*Hammett Correlations in the Chemistry of Thallium (III)-Induced Oxidation of Benzoic and m-Chlorobenzoic Acid Hydrazides -in Acidic Medium*

*Section A-Research paper*

# HAMMETT CORRELATIONS IN THE CHEMISTRY OF THALLIUM (III)-INDUCED OXIDATION OF BENZOIC AND M-CHLOROBENZOIC ACID HYDRAZIDES -IN ACIDIC MEDIUM

**Amit Varale[1*], Samadhan Nikalaje[2]**

### Abstract

In a perchloric and hydrochloric acid medium mixture, thallium (III) reacts with benz and m-chloro benz acid hydrazide. The process of the reaction begins with the creation of a complex with the reactant, which breaks down later to produce the product. Acrylonitrile's reaction indicates that no free radicals are produced. As $[H^+]$ and $[Cl^-]$ rise, the reaction's rate decreases. A rise in ionic strength has no impact on the reaction's speed. At four various temperatures ranging from 288K to 303K, temperature effects were examined. A mechanism has been investigated, as well as the activation parameters. For BAH and m-chloro BAH, to calculate the reaction constant ($\rho$) and the substituents constant ($\sigma$).

**Keywords:** kinetics, Thallium (III), Oxidation, benzoic acid hydrazide (BAH) and m-chloro benzoic acid hydrazide (m-BAH)

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## 1.      INTRODUCTION

One of the goals of physical chemistry is to explain and correlate empirical chemical data. The Hammett equation is one of the more helpful conclusions of organic chemistry. [1] To explain the reactivity at an atom directly bound to an aromatic, meta-, or Para-substituent, Hammett constants were initially established and used. [2] "It is incredible that constants obtained simply from the ionization of organic acids in solution can frequently predict equilibrium and rate constants for a variety of individuals of reactions in solution, even though the Hammett methodology has been objected to by theoreticians due to its empirical foundation. The Hammett equation, or its developed form, has been used to model almost every type of organic reaction." [3] This study uses and substitutes at places on the aromatic ring a containing a range of the typical Hammett -values.[4]

In organic synthesis uses hydrazides as adaptable intermediates for a number of reactions. [5] These types of hydrazide compounds have biological properties that include anticancer, antibacterial, antimicrobial, antidepressant, and anti-inflammatory activity. [6] Hydrazides are frequently used in the production of polymers and glues, as well as in the industrial preservation of plants. [7] Although the usage of thallium (III) in the oxidation of organic molecules has increased recently, little research has been done in this area. [8] Compared to its neighbours in the periodic table, mercury (II) and lead (IV), thallium (III) has a higher selectivity and performs better as an oxidant. [9] "The area of physical chemistry known as reaction kinetics is concerned with determining the speeds of chemical processes. It is intended to be related to thermodynamics, which is concerned with how a process occurs but expresses nothing about its rate." [10]

Nitric acid, chromic acid, permanganates, ceric sulphate, lead tetra acetate, Thallium, Ti(CH3COO)3, Cr(VI) oxide, peroxydisulphate, Mn(II) pyrophoshate, Mn(II) acetate, Mn(III) sulphate, vanadium, selenium dioxide, hexacyanoferrate(III), aluminium alkoxid Many of them are highly selective in their effect on various functional groups, and they are commonly used to research the oxidation of various organic compounds.

The thallium (III) has a higher selectivity and is a better oxidant compared to its neighbours in the periodic table.[11]

Our focus is on calculating the equilibrium constant and studying how the solvent affects reaction speed. In addition, we will correlate the reaction rate with the Hammett parameter and the reaction constant.

## 2. EXPERIMENTAL

Thallium (III) solution [12] was produced by ionizing $Tl_2O_3$ (ACROS) in 1.0 mol/dm$^3$ Iodometric titration was used to determine the concentration of HCl. The benzoic and m-chloro benzoic acid hydrazide were synthesized using the described process, and their melting temperatures were used to identify products. In 50% v/v 1,4-dioxan, a stock solution of benzoic and m-chloro benzoic acid hydrazide was made. The ionic force remained constant.

