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KINETIC STUDY AND HAMMETT CORRELATIONS IN THE CHEMISTRY OF SELECTED ACID HYDRAZIDES BY USING THALLIUM (III) IN 1,4-DIOXANE MEDIUM

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ABSTRACT

In the medium of $HClO_4$ in addition to HCl, Thallium (III) was reacted with benzoic (benz) and m-nitro benz hydrazide. The complex created when thallium reacts with benz and m-nitro benzhydrazide undergoes decomposition to give a product. Acetonitrile is employed as a solvent to check the formation of free radicals and the results show that they are not formed. The decrease in the rate of reaction is caused by a rise in $[H^+]$ and $[Cl^-]$ ions. Additional kinetic research demonstrates that ionic strength has no effect on the rate of reaction. The temperature effect for the kinetic research was computed at temperatures between 15°C and 30°C. The analysis of reaction constants (ρ) and substituent constants (σ) for m-nitro benzhydrazide indicates good agreement with the values from the literature.

Keywords: m-nitro benz acid hydrazide (m-NO_2BAH), Oxidation, Hammett Parameter, Kinetics,Thallium(III) and Thermodymamic Parameter

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INTRODUCTION

Hammett equation helps to study the effect of substituents on any reaction. Hammett defined a substituent parameter (**σ**) for benzoic acid and substituted benzoic acid. Hammett parameters may be able to determine the effect of substituents on any reaction. The Hammett equation explains how organized changes in the ability of substitutes to donate or withdraw electrons are produced by changes in equilibrium, rate constants, and physical properties with different structural characteristics.[1] In this connection, the rate of reaction of chemical processes is the main objective of the physical chemistry branch known as chemical kinetics.[2] Additionally, it covers the use of metal oxide in the spectroscopic study of aromatic acid hydrazides, which is essential in organic and pharmaceutical chemistry. It is employed to create molecules with significant medicinal effects. When developing different substituted substrates and reactions that are related to the Hammett parameter.[3] QSAR has been a very helpful tool for the study of substituent effects on the rate of reaction. Hydrazides are products prepared from hydrazine hydrate, ester, and carboxylic acid.[4] In aqueous alkali media, a recent initial review based on the oxidation of aromatic acid hydrazides using hexacyanoferrate-(III) has been reported.[5,6] There is no change in ionic strength, according to a recent report on the kinetics study and mechanism of fluorenone hydrazines permanganate oxidation in alkaline media.[7] A recent study suggests that vanadium(IV) bromate is employed as a catalyst in the oxidation of benzohydride in an aqueous solution.[8] Additionally, a positive outcome was seen for the reaction in which diphenyl and dimethyl sulfoxide were being oxidized with the help of tetrabutyl ammonium tribromide as a catalyst.[9] In a recent publication, Anderson-type hexamolybdochromate(III) catalyzes the rate at which bromate oxidizes benzoic acid hydrazide in an acidic aqueous medium.[10]

The oxidizing agents such as nitric acid, chromic acid, permanganates, ceric sulphate, lead tetra acetate, Thallium, $Ti(CH_3COO)_3$, Cr(VI) Oxide, peroxydisulphate, Mn(II) pyrophosphate, Mn(II) acetate, Mn(III) sulphate, Vanadium, selenium dioxide, hexacyanoferrate(III), aluminum alkoxide, Osmium tetroxide,

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pyridine complex, organic peracids, periodic acid, peroxytrifluoroacetic acid, chloramine-T, bromamine-T, N-bromosuccinamide, etc., have been extensively used to study the oxidation of different organic compounds. Many of them act on different functional groups with a high degree of selectivity and show remarkable results in kinetic and mechanistic studies. Due to the significant amount of recent work being done, the potential of Thallium (III) oxidant is being understood more and more. Compared to Hg(II) and Pb (IV), Tl (III) has superior oxidant performance and a higher selectivity. Our focus is on understanding how the solvent affects reaction rate and equilibrium constant. We can also relate the reaction rate to the reaction constant and the Hammett parameter.

