Study of Various factors on Oxidation of *p-nitro benzoic acid hydrazide*-A Kinetic and Mechanistic Approach
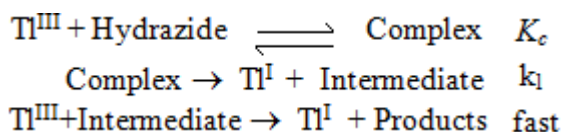
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Abstract: *The kinetics of oxidation of p-nitro benzoic acid hydrazide by Thaliium (III) in a mixture of perchloric and hydrochloric acid medium at a constant ionic strength has been planned to study iodometrically.*

$$Tl^{III} + Hydrazide \rightleftharpoons Complex \quad K_c$$
$$Complex \rightarrow Tl^{I} + Intermediate \quad k_1$$
$$Tl^{III} + Intermediate \rightarrow Tl^{I} + Products \quad fast$$

The increase in [H$^+$] and [Cl$^-$] decreases the rate of the reaction. The activation parameters were also determined and a mechanism is predicted.

Keywords: Kinetics, Thermodynamics, Thallium (III), Oxidation, Hydrazide.

1. Introduction

The Chemical kinetics focuses primarily on the fundamental physical and chemical processes that control the conversion of chemical to thermal energy in high-temperature, high-activation reacting flows. The approach taken is interdisciplinary, as it addresses the interplay of chemical thermodynamics. The results of this research are of immediate interest to Engineering and to study enzyme catalyzed reactions. The experience obtained in the Research Laboratory prepares students and researchers to advance their careers in, Chemical kinetics, Thermodynamics as well as in other fields including materials, nanotechnology, and bioengineering in which there is also interplay of similar and/or analogous processes.

Oxidation of organic compound carried out by oxidising agent like chloramine-T, chloramine-B, N-bromosuccinimide, Nbromobenzamide[1] p-methyl[2] and other halomides[3] potassium dichromate Cr (VI).[4,5,6] is available but very little information is available on oxidation of hydreazides by Thallium(III). Other investigations have included those of the oxidation of captive oxalate [7] the reaction of phenyl thallium dicarboxylate with tetramethyltin in methanol [8] oxythallation of norbornene derivatives in aqueous solution and in methanol [9] the oxidation of aryl dialkyl amines [10] the thallium (III) promoted hydrolysis of thiol esters [11] and the thallium (III) oxidation of catechol in chloride containing media [12]. An interesting study of oxidation of anilines by thallium (III) acetate in aqueous acetic acid is also reported [13].

The hydrazides are pharmaceutically important compounds used as antitubercular and antibacterialagents, some of them have been reported to possess anti-inflammatory and diuretic activities.

The objective of the present study is not only to develop method for the oxidation of p-nitro benzoic acid hydrazide to their corresponding carboxylic acids but also to determine order of reaction and to propose the plausible mechanism of the reaction.

2. Material and Methods

The stoichiometry of the reaction was determined using a known excess of thallium (III) over hydrazide and determining remaining oxidant iodometrically after 24 hrs. The results consistent with equation-(1) were obtained. The corresponding carboxylic acid was characterized by determining its MP.

$$RCONHNH_2 + 2\,Tl(III) + H_2O \rightarrow R\text{-}COOH + N_2 + 4H^+ + 2\,Tl(I) \quad (1)$$
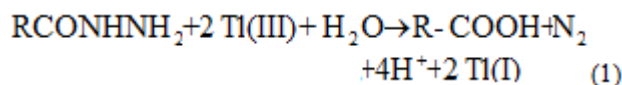
3. Results and Discussion

The reaction occurs rapidly in perchloric acid medium but in the presence of hydrochloric acid the rate is measurable. Therefore the reaction was carried out in a mixture of both the acids. The effect of reactants on the reaction was studied at constant [HCl] and [HClO$_4$] of 0.1 mol dm^{-3} each and ionic strength of 0.6 mol dm^{-3}. Concentration of oxidant was varied from 6.4×10^{-4} to 6.4×10^{-3} mol dm^{-3} keeping the [hydrazide] constant at 1×10^{-1} mol dm^{-3}.Since,the pseudo first order rate constants were fairly constant (1.12 +_ 0.1×10^{-4} S^{-1} for p-Nitro BAH at 25^{0}C, the order with respect to [oxidant] is unity. The effect of [hydrazide] was studied between the concentration range from 1×10^{-2} to 1×10^{-1} mol dm^{-3} keeping the [oxidant] constant at 3.0×10^{-3} moldm^{-3}.The pseudo first order rate constants increases with increase in

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concentration and the order with respect to hydrazide is found to be fractional.

To study the effect of $[H^+]$ and $[Cl^-]$,[oxidant], [hydrazide] and ionic strength were kept as 3.0×10^{-3}, 1×10^{-1} and 0.6 mol dm^{-3} respectively. To vary $[H^+]$ and $[Cl^-]$, $HClO_4$ and NaCl were used. Increase in $[H^+]$ from 7×10^{-2} to 5.4×10^{-1} mol dm^{-3} decreases 10^{-4} k(S^{-1}) from 0.43 to 0.055 for p-Nitro BAH at 25^0C. Increase in $[Cl^-]$ from 7×10^{-2} to 5.4×10^{-1} mol dm^{-3} decreases 10^{-4} k(S^{-1}) from 0.69 to 0.076 for p-Nitro BAH at 25^0C. The relative permittivity was varied by changing the 1,4-dioxan content from 5 to 40 % v/v. The rate was found to decrease with decrease in relative permittivity.

