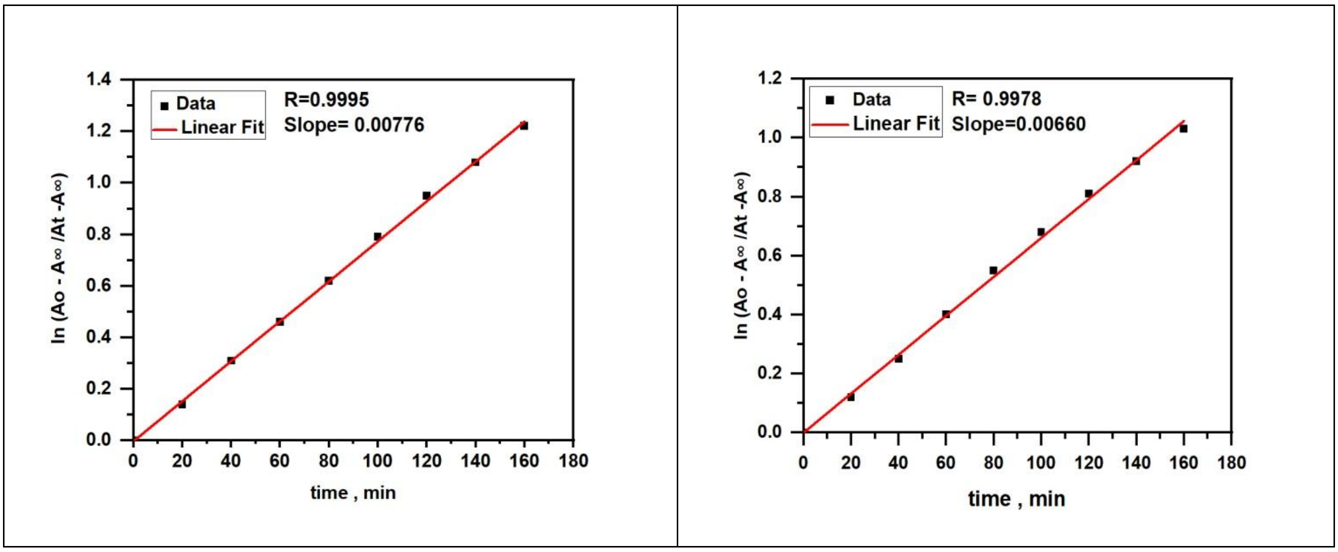


Figure 1. The plot of ln (Ao-A∞ /At-A∞) versus time for hydrolysis of compounds (M1 and M2) at pH = 7 and Temp. 298 °K

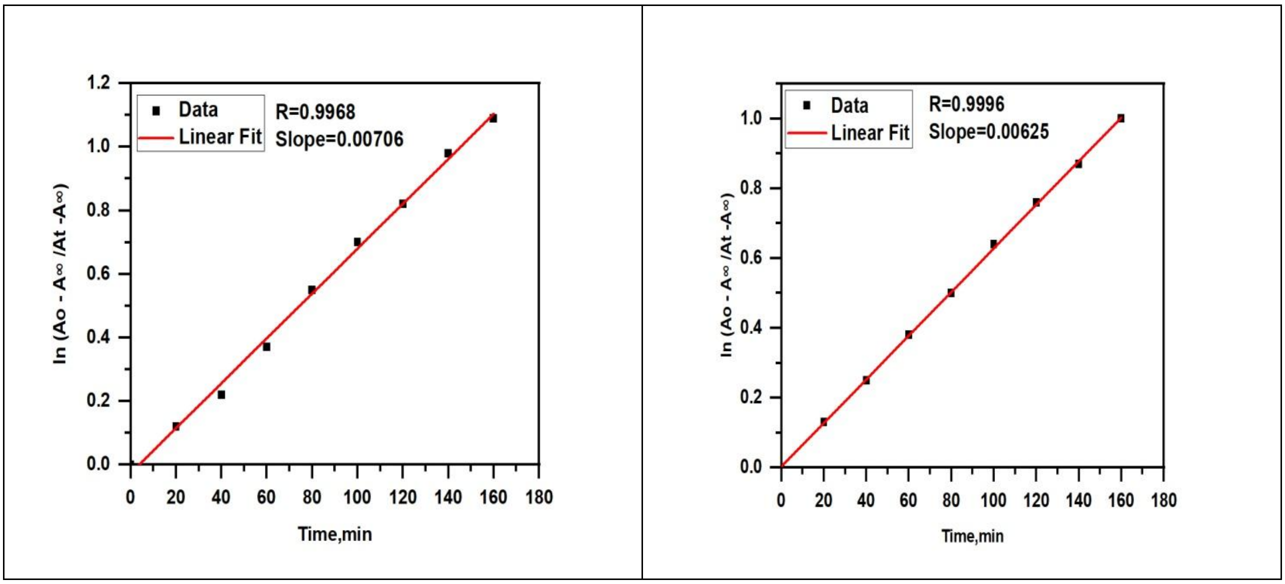


Figure 2. The plot of ln (Ao-A∞ /At-A∞) versus time for hydrolysis of compounds (M3 and M4) at pH = 7 and Temp. 298 °K