EXPERIMENTAL

All of the chemicals were obtained from SD Fine Chem., and were utilized directly. Tl_2O_3 (ACROS) was dissolved in 1.0 mol dm-3 HCl., Thallium (III) solution[11] stood prepared, and its concentration was assessed using an iodometric titration. The stated process was used to create the benz and m-nitro benz acid hydrazides, which were subsequently determined by their melting points. In 50% v/v 1,4-dioxan, benz and m-nitro benz acid hydrazide stock solution was made up. The strength of the ions didn't change. The reactions were to be performed in pseudo-unimolecular reaction conditions in 50% v/v 1, 4 dioxane with an important hydrazide over oxidant excess.

The reactant and other constituent solutions were thermally equilibrated separately, and mixed, and the volume of Thallium (III) that hadn't reacted in the mixture was determined by iodometric titration in comparison to a sodium thiosulphate reference solution. The calculation of the pseudo-unimolecular order velocity constants was done using the [Tl(III)]'s linearity in relation to time graphs. Results were accurate and reliable up to 4%. The kinetic runs have been shown to be three reaction half-lives. Under the test conditions, It did not oxidize, 1,4-dioxan.

End Product Analysis

The progress of the reaction was done in an aqueous media of hydrazide, Thallium(III), in an acidic medium to determine the products. To finish the reaction, in a flask with a thermostated water bath, the reaction mixture was placed. that was held at 50ºC for 24 hours. The residue was then filtered and it was analyzed for acid as follows: Bicarbonate was used as a test substance; it showed the presence of Benz and m-nitro benz acid group. The FTIR analysis of acids and melting point measurements confirmed the final product.

$$RCONHNH_2 + 2\,Tl(III) + H_2O \rightarrow R\text{-}COOH + N_2 + 4H^+ + 2\,Tl(I)$$

RESULTS AND DISCUSSION

It should be mentioned that the reaction went forward satisfactorily by using a combination of HCl and $HClO_4$. At constant concentrations of [HCl] and [$HClO_4$] and ionic strength of 0.6 mol /dm^3, the influence of reactants on the kinetics of the reaction was investigated. Oxidant concentration was diversified since $6.5x10^{-4}$ near $6.5x10^{-3}$ mol/ dm^3 and maintaining the hydrazide concentration at $10x10^{-2}$ mol/dm^3. The pseudo-uni-molecular velocity constant is constant for BAH and m-nitro BAH and is $3.58 \pm 0.1x10^{-4}$ s^{-1}, $8.32 \pm 0.1x10^{-4}$ per second the order is equal to one when compared to the order of the [oxidant]. In the further study, the concentration of hydrazide was determined by changing concentration from 0.01 to 0.1 mol /dm^3 by putting the concentration of oxidant constant at $3.0x10^{-3}$ mol/ dm^3. It is observed that the big rise in the pseudo-first-order velocity constants from 0.062 x 10^{-3} s^{-1} to 0.354 x 10^{-3} s^{-1} for BAH and 0.153 x 10^{-3} s^{-1} to 1.296 x 10^{-3} s^{-1} for m-nitro BAH with hydrazide. The fractional contains the reaction's order.

To investigate the effect of [H^+] and [Cl^-] on the rate of reaction BAH and m-nitro BAH, the [oxidant], [hydrazide], and ionic strength remained constant and these are 0.003, 0.1, μ = 0.6 mol/ dm^3 respectively. For the determination of [H^+] and [Cl^-], the chemical reagents used are $HClO_4$ and NaCl.

It is observed that a rise in [H^+] from 0.13 to 0.6 mol /dm^3 reduces 10^{-3} k(s^{-1}) from 0.422 to 0.015 for BAH and 0.306 to 0.099 x10^{-3} k(s^{-1}) m-nitro BAH at 25ºC. Further the rise in [Cl^-] from 0.13 to 0.6 mol /dm^3 decreases 10^{-3} k(s^{-1}) from 0.287 to 0.0095 for BAH and 0.106 to 0.022 x10^{-3} k(s^{-1}) m-nitro BAH at 25ºC. By adjusting the solvent concentration from 5 to 40% v/v, the relative dielectric phenomena were changed. It is detected that the rate of reactions for BAH and m-nitro BAH was reduced by reducing the percentage of 1, 4-dioxan. The values for the Michaelis-Menten plot for m-nitro BAH are revealed in Table-1. Figure-1 displays the Michaelis-Menten plot for temperatures between 15°C and 30°C.