Under pseudo-unimolecular reaction conditions, the reactions were examined in 50% v/v 1-4 dioxane (s.d. fine chem), while retaining a significant excess of hydrazide over oxidant. The solutions with the reactants and all other constituents were thermally equilibrated separately, combined, and the reaction combination's iodometric titration against a reference sodium thiosulphate solution was used to calculate the amount of unreacted thallium (III) in the mixture. The slopes of linearity of [Tl (III)] against time graphs were used to derive the pseudo-unimolecular rate constants. Up to 4%, the results were accurate and repeatable. About three reaction half-lives were found to be the kinetic runs. Solvent did not oxidise under the testing conditions.

**End Product Analysis**
The reaction occurred using an aqueous solution of hydrazide, Thallium (III), HCl, and $HClO_4$ for the purpose of product identification. After filtration of the reaction

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mixture in the flask, the residue was tested for acid using the following procedure in a thermostated water bath that was held at $50^0C$ for 24 hours.

i. Using bicarbonate as a test substance, benzoic and m-chloro benzoic acid groups were found to be present.

ii. Acid's melting point and infrared reflectance were used to confirm the end product.

$$RCONHNH_2 + 2\,Tl(III) + H_2O \rightarrow R\text{-}COOH + N_2 + 4H^+ + 2\,Tl(I) \qquad \text{... (1)}$$
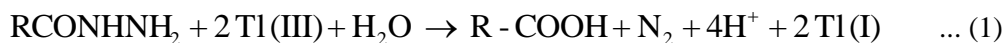
## 3. RESULTS AND DISCUSSION

It is observed that, the reaction takes place quickly in a perchloric acid solution, but the rate is observable when hydrochloric acid is present. As a result, both acids were combined to carry out the reaction.

| Sr.No. | Effect | Concentration in mol/dm$^3$ | Kobs x 10$^{-4}$ | |
|---|---|---|---|---|
| | | | m-ClBAH | BAH |
| 1 | [Hydrazide] | 1 x 10$^{-2}$ | 1.44 | 0.62 |
| | | 3 x 10$^{-2}$ | 3.44 | 1.57 |
| | | 5 x 10$^{-2}$ | 4.51 | 1.84 |
| | | 6.4 x 10$^{-2}$ | 5.48 | 1.96 |
| | | 10 x 10$^{-2}$ | 7.18 | 3.54 |
| 2 | [Tl (III)] | 0.65 x 10$^{-3}$ | 8.04 | 3.60 |
| | | 6.5 x 10$^{-3}$ | 8.52 | 3.60 |
| 3 | [H$^+$] | 7 x 10$^{-2}$ | 2.61 | 4.2 |
| | | 7 x 10$^{-2}$ | 0.32 | 0.15 |
| 4. | [Cl$^-$] | 7 x 10$^{-2}$ | 1.45 | 2.87 |
| | | 7 x 10$^{-2}$ | 0.13 | 0.095 |
| 5 | [NaClO$_4$] | 4.4 x 10$^{-1}$ | 1.39 | 1.57 |
| | | 1.2 x 10$^{-1}$ | 1.18 | 1.58 |
| 6 | [Acrylonitrile] | 5% | 1.03 | 1.57 |
| | | 40% | 0.90 | 0.32 |
| 7 | Dielectric constant | 5% (dioxane) | 1.37 | 1.80 |
| | | 40% (dioxane) | 0.64 | 0.23 |

At constant [HCl] and [HClO4] concentrations, the reaction's impact of the reactants was determined of 5 x 10$^{-1}$mol/dm$^3$ respectively and ionic strength of 6 x 10$^{-1}$mol/dm$^3$. Oxidant concentration ranged from 0.65x10$^{-5}$ to 0.65x10$^{-4}$ mol/dm$^3$ maintaining the [hydrazide] level at 1x10$^{-3}$ mol/dm$^3$. Due to the fact that the pseudo-unimolecular rate constants were actually consistent 3.58 ± 0.1x10$^{-4}$ per second for BAH and 8.042 ± 0.5x10$^{-4}$ per second m-chloro BAH at, the [oxidant] is in a state of unity. Studying the affect of [hydrazide] between the concentration range from 0.01 to 0.1 mol/dm$^3$ maintaining the [oxidant] at 0.3x10$^{-4}$ mol/dm$^3$.The pseudo unimolecular rate constants increases 0.62 x 10$^{-4}$ per second to 3.54 x 10$^{-4}$ per second for BAH and 1.44 x 10$^{-4}$ per second to 7.184 x 10$^{-4}$ per second for m-chloro BAH as concentration rises, it is discovered that the order in relation to hydrazide is fractional.