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[18]. The results were documented in (Table 3), displaying the rate constants for the six compounds (M1-M4) at pH levels of 5, 7, and 9.

Table 3. Rate constants (k, s-1) for hydrolysis of the compounds (M1-M4) at pH3, pH5, pH9 at Temp 298

PH	M1	M2	M3	M4
PH=5	0.00793	0.00697	0.00713	0.00632
PH=7	0.00776	0.00660	0.00706	0.00625
PH=9	0.00783	0.00702	0.00722	0.00636

The findings derived from our ongoing investigation as displayed in the aforementioned table reveal that: First, the disparity in the rate constant values is rather small between resonance-donating substituent groups of compounds (M1, M2, M3, and M4) and the resonance-withdrawing ones of compound (M2) when compared to the unsubstituted compound (M1) in general. Second, the high value of the rate of the hydrolysis reaction, specifically the heightened values of the rate constant (indicating reduced stability) observed in the case of compound (M2), 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 [25]. Third, the decrease in the rate constant (indicating increased stability of the intermediate state) during the hydrolysis process of compounds (M1, M2, M3, and M4) is linked to the presence of substituents (-OH, NO_2, $-OCH_3$, 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 by counteracting the negative induction (-I). Fourth, 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[26].

3.1. The Reaction Rate Changes with Temperature

The influence of temperature is a crucial factor in 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 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 1x10-4 and a pH of 7.

The data depicted in figures (3-4) demonstrate that the rate constants of the examined compounds exhibit an upward trend with rising temperatures. This indicates that the hydrolysis of these compounds becomes easier, leading to a decrease in their stability.

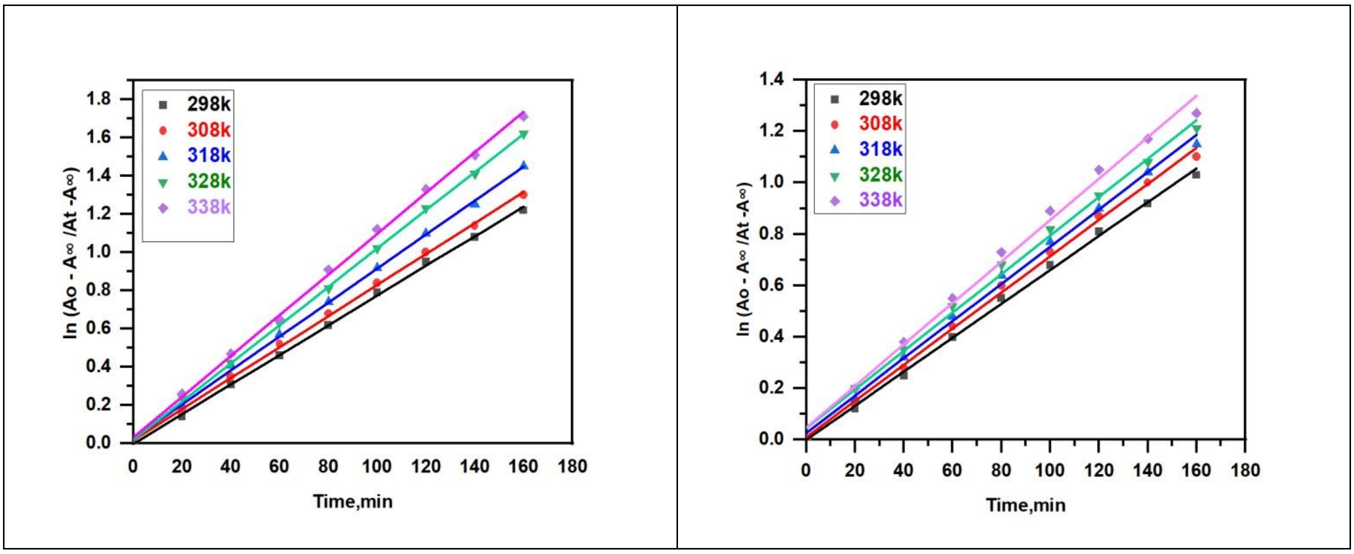


Figure 3 Plot of ln (Ao-A∞ /At-A∞) versus time for hydrolysis of compound (M1 and M2) at pH = 7 and Temperatures (298, 308, 318, 328,338°K)