Table-1: m-nitro BAH Michaelis-Menten Plot

Temperature	meta-nitroBAH	1/ meta-nitroBAH	Kobs x 10^{-4} s^{-1}	1/ Kobs x 10^{-4} s^{-1}
15°C	0.01	100.33	0.75	1.3333
	0.03	33.33	1.25	0.8000
	0.05	20.00	2.51	0.3920
	0.064	15.625	4.79	0.2087
	0.1	10.00	6.12	0.1633
20°C	0.01	100.33	1.14	0.8771
	0.03	33.33	1.72	0.5813
	0.05	20.00	3.14	0.2673
	0.064	15.625	7.28	0.1373
	0.1	10.00	9.32	0.1072
25°C	0.01	100.33	1.53	0.6535
	0.03	33.33	2.52	0.3968
	0.05	20.00	5.01	0.1996
	0.064	15.625	9.77	0.1023
	0.1	10.00	12.96	0.0771
30°C	0.01	100.33	2.26	0.4424
	0.03	33.33	3.40	0.2941
	0.05	20.00	7.42	0.1347
	0.064	15.625	14.20	0.0704
	0.1	10.00	18.20	0.0552

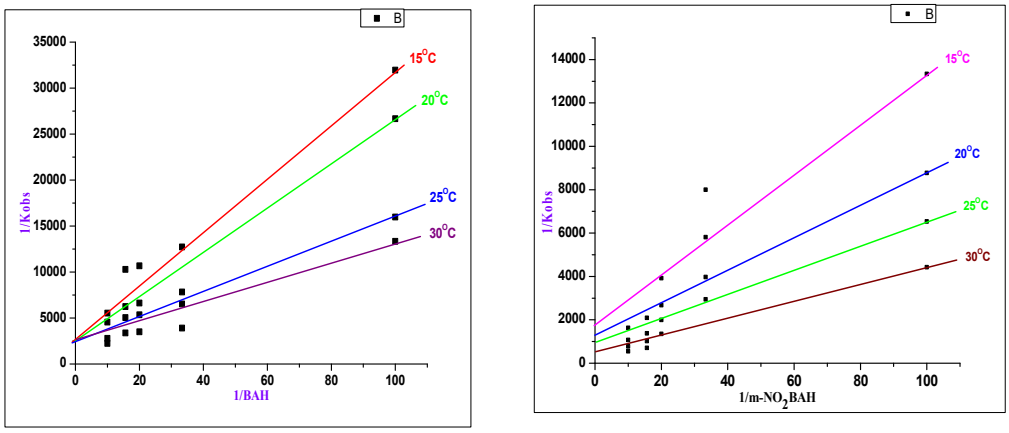


Fig.-1: Effect of Temperature and Michaelis-Menten Plots

Table-2: Calculating Kc and K_1

[HCl] = 0.1 mol dm^{-3}, [$HClO_4$] = 0.1 mol dm^{-3}, [Tl^{III}] = 0.3 x 10^{-2} mol dm^{-3}, μ = 0.6 mol dm^{-3}

Hydrazide for kinetic sudy	Kc. (mol dm^{-3})			
	15°C	20°C	25°C	30°C
BAH	9.30	9.59	9.29	9.11
meta-nitro BAH	14.50	14.47	14.94	14.53

From the kinetic study of the reaction, it was found that the order of hydrazide is fractional and it is unity with respect to Thallium (III) oxidizing reagent. The complex formed in the reaction has an equilibrium with the substrates. This shows an effect on the fractional order of substrate concentration.[11] Due to the complex's production throughout the reaction, against 1/[Hydrazide] the 1/kobs Michaelis-Menten graphs had an intercept and were linear. As a result, findings, Scheme-1 can be used to identify the reaction's probable mechanism.

Tl^{III} + Hydrazide $\rightleftharpoons$ Complex K_c

Complex $\rightarrow$ Tl^{I} + Intermediate k_1

Tl^{III}+Intermediate $\rightarrow$ Tl^{I} + Products Fast

Scheme-1

By plotting the graph of per k_{obs} versus per[Hydrazide] at varying temperatures, the rate law is validated. Kc and k1 values were calculated. using the value of slopes and intercepts obtained through graphs shown in Table-2. These depict marginally positive intercept values. It has been noted that the reaction is influenced by the concentrations of hydrogen and chloride ions due to the protonation of hydrazides[12] and the presence of various chloro-complexes[13] of Thallium (III). Ionic strength and the finding that one of the reactants employed in the reaction is neutral support the idea that free hydrazide plays a significant role in this reaction. "Oxidant forms solid complexes with chloride ions that have the formula $TlCl^{3-n}$, where n is the number of complexes with chlorides. The values of specific stability constants"[14] are as follows:

$K_1 = 13.8 \times 10^7$, $K_2 = 39.8 \times 10^{12}$, $K_3 = 60.2 \times 10^{14}$ and $K_4 = 10 \times 10^{17}$ per mole dm3.