Ionic strength, oxidant, hydrazide, and [oxidant] were maintained as constants to evaluate the effects of [H$^+$] and [Cl$^-$], 0.003,0.1 and 6 x 10$^{-1}$mol/dm$^3$ respectively. We used HClO4 and NaCl to change [H+] and [Cl-]. Raised [H+] from 1.3 to 6.0 x 10$^{-1}$mol/dm$^3$ decreases 10$^{-4}$ k(per second) from 4.22 to 0.15 for BAH and 2.61 to 0.32 m-chloro BAH at 298K. Raised in [Cl$^-$] from 1.3 to 6.0 x 10$^{-1}$mol/dm$^3$ reduced 10$^{-4}$ k(per second) from 2.87 to 0.095 for BAH and 1.45 to 0.13 m-chloro BAH at 298K. There was a range in the relative permittivity. with a 40% v/v increase in the solvent concentration from 5%. It has

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been found that rate reduces as solvent percentage lowers.

**Table: Michaelis-Menten Plot for m-chloro BAH**

| Temperature | m-chloroBAH | 1/ m-chloroBAH | $K_{obs} \times 10^{-4}$ per second | $1/ K_{obs} \times 10^{-4}$ per second |
|---|---|---|---|---|
| 288K | 0.01 | 100.33 | 0.72 | 1.3888 |
|  | 0.03 | 33.33 | 1.70 | 0.5882 |
|  | 0.05 | 20.00 | 2.24 | 0.4464 |
|  | 0.064 | 15.625 | 2.70 | 0.3703 |
|  | 0.1 | 10.00 | 3.48 | 0.2873 |
| 293K | 0.01 | 100.33 | 1.08 | 0.9259 |
|  | 0.03 | 33.33 | 2.57 | 0.3891 |
|  | 0.05 | 20.00 | 3.38 | 0.2958 |
|  | 0.064 | 15.625 | 4.10 | 0.2439 |
|  | 0.1 | 10.00 | 5.32 | 0.1879 |
| 298 K | 0.01 | 100.33 | 1.44 | 0.6944 |
|  | 0.03 | 33.33 | 3.44 | 0.2906 |
|  | 0.05 | 20.00 | 4.52 | 0.2212 |
|  | 0.064 | 15.625 | 5.49 | 0.1821 |
|  | 0.1 | 10.00 | 7.18 | 0.1392 |
| 303K | 0.01 | 100.33 | 2.16 | 0.4629 |
|  | 0.03 | 33.33 | 5.14 | 0.1945 |
|  | 0.05 | 20.00 | 6.76 | 0.1479 |
|  | 0.064 | 15.625 | 8.20 | 0.1219 |
|  | 0.1 | 10.00 | 10.64 | 0.0939 |
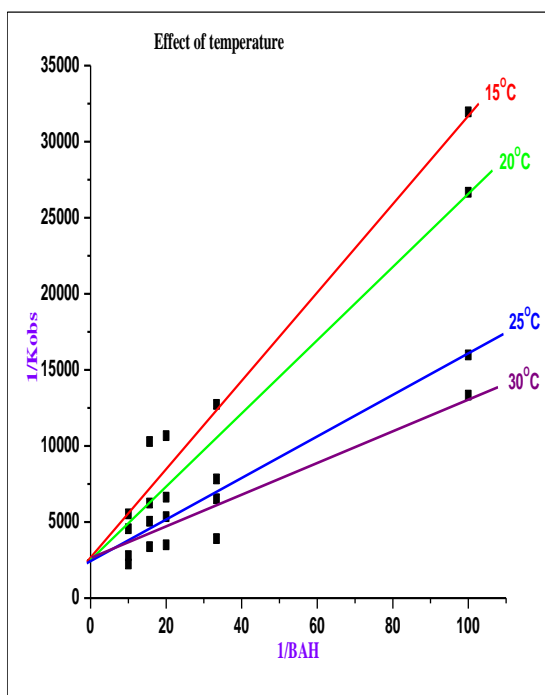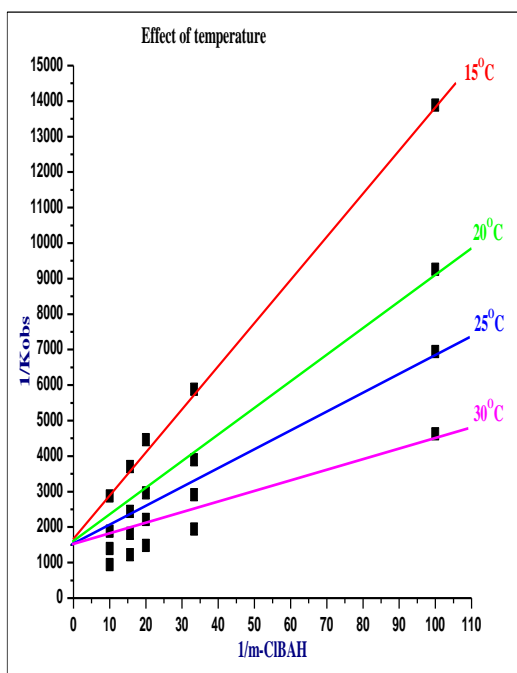