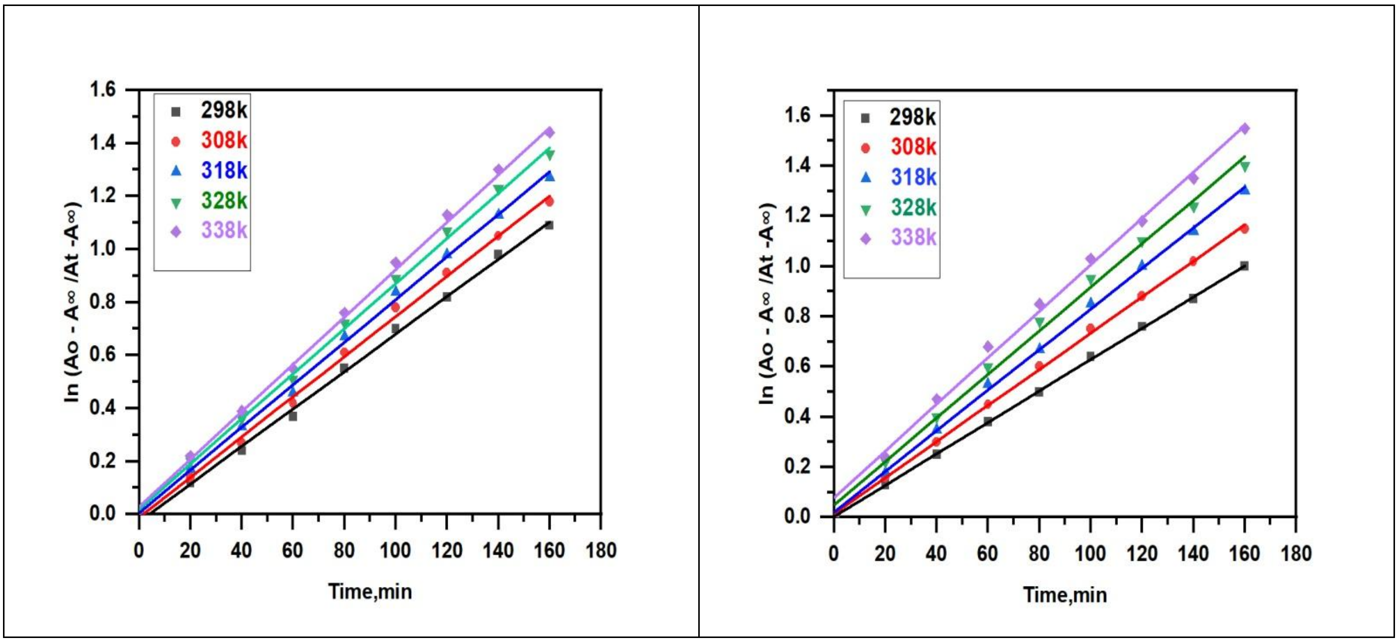


Figure 4. Plot of ln (Ao-A∞ /At-A∞) versus time for hydrolysis of compound (M3 and M4) at pH = 7 and Temperatures (298, 308, 318, 328,338°K)

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 (Ea) for each compound were determined using the Arrhenius equation.

$Lnk = lnA-Ea/RT$..................(1)

The findings are 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).

$\Delta G = -nRTlnk$ .... (2)

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 taking place and if it can occur spontaneously. There was a need for specific external conditions to be available for starting the reaction. Furthermore, this study allowed for the determination of both the quality of the reaction and the underlying factors that cause it.