Thallium (III) will be present in this reaction as $TlCl^{2+}$ and A.15 illustrates its concentration. $[TlCl_2]^+$free where, $\beta_1=K_3/K_2=151$ and $\beta_2=K_4/K_3=166$.

$TIC1_2^+$ + Hydrazide $\rightleftharpoons$ Complex K_c

Complex $\rightarrow$ $RCONHNH + T1C1_2- + H^+$ k_1

$RCONHNH+H_2O+T1C1_2^+ \rightarrow RCOOH+N_2+2H^+ + T1C1_2^-$ Fast

Where R –Alkyl group

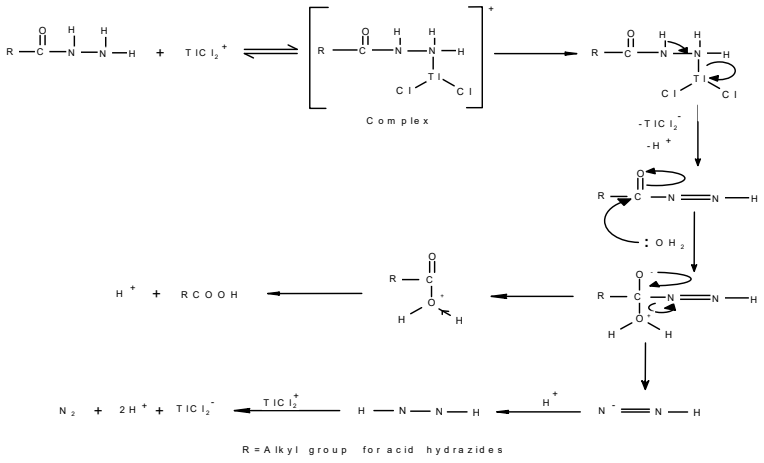
Scheme-2

The rate laws were confirmed when plotting per kobs against both per [Hydrazide] and per [H+], both of which linearity was found with positive intercepts. as shown in Fig.-1. The values were determined using the slopes and intercepts of graphs of KH and Kc. The Kc values can be found in Table-1. For BAH and m-nitro BAH, they were found to be 13 and 16 per mol dm3 respectively. The Thallium (III) chloro complex with the highest electrophilicity, $TlCl_2^+$ is the reactive species.

$$\text{Rate} = \frac{k_1K_c\,[\text{Hydrazide}]_{\text{total}}\,[T1C1_2^+]_{\text{total}}}{(1+K_c\,[\text{Hydrazide}])\,(1+K_H\,[H^+])\,(1+\beta_1\,[Cl^-]+\beta_2\,[Cl^-]^2)}$$

$$K_{obs} = \frac{k_1K_C\,[\text{Hydrazide}]_{\text{total}}}{(1+K_c\,[\text{Hydrazide}])\,(1+K_H\,[H^+])\,(1+\beta_1\,[Cl^-]+\beta_2\,[Cl^-]^2)}$$

Below is an illustration of the plausible mechanism for the entire reaction:



Scheme-3

An N-Tl bond is created by the electrophilic substitution of the hydrazide's in the mechanism. The intermediate is produced via a two-electron shift from substrate to oxidant. This N-Tl bond formation is