**Effect of Temperature for BAH and m-chloroBAH**
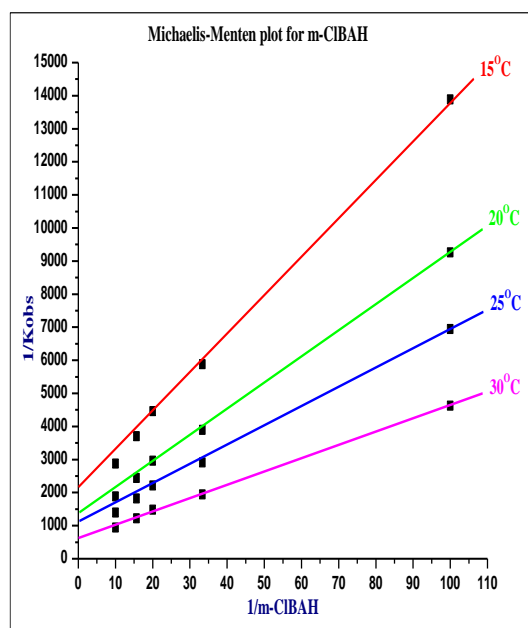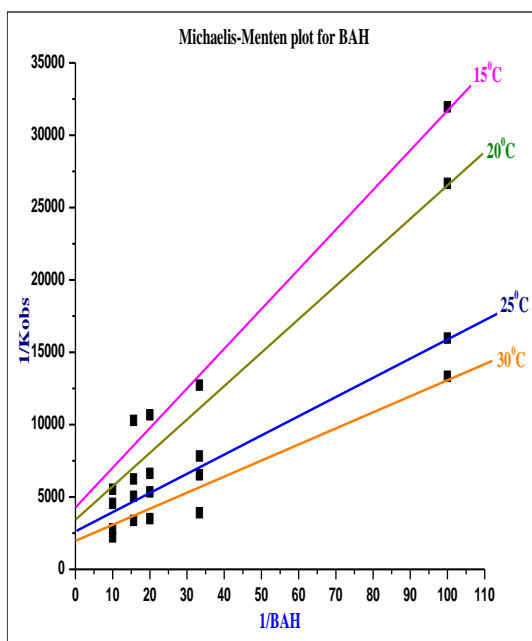
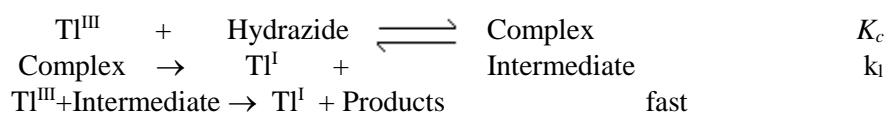**Michalie's-Menten plots for BAH and m-chloroBAH**

Table 1 – values of $K_1$ and $k_c$      [HCl] = 1 x $10^{-1}$mol/dm$^3$, [HClO$_4$] = 1 x $10^{-1}$mol/dm$^3$
[Tl$^{III}$] = 0.003 mol/dm$^3$,  µ = 6.0 mol dm$^{-3}$

| Hydrazide | Kc. (mol/dm$^3$) | | | |
|---|---|---|---|---|
| | 288K | 293K | 298K | 303K |
| BAH | 9.33 | 9.60 | 9.33 | 9.00 |
| m-chloro BAH | 20.43 | 20.00 | 20.00 | 20.00 |