$\Delta G = \Delta H -T\Delta S$ .... (3)

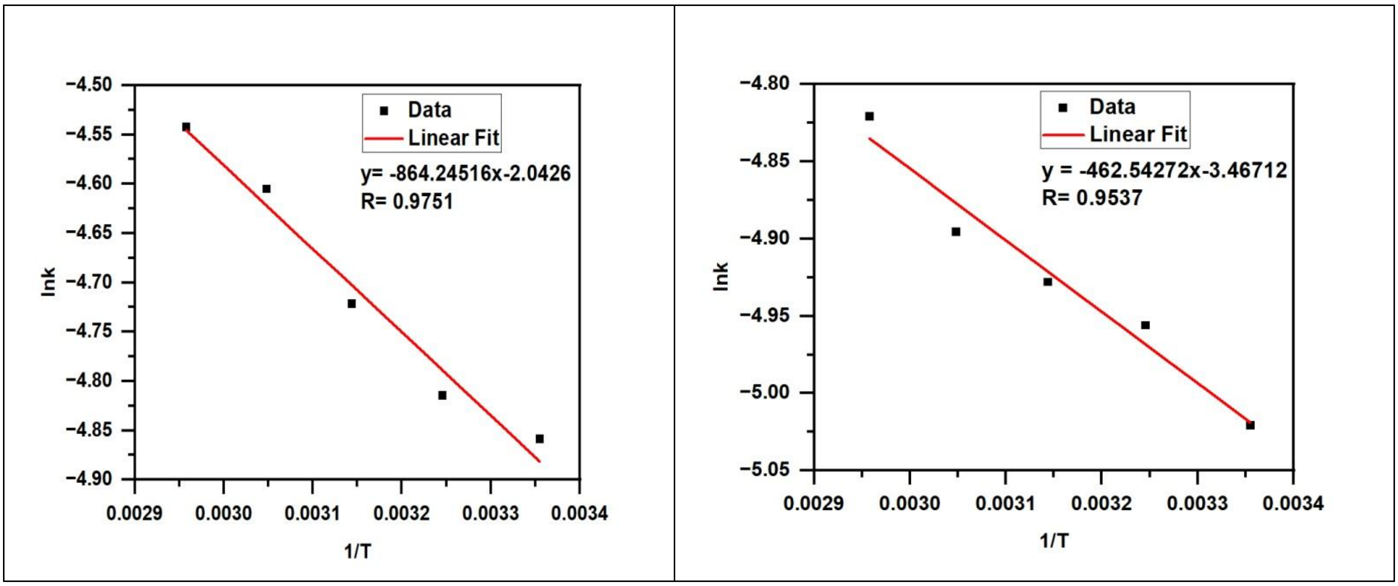


Figure 5. Plot of ln k against 1/T for compound M1 and M2 at pH=7

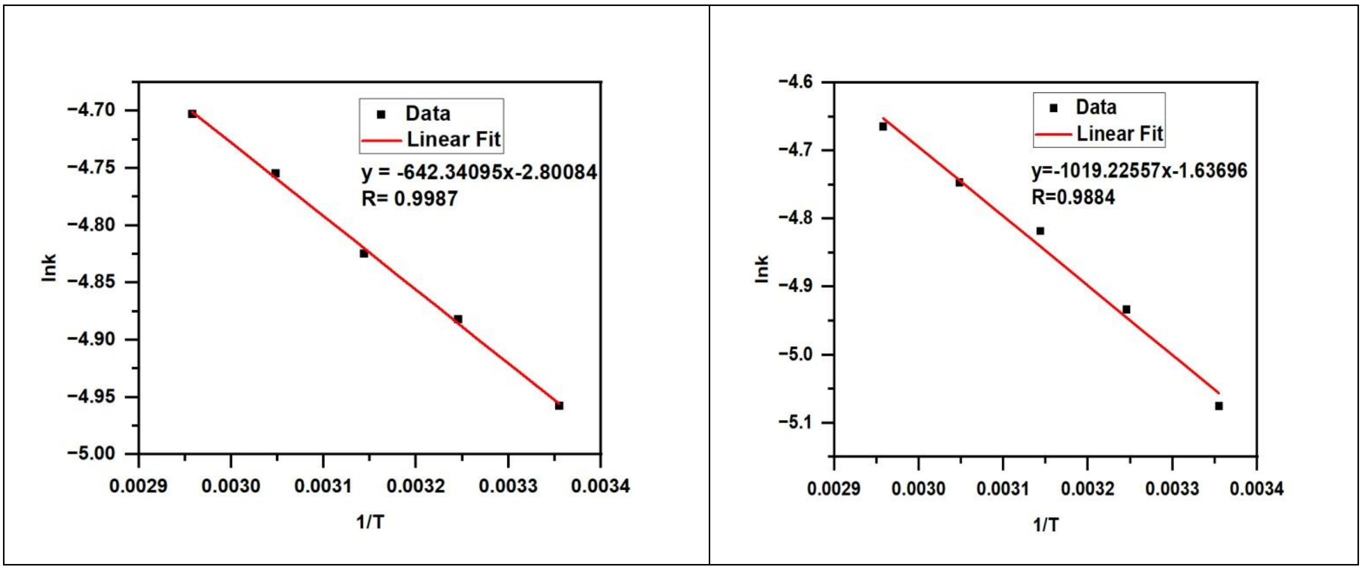


Figure 6. Plot of ln k against 1/T for compound M3 and M4 at pH=7

Table 4. Thermodynamic parameters of the compounds (M1-M4)