4. Effect of Temperature for p-Nitro BAH
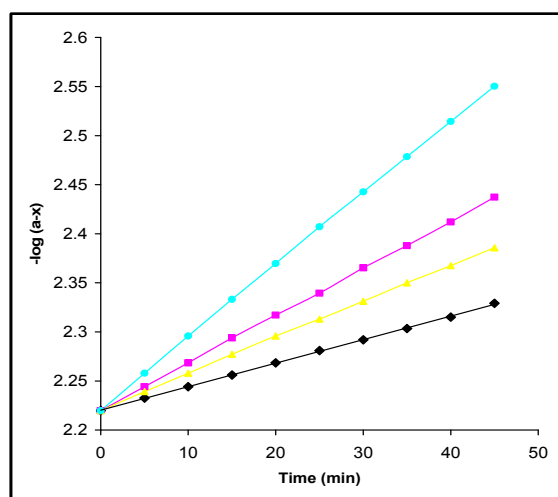
Since there is no formation of free radicals in the reaction, the reaction proceeds with two-electron transfer step. The Michealis - Menten plots of $1/k_{obs}$ versus 1/[Hydrazide] were linear with an intercept in support of the complex formation. The rate law was verified by plotting $1/k_{obs}$ against 1/[Hydrazide] and $1/k_{obs}$ against $[H^+]$ which were found to be linear. From the slopes and intercepts of these plots the values of K_c and K_H were determined [14-15].

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

$$k_{obs} = \frac{k_1 K_c [Hydrazide]_{total}}{(1 + K_c [Hydrazide])(1 + K_H[H^+])(1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2)} \quad (3)$$

The values of K_c are given in Table 1 and those of K_H were found to be 13 and 16 mol^{-1} dm^3 for benzoic and p-Chloro benzoic acid hydrazides respectively. The electrophilic character of $TlCl_2^+$ among the thallium (III) chlorocomplexes is highest thus making it the reactive species.
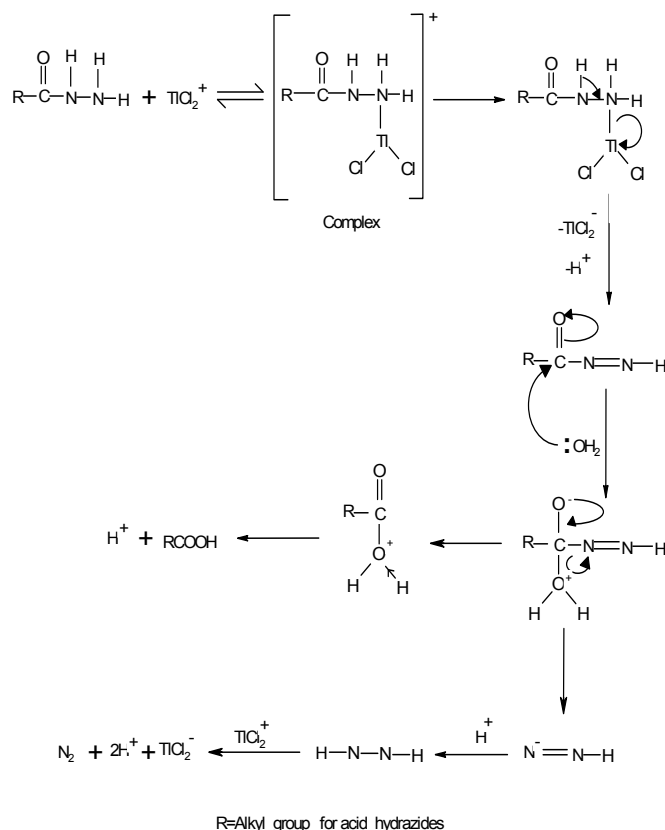
Table 1: Values of Kc and k_1
$[Tl^{III}] = 3.0 \times 10^{-3}$ mol dm^{-3}, I = 0.6 mol dm^{-3}
[HCl] = 0.1 mol dm^{-3}, $[HClO_4]$ = 0.1 mol dm^{-3}

Hydrazide	Kc. (mol dm^{-3})				$10^4 \times k_1$ (s^{-1})			
	15°C	20°C	25°C	30°C	15°C	20°C	25°C	30°C
p-NO₂ BAH	9.60	9.40	9.60	9.60	1.11	1.66	2.50	3.33

5. Mechanism

R=Alkyl group for acid hydrazides

6. Activation Parameters for p--nitro benzoic acid hydrazide

Hydrazide	Ea ($KJ\ mol^{-1}$)	$\Delta H^{\#}$ ($KJ\ mol^{-1}$)	$\Delta G^{\#}$ ($KJ\ mol^{-1}$)	$\Delta S^{\#}$ ($KJ\ mol^{-1}$)
BAH	67.45	59.74	87.94	-94.64
p-NO₂ BAH	33.72	19.27	81.81	-209.89

7. Relative Reactivities of Hydrazides

The order of reactivities of Benzoic and substituted benzoic acid hydrzides under investigation is –
p – Nitro BAH < BAH
Nitrogen has electron withdrawing inductive effect but an electron-donating mesomeric effect since it is in the para position.

8. Acknowledgement

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