It was discovered that the thallium (III) order was uniform and the order was fractional in regard to hydrazide. In terms of substrate concentration, the fractional order is a result of the substrate equilibrium during complex formation.

| | | | | | |
|---|---|---|---|---|---|
| Tl$^{III}$ | + | Hydrazide ⇌ | Complex | | $K_c$ |
| Complex | → | Tl$^{I}$ + | Intermediate | | $k_l$ |
| Tl$^{III}$+Intermediate → | | Tl$^{I}$ + Products | | fast | |

**Scheme 1**
The 1/kobs vs 1/[Hydrazide] Michealis-Menten graphs were linear with an intercept in the direction of the complicated growth. Thus, using Scheme 1, the observed results can be applied to show the reaction's mechanism. Equation 2 gives the rate that Scheme1 can afford. Then, Equation 6 defines the [Tl(III)] free since total [Tl(III)] both the complex [Tl(III)] and free [Tl(III)] form (Equation 3). Equation 7 and Equation 8's pseudo-first order rate constant, kobs, can be applied to explain the final rate law.

Rate = $k_1$ [Complex] = $k_1K_c$      [Hydrazide] $_{free}$ [Tl$^{III}$] $_{free}$                                   (1)
[Tl$^{III}$] $_{total}$ = [Tl$^{III}$] $_{free}$ + [Complex]                                                                         (2)
[Tl$^{III}$] total = [Tl$^{III}$] $_{free}$ $_+$ $K_c$ [Hydrazide] [Tl$^{III}$] $_{free}$                                           (3)
[Tl$^{III}$] $_{free}$ $_=$ [Tl$^{III}$] $_{total}$/ (1 + $K_c$ [Hydrazide])                                                       (4)
Rate = $k_1K_c$ [Hydrazide] [Tl$^{III}$] $_{free}$                                                                                (5)

$$Kobs = k_1 K_c [Hydrazide]/ (1 + K_c [Hydrazide]) \qquad (6)$$

1/kobs vs 1/ [Hydrazide] at four distinct temperatures was graphed., rate law 8 is confirmed. The values of k1 and Kc were derived from the incline and intercepts of these graphs and are illustrated in Table 1.

Because hydrazides and other chloro-complexes are protonated [13] of the solution contains thallium (III), hydrogen and chloride ion concentrations have an impact on the process. Equation 9 states that in an acidic medium. Given that hydrazides are known to be protonated, Equation 10 may be used to express total [Hydrazide], and Equation 12 can be used to indicate that free [Hydrazide] had no effect. Ionic strength on the reactions is confirmed by the fact that free hydrazide is the active species and that the rates of reaction fall as [H+] increases, establishing the neutrality of one of the reactants.

$$RCONHNH_2 + H^+ \rightleftharpoons RCONHNH_3^+ \qquad K_H \qquad (7)$$
$$[Hydrazide]_{total} = [Hydrazide]_{free} + [Hydrazide]_{protonated} \qquad (8)$$
$$[Hydrazide]_{total} = [Hydrazide]_{free} + K_H [Hydrazide]_{free} \qquad (9)$$
$$[Hydrazide]_{free} = [Hydrazide]_{total} / (I + K_H [H^+]) \qquad (10)$$

When chloride ions are combined with thallium (III), solid complexes with the formula $TlCl_n^{3-n}$, where n is the maximum number of thallium (III) chloride complexes that can be seen in equilibrium, which ranges from 13 to 16. The applicable stability constants' values

$K_1 = 13.8 \times 10^7$, $K_2 = 39.8 \times 10^{12}$, $K_3 = 60.2 \times 10^{14}$ and
$K_4 = 10 \times 10^{17}$ dm$^3$per mole.