Comp	T(K)	1/T (K^{-1})	Ln K	$t^{1/2}$	ΔG° ($J.mol^{-1}$)	ΔS ($J.mol^{-1}. K^{-1}$)	ΔH° ($J.mol^{-1}$)
M1	298	0.003355	-4.8587	89.304123	12037.77908	-16.98217	7185.33376
	308	0.003246	-4.8146	85.45	12328.8039952		
	318	0.003144	-4.7217	77.865168	12483.4759884		
	328	0.003048	-4.6051	69.3	12558.0708592		
	338	0.002958	-4.5421	65.625	12763.9005572		
M2	298	0.003355	-5.0206	105	12438.8979832	-28.82563	3845.58017
	308	0.003246	-4.9561	98.4375	12691.1447432		
	318	0.003144	-4.9281	95.71823204	13029.1670412		
	328	0.003048	-4.8955	92.64705882	13349.989336		
	338	0.002958	-4.8208	85.98014888	13547.0843456		
M3	298	0.003355	-4.9575	98.5775248	12282.56319	-23.28618	5340.42265
	308	0.003246	-4.8822	91.424802110	12501.9081264		
	318	0.003144	-4.8245	86.301369863	12755.263974		
	328	0.003048	-4.7548	80.4878048	12966.3015616		
	338	0.002958	-4.7027	76.4057331	13215.20777564		
M4	298	0.003355	-5.0751	110.88	12573.925672	-13.60968	8473.84138
	308	0.003246	-4.9336	96.25	12631.992296		
	308	0.003144	-4.8183	85.767326732	12738.8720916		
	328	0.003048	-4.7467	79.838709677	12944.2129264		
	338	0.002958	-4.6649	73.566878980	13108.9847668		

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-(Ea/RT)), which establishes an inverse correlation between the reaction rate, represented by the rate constant (k), and the value of activation energy (Ea).

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 finding

3. Positive values of (ΔH) reveals that the studied chemicals underwent an endothermic thermal breakdown reaction. Consequently, the produced compound's transition from a stable state is characterized by lower potential energy compared 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.

3.2. Density Functional Theory Calculations

Molecules with wide HOMO-LUMO gaps are generally stable and unreactive, whereas molecules with tiny gaps are reactive. The higher the HOMO energies, the easier it is for HOMO to donate electrons, and the lower the LUMO energies, the easier it is for LUMO to accept electrons. Theoretical study showed little effect of synthesized M1-M4 by substitution of halogen except for M increasing the LUMO energy level and the molecule becomes more stable compared to other compounds. HOMO and LUMO orbitals and their energy gap for A1-A4 compounds. The electronic properties such as electron affinity A, Ionization potential I, absolute electronegativity μ, absolute hardness η, and electrophilicity ω were calculated by the following equations, results are given in Table 2.

$$A = -(E_{LUMO}) \qquad I = -(E_{HOMO}) \qquad \omega = \frac{\mu^2}{2\eta}$$

$$\mu = \frac{E_{LUMO} + E_{HOMO}}{2} \qquad \eta = \frac{E_{LUMO} - E_{HOMO}}{2}$$

Table 5. HOMO, LUMO, and Some electronic properties for synthesized M1-M4 compounds

Comp. No.	EHOMO	ELUMO	ω	η	M	Ip	EA	ELUMO-HOME
	eV	eV	eV $\mu^2/2\eta$	eV ELUMO-EHOMO/2	Ev ELUMO+EHOMO/2	eV -EHOMO	eV -ELUMO	eV
M1	- 7.554	0.757	1.3897	4.1555	-3.3985	7.554	-0.757	8.311
M2	-7.578	-0.546	2.3494	3.516	-4.0620	7.578	0.546	7.023
M5	-7.373	1.104	1.1590	4.2385	-3.1345	7.373	-1.104	8.477
M11	-7.132	1.190	1.0606	4.161	-2.9710	7.132	-1.190	8.322

3.3. **The frontier molecular orbitals**

The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are the types of frontier molecular orbitals. The HOMO has the capacity to donate an electron whereas LUMO represents the ability to accept electrons. These orbitals are important to decide the stability of the chemical compound. The HOMO and LUMO energy values were calculated through the DFT method using the B3LYP/ def2-SVP level of theory is shown in Table (5). The transfer of electrons from the ground state to the excited state is labeled by one electron from the highest occupied molecular orbitals to the lowest unoccupied molecular orbitals. The displayed diagram of HOMO-LUMO energy value is shown in Fig. 7 . The energy gap between HOMO and LUMO gives the detailed interaction between the molecules and chemical stability [27].