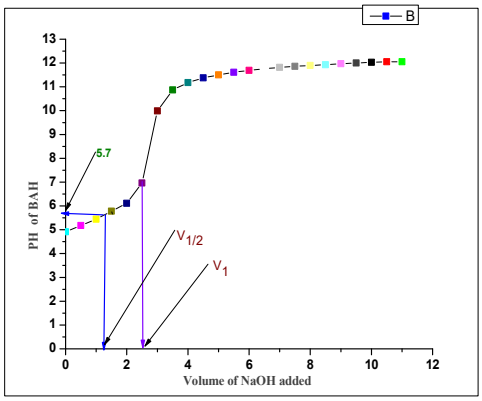
thought to result from the oxidation of nitrogen-containing molecules by thallium (III).[15] The computed values for thermodynamic variables are ΔH(KJmol^{-1}), ΔG(KJmol^{-1}) and ΔS(KJmol^{-1}) remained 59.74, 62.56, and -94.64 for BAH and 16.64, 21.37, -15.92 for m-nitro BAH. According to Scheme-3, The establishment of a transition stage that is more organized results in a sizable decrease in the entropy of activation. The reaction can be tolerated by the shift in ionic strength since the method uses the active substrate, hydrazides are neutral. The rate reduces as the concentration of 1, 4-dioxan increases; this effect of the solvent is brought about by the complex equilibrium between the reactants[16] in a medium with a low relative permittivity.[17-19]

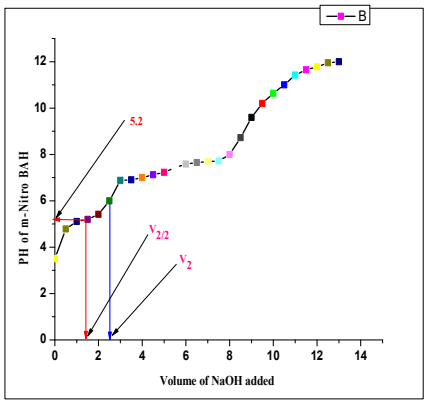
Calculation of Hammett Parameters

The value of pKa for BAH at ($V_{1/2}$) is 5.7 and the pKa value of the m-nitro BAH ($V_{2/2}$) is 5.2 (δ = 1.69 for 50% ethanol). The substituent constant (**σ**) value of the m-nitro BAH is 0.30 and the reaction constant (**ρ**) value of m-nitro BAH is 1.67. pH metry method is used to determine the substituents constant (**σ**) and the reaction constant (**ρ**) value of m-nitroBAH. Moreover, the purpose of this research work was to use the Hammett equation to determine how the BAH and m-substituted BAH's substituents affect their equilibrium constants or up of reactions.

$$Pk_o - pK_a = \boldsymbol{\rho\sigma}$$

Where Pk_o and pKa represent the acid dissociation constant of BAH and substituted BAH, **σ** is a reliable constant. the presence of substituents m-NO_2 independent of the substituents. The ionic strength (0.6) was kept constant during the experimental condition. pH measurements were performed using serial number 259731 for an Adel model Equipped with a combined pH electrode E-201-C, the pH ionometer from Bio Era Life Sciences. In aqueous 50% ethanol (v/v), pH metry measurements were prepared at room temperature. The value was recorded at the beginning of the pH metry titration (in the acidic area). with the value of pH at the end of titration where the titration solution was sufficiently basic. At regular intervals throughout the titration, pH was monitored. (2-3 min) for equilibrium after every 0.2 N NaOH solution addition. Pk_o, pKa value of BAH, and substituted BAH were calculated from this method and pH measurement data.[20-21]





Hammett Parameter meta-nitro BAHydrazide	
σ -value	**ρ**- value
0.30	1.67

Fig.-2

CONCLUSION

The examined hydrazides are reactive in the following order:

m-nitro BAH < BAH

The increased electron-withdrawing inductive action of the alkyl group has no impact on reactivity in the instance of m-nitro benz hydrazide. The calculation of the Hammett parameters yields the reaction constant (ρ) value of 1.67 for the m-nitro BAH and the substituent constant (σ) value of 0.30. Because they raise the ionization constant in comparison to parent benzoic acid, Sigma values for electron-withdrawing groups

are positive, whereas those for electron-donating groups are negative. These constants provide us with a qualitative and quantitative sequence effect caused by electron-donating and withdrawing groups on the rate of reaction in addition to providing us with an understanding of whether a specific substituent is relative to hydrogen electron-withdrawing or electron-donating. Reaction rates are slowed or equilibrium is suppressed by electron-withdrawing groups.

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CONFLICT OF INTERESTS

The authors confirm that none of their known financial conflicts of interest or close personal connections might have seemed to have influenced the research presented in this study.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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