$$Tl^{3+} + Cl^- \rightleftharpoons TlCl^{2+} \qquad K_1 \qquad (11)$$
$$TlCl^{2+} + Cl^- \rightleftharpoons TlCl_2^+ \qquad K_2 \qquad (12)$$
$$TlCl_2^+ + Cl^- \rightleftharpoons TlCl_3^+ \qquad K_3 \qquad (13)$$
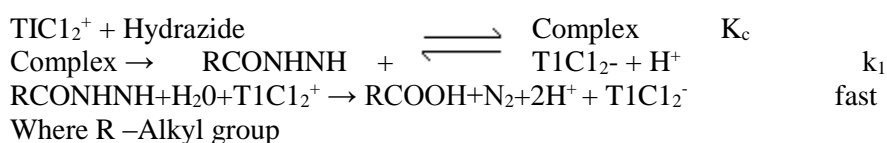$$TlCl_3 + Cl^- \rightleftharpoons TlCl_4^+ \qquad K_4 \qquad (14)$$
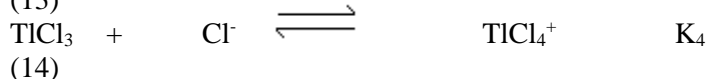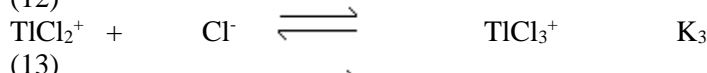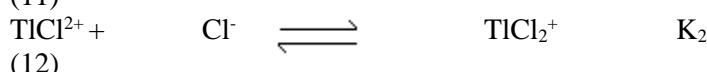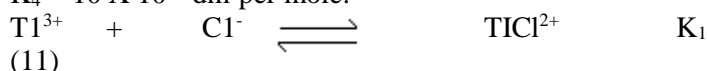
Equation 17 can be used for expressing the concentration of all thallium (III) as $TlCl2^+$. Equations 18 and 19 were used to calculate the concentrations of $[TlCl2]^+$free, $TlCl_3$, and $TlCl4^-$ the change in rate constant as the chloride ion concentration changed at different chloride ion concentrations. Equation (19) can now be used to calculate the $[TlCl2]^+$free., where b1 = K3/K2 = $1.51 \times 10^2$ and b2 = K4/K3 = $1.66 \times 10^2$

$$[Tl(III)]_{total} = [TlCl_2^+]_{total} = [TlCl_2^+]_{free} + [TlCl_3] + [TlCl_4] \qquad (15)$$
$$[TlCl_2^+]_{total} = [TlCl_2^+]_{free} (1+\beta_1 [Cl^-] + \beta_2 [Cl^-]^2) \qquad (16)$$
$$[TlCl_2^+]_{free} = [TlCl_2^+]_{total} / (1 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2) \qquad (17)$$

The only active species is $[TlCl2^+]$ free, and the order of $[Cl^-]$ is -1.5. As $[Cl^-]$ fluctuates, the concentrations of $[TlCl2^+]$ free and TlCl3 follow the values of the rate constants.

$$TlCl_2^+ + Hydrazide \rightleftharpoons Complex \qquad K_c$$
$$Complex \rightarrow RCONHNH + TlCl_2- + H^+ \qquad k_1$$
$$RCONHNH + H_2O + TlCl_2^+ \rightarrow RCOOH + N_2 + 2H^+ + TlCl_2^- \qquad fast$$
Where R –Alkyl group

**Scheme 2**
Now that the free hydrazide of the substrate and $TlCl2^+$ of the oxidant have been recognized as the species in progress, Scheme 2 can depict the mechanism by using the proper rate law and equations for