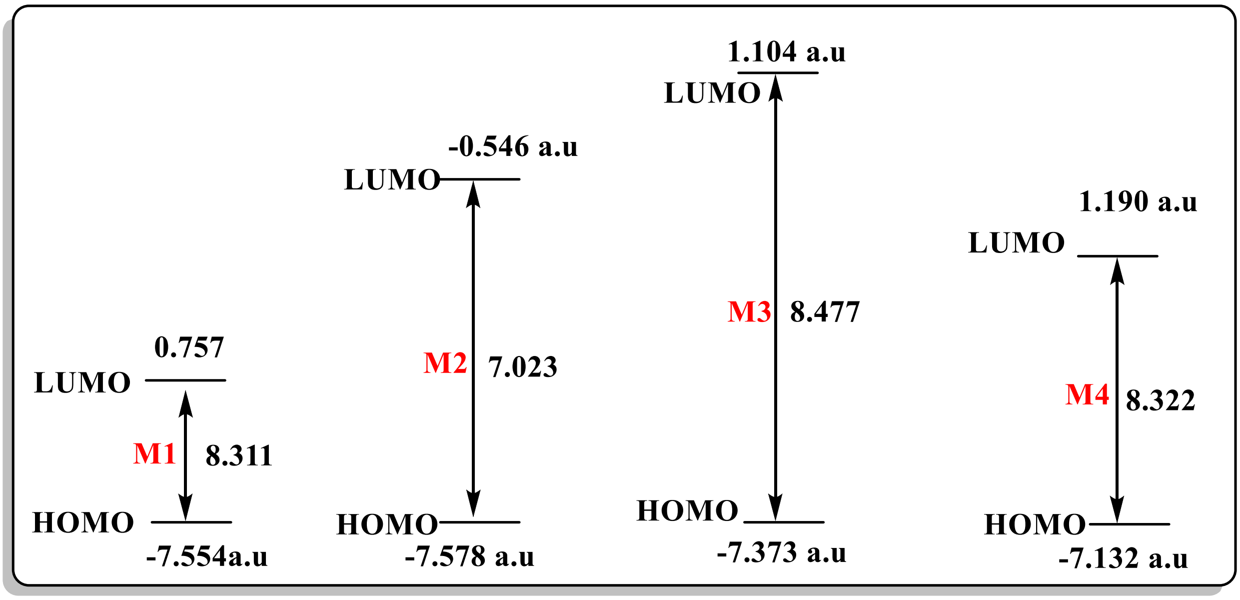
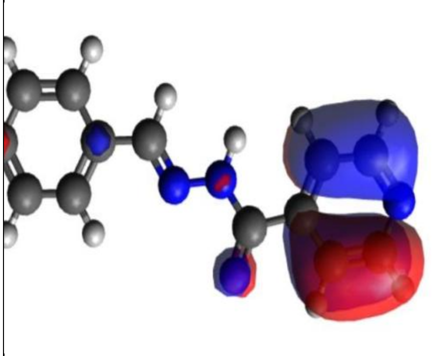
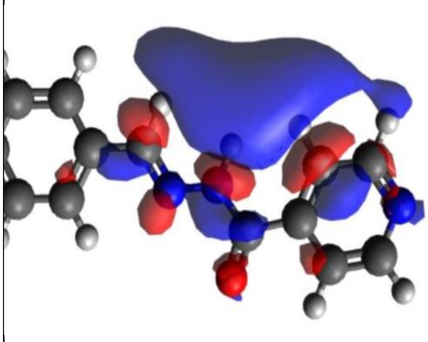
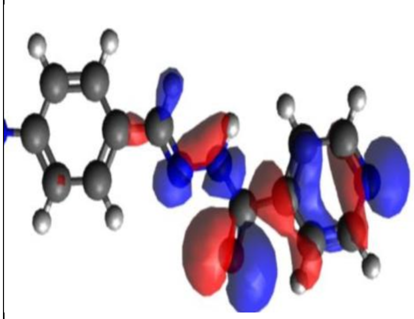
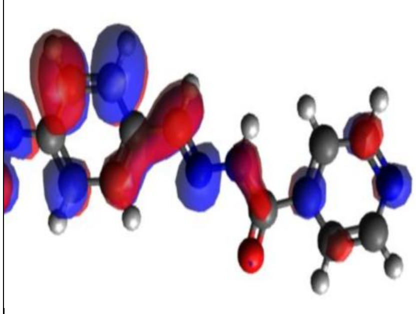


Fig. 7. HOMO-LUMO energy value and The energy gap

The HOMO electronic density distribution for Schiff bases is plotted in Fig. 8.

Code	HOMO	LUMO
M1		
M2		

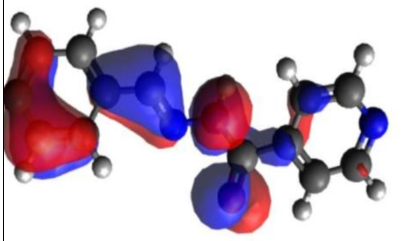
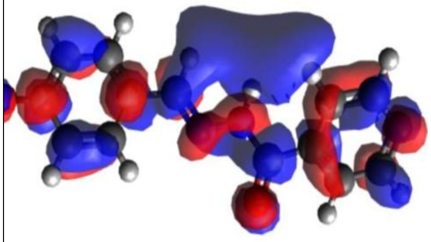
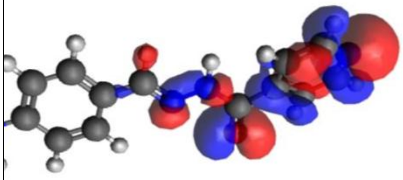
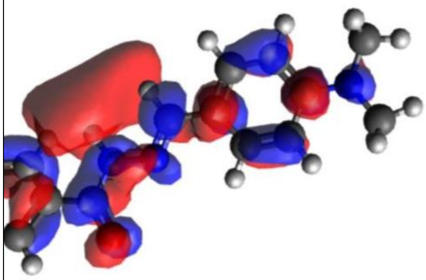
M3		
M4		

Fig. 8. The HOMO and LUMO of compounds M1-M4

4. Conclusion

There is no discernible disparity in the rate constant values during the investigation of the hydrolysis kinetics of the compounds under study (M1, M2, M3, and M4). 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. In this paper, the synthesized new Spiro derivatives were successfully synthesized, and this has been proved by spectral analyses. The study of energies of the HOMO and LUMO orbitals negative indicates that compounds A1-A4 are stable compounds, Hardness results indicate that compound A2 has more aromatic character compared to other compounds.

REFERENCES

[1] Goodman LS, Gilman A. The Pharmacological basis of therapeutics. 3rd ed. New York: Macmillan Company; 1965.

[2] Kolyva AS, Karakousis PC. Old and new TB drugs: Mechanisms of action and resistance, understanding tuberculosis - New approaches to fighting against drug resistance. Pere-Joan Cardona (Ed.); 2012.

[3] Rodrigues FAR, Oliveira ACA, Cavalcanti BC, Pessoa C, Pinheir AC, De Souza MVN. Biological evaluation of isoniazid derivatives as an anticancer class. Scientia Pharmaceutica. 2014;82:21–28.

[4] Hearn MJ, Cynamon MH. Design and synthesis of anti-tuberculous: Preparation and evaluation against Mycobacterium tuberculosis of an isoniazid schiff base. J.Antimicrobial Chemo. 2004;53:185–191.

[5] Eldehna WM, Fares M, Abdel-Aziz MM, Abdel-Aziz HA. Design, synthesis, and antitubercular activity of certain nicotinic acid hydrazides. Molecules. 2015;20:8800- 8815.

[6] Yadav G, Mani JV. Green synthesis of Schiff bases by natural acid catalysts. Int. J. Sci. Res. 2015;4(2):121-127.

[7] Sinn, E., & Harris, C. M. (1969). Schiff base metal complexes as ligands1. *Coordination Chemistry Reviews*, *4*(4), 391-422.

[8] Yass, I. A., Aftan, M. M., Dalaf, A. H., & Jumaa, F. H. (Nov. 2020). Synthesis and Identification of New Derivatives of Bis-1,3-Oxazepene and 1,3-Diazepine and Assess their Biological and Laser Efficacy for Them. The Second International & The Fourth Scientific Conference of College of Science – Tikrit University. **(P4)**: 77-87.

[9] Salih, B. D., Dalaf, A. H., Alheety, M. A., Rashed, W. M., & Abdullah, I. Q. (2021). Biological activity and laser efficacy of new Co (II), Ni (II), Cu (II), Mn (II), and Zn (II) complexes with phthalic anhydride. Materials Today: Proceedings, 43, 869-874.