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pseudo-unimolecular Equations 20 and 21 provide reaction constants. The rate law 21 was confirmed by establishing 1/kobs versus 1/[Hydrazide] and 1/kobs against [H$^+$], both of which were shown to be linear. The values of Kc and KH have been derived from these plots' slopes and intercepts. the corresponding Kc and KH values for BAH and m-chloro BAH are shown in Table 1 and are 13 and 16 per mole dm3, respectively.
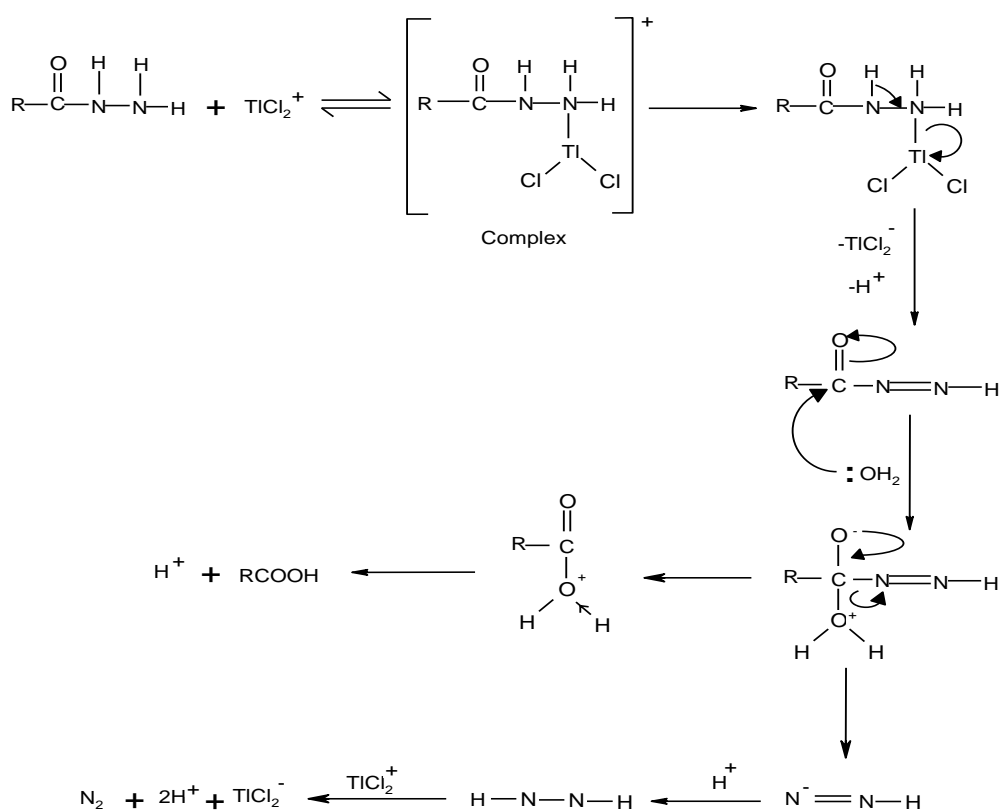
| Sr.No. | Thermodynamic Parameter | m-chloroBAH | BAH |
|---|---|---|---|

$$\text{Rate} = \frac{k_1 K_c \, [\text{Hydrazide}]_{total} \, [TlCl_2^+]_{total}}{(1+K_c\,[\text{Hydrazide}])\,(1+K_H\,[H^+])\,(1+\beta_1\,[Cl^-]+\beta_2\,[Cl^-]^2)} \qquad (18)$$

$$\text{Kobs} = \frac{k_1 K_C \, [\text{Hydrazide}]_{total}}{(1+K_c\,[\text{Hydrazide}])\,(1+K_H\,[H^+])\,(1+\beta_1\,[Cl^-]+\beta_2\,[Cl^-]^2)} \qquad (19)$$

TlCl2$^+$ is the thallium (III) chloro complex that is most electrophilic, making it the reactive species.

**MECHANISM**



R=Alkyl group for acid hydrazides

**Scheme 3**
Direct two-electron transfer from hydrazide to thallium produces an intermediate in the exact mechanism, which is followed by quick stages. When the hydrazide's nitrogen is electrophilically substituted, the intermediate is formed of the N-Tl bond, it breaks down in the next stage. (Plan 3). It has been hypothesized that this N-T1 bond formation occurs when compounds containing nitrogen are subjected to thallium (III) oxidation.[14]

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| 1 | Ea (KJ mol$^{-1}$) | 12.584 | 16.466 |
|---|---|---|---|
| 2 | $\Delta H^{\#}$ (KJ mol$^{-1}$) | 14.976 | 15.564 |
| 3 | $\Delta G^{\#}$ (KJ mol$^{-1}$) | 21.462 | 40.113 |
| 4 | $\Delta S^{\#}$ (e.u.) | -22.164 | -19.690 |
| 5 | Temperature co-efficient | 1.8333 | 1.9888 |
| 6 | Frequency factor | 1.2589 x 10$^{-4}$ | 1.5848 x 10$^{-5}$ |

the activation constants for BAH and m-chloro BAH, respectively. Due to the development of a more regulated transition state, as illustrated in Scheme 3, the entropy of activation has been significantly reduced. Ionic force variations have little impact on the reaction. due to technique employs neutral hydrazides as the active substrate. The maintenance of the inter reactant complex that was created [15] in a low relative permittivity medium [16] [17] [18] explain the decrease in rate as 1, 4-dioxan concentration rises..