[10] Raczuk, E., Dmochowska, B., Samaszko-Fiertek, J., & Madaj, J. (2022). Different Schiff bases—structure, importance, and classification. *Molecules*, *27*(3), 787.

[11] Khalaf, S. D., Ahmed, N. A. A. S., & Dalaf, A. H. (2021). Synthesis, characterization, and biological evaluation (antifungal and antibacterial) of new derivatives of indole, benzotriazole, and thioacetyl chloride. MaterialsToday: Proceedings. 47(17), 6201-6210.

[12] Dalaf, A. H., Jumaa, F. H., & Salih, H. K. (2021). Preparation, Characterization, Biological Evaluation and Assess Laser Efficacy for New Derivatives of Imidazolidin-4-one. International Research Journal of MultidisciplinaryTechnovation, 3(4), 41-51.

[13] Dalaf, A. H., Jumaa, F. H., & Salih, H. K. (2021). MULTIDISCIPLINARY TECHNOVATION. Red, 15(A2),C44H36N10O8.

[14] Dalaf, A. H., Jumaa, F. H., Aftana, M. M., Salih, H. K., & Abd, I. Q. (2022). Synthesis, Characterization, Biological Evaluation, and Assessment of Laser Efficacy for New Derivatives of Tetrazole. In Key Engineering Materials (Vol.911, pp. 33-39). Trans Tech Publications Ltd.

[15] Dalaf, A. H., Jumaa, F. H., & Yass, I. A. (2022, November). Synthesis, characterization, biological evaluation, molecular docking, assessing laser efficacy, thermal performance, and optical stability study for new derivatives of bis-1, 3-oxazepam, and 1, 3-diazepine. In AIP Conference Proceedings (Vol. 2394, No. 1, p. 040037). AIP Publishing LLC.

[16] Hamad, A. M., Atiyea, Q. M., Hameed, D. N. A., & Dalaf, A. H. (2023). Green synthesis of copper nanoparticles using strawberry leaves and study of properties, anti-cancer action, and activity against bacteria isolated from COVID-19 patients. Karbala International Journal of Modern Science, 9(1), 12.

[17] Mohammed, L. J., Hamad, A. M., Atiyea, Q. M., Jwair, W. A., Dalaf, A. H., Jasim, A. S., Elsaigher, S. M., Ragab, A., and Hassan, Z. H. S. (2022). In vitro Comparison of the Effect of Zinc Oxide Nanoparticles and Hibiscus sabdariffa Extract on Streptococcus mutans Isolated from Human Dental Caries. The Third International and The Fifth Scientific Conference for College of Science –Tikrit University. 2(2): 5-14.

[18] Kirdant, A. S., Shankarwar, S. G. and Chondhekar, T. K., (2010). Kinetics study and mechanism of hydrolysis of N-Salycylidene-m-chloroaniline. Int. J. Chem. Sci.: 8(1), 279-289,

[19] Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. Phys. Chem. Chem. Phys. 2006, 8, 1057–1065.

[20] Kirdant, A. S., Shankarwar, S. G. and Chondhekar, T. K., (2010). Kinetics study and mechanism of hydrolysis of N-Salycylidene-m-chloroaniline. Int. J. Chem. Sci.: 8(1), 279-289,.

[21] Dash, A. C., Dash, B., Mahapatra, P. K., & Patra, M. (1983). Hydrolysis of imines. Part 2. Kinetics and mechanism of hydrolysis of N-salicylidene-2-aminopyridine in the presence and absence of copper (II) ion. A study of the catalytic effect of some mixed-ligand complexes of copper (II). *Journal of the Chemical Society, Dalton Transactions*, (8), 1503-1509.

[22] Neese, F. The ORCA Program System. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2012, 2, 73.

[23] Neese, F. Software Update: The ORCA Program System, Version 4.0. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2018, 8, No. e1327.

[24] Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. Phys. Chem. Chem. Phys. 2006, 8, 1057–1065.

[25] Bruyneel, W., Charette, J. J., & De Hoffmann, E. (1966). Kinetics of hydrolysis of hydroxy and methoxy derivatives of N-benzylidene-2-aminopropane. *Journal of the American Chemical Society*, *88*(16), 3808-3813.

[26] Prabhu, D. V., Lalitha, K., & Laxmeshwar, N. B. (2004). Kinetics and reaction mechanism of the metal ion catalyzed hydrolysis of some substituted salicylates. *J. Indian Chem. Soc*, *81*, 1103-1109.