**Determination of Hammett Parameters-**
BAH has a pKa value of 5.7 at ($V_{1/2}$) and a pKa value of 5.3 at ($V_{2/2}$) ($\delta$ = 1.69 for 50% ethanol). The m-chloro BAH has a substituent constant ($\sigma$) value of 0.24 and a reaction constant ($\rho$) value of 1.66.
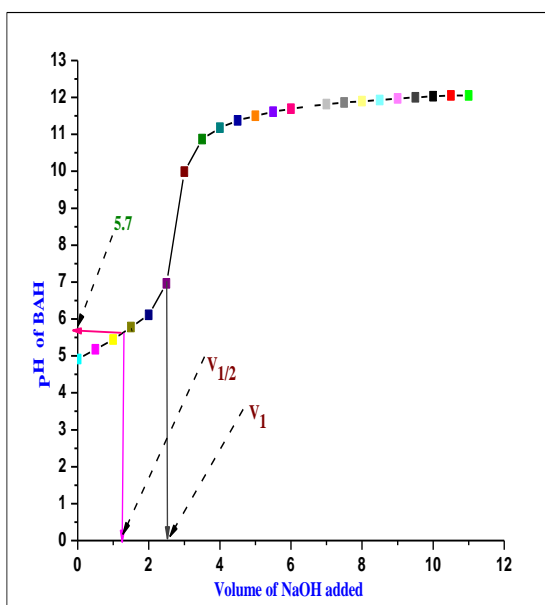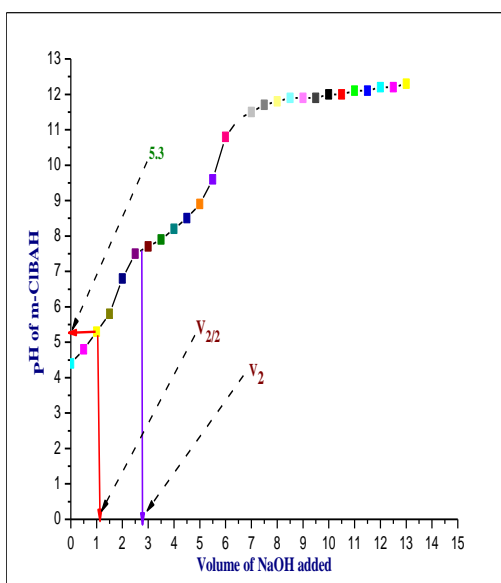
BAH and m-chloro BAH's substituent constant ($\sigma$) and reaction constant ($\rho$) values are calculated using the pH metry method. Furthermore, the aim of this research was to calculate the influence of the substituent of BAH and m-substituted BAH on their rate of reactions or equilibrium constants using the Hammett equation.

$$pK_0 - pK_a = \rho\sigma$$

Where, The acid dissociation constants of BAH and m-chloro are represented by $pK_0$ and pKa. BAH, a constant that is unaffected by the substituents m-Cl, is characterised by the other two. The ionic strength (6 x 10$^{-1}$) kept constant during the experimental condition [19]

An Adel model serial number 259731 Bio Era life sciences pH ionometer outfitted with combination pH electrode E-201-C was used to monitor pH. At room temperature, pH metry measurements were prepared in aqueous 50% ethanol (v/v). The initial pH values of the pH metry titration (in an acidic medium) and completion of the titration, In the event that the measurement solution was appropriately basic, were recorded.pH was measured during the titration at appropriate intervals (1-2 min) for equilibrium following each addition of 0.2 N NaOH solution. Using this technique and the results from the pH measurement, the $pK_0$ and pKa values of BAH and m-chloro BAH were determined. [20]

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## Determination of Hammett Parameters

| Hammett Parameter | |
|---|---|
| **σ** m-chloro BAH | **ρ** m-chloro BAH |
| 0.24 | 1.66 |

## 4. CONCLUSION

The experimental condition, m-chloro benzhydrazide, interacts in the following order:
BAH < m-chloro BAH.
In the case of m-chloro benzhydrazide, the alkyl group's higher electron-withdrawing inductive effect has no impact on reactivity.
The m-chloro BAH's substituent constant ($\sigma$) value is 0.24, and its reaction constant ($\rho$) value is 1.66, based to the Hammett parameter.

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