

Kinetic and Mechanistic study of oxidation of benzoic and p-Nitro benzoic acid hydrazides to their corresponding acids by Thallium (III) in acidic medium

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ABSTRACT

The kinetics of oxidation of benzoic and p-Nitro benzoic acid hydrazides by Thallium(III) in a mixture of perchloric and hydrochloric acid medium at a constant ionic strength has been planned to study iodometrically. The reaction proceeds through formation of complex with reactant, which decomposes in subsequent steps to give product. The increase in $[H^+]$ and $[Cl^-]$ decreases the rate of the reaction. The thermodynamic parameters were also determined and a mechanism is predicted.

Key words: Kinetics, thallium(III), Oxidation.

INTRODUCTION

The kinetics and Mechanism of oxidation of benzoic and p-Nitro benzoic acid hydrazides has been well studied. Thallium oxide being one of the most versatile oxidizing agents, reacting with diverse substrates. The oxidation of benzoic and p-Nitro benzoic acid hydrazides continues to be of interest. The oxidant used is a versatile that deserves further investigation. Literature survey reveals that, although several oxidants are used for oxidation of hydrazides and their mechanisms have been established, there is no report on the oxidation of hydrazides by Thallium(III).

The reaction of hydrazides with most oxidants give the corresponding acids¹ and in some cases² esters or amides. Thallium(III) salts are well known oxidants³ in organic synthesis. The redox potential of $Tl(III)/Tl(I)$ couple is sensitive to the anion present in the solution. In perchloric and sulphuric acid media⁴ it has the highest value of 1.23V with either free Tl^{3+} , $TlOH^{2+}$ or thallium(III) sulphate complexes as active species respectively. Therefore, thallium(III) can be utilized both as a strong

(in perchloric acid and sulfuric acid media) and as a mild oxidant (in hydrochloric acid medium) by changing the reactive species. Although thallium(III) has been utilized for splitting of carbon-nitrogen bonds⁵ no mechanistic investigation has been carried out. The present work deals with kinetic and mechanistic study of oxidation of benzoic and p-Nitro benzoic acid hydrazides in a mixture of perchloric and hydrochloric acid medium.

MATERIAL AND METHODS

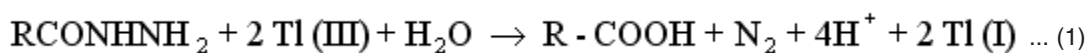
Thallium (III) solution was prepared by dissolving Tl_2O_3 (ACROS) in 1.0 moldm⁻³ HCl and the concentration was ascertained by iodometric titration. The benzoic (BAH) and p-Nitro benzoic acid (p-NO₂ BAH) hydrazides were prepared from reported⁶ procedure and characterized by determining their melting points. Stock solution of benzoic and p-Nitro benzoic acid hydrazides were prepared in 50 % v/v, 1,4-dioxane. Ionic strength was kept constant.

The reactions were carried out in 50 % v/v 1-4 dioxane (s.d.fine.chem) under pseudo first

order conditions keeping concentration of hydrazide in large excess over that of the oxidant. The solutions containing the reactants and all other constituents were thermally equilibrated separately, mixed and the reaction mixture was analysed for unreacted thallium (III) iodometrically by titrating against standard thiosulphate. The pseudo-first order rate constants were determined from the slopes of linear $\log[Tl(III)]$ versus time plots. The results were reproducible up to $\pm 5\%$. Kinetic runs were followed to about three half-lives of the reactions. Under

the experimental condition oxidation of 1,4-dioxan did not occur.

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 (114°C for benzoic acid and 239°C for p-Nitrobenzoic acid)



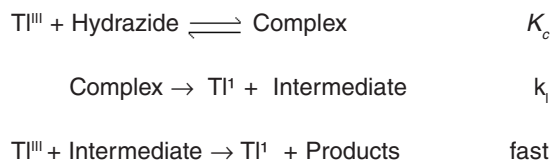
RESULTS AND DISCUSSION

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 $6.4 \times 10^{-3} \text{ mol dm}^{-3}$ keeping the [hydrazide] constant at $1 \times 10^{-1} \text{ mol dm}^{-3}$. Since, the pseudo first order rate constants were fairly constant ($3.83 \pm 0.1 \times 10^{-4} \text{ S}^{-1}$ for BAH at 25°C and $1.12 \pm 0.1 \times 10^{-4} \text{ S}^{-1}$ for p-Nitro BAH at 25°C , the order with respect to [oxidant] is unity. The effect of [hydrazide] was studied between the concentration range from 1×10^{-2} to $1 \times 10^{-1} \text{ mol dm}^{-3}$ keeping the [oxidant] constant at $3.0 \times 10^{-3} \text{ mol dm}^{-3}$. The pseudo first order rate constants increases with increase in concentration and the order with respect to hydrazide is found to be fractional (0.62 for BAH and 0.22 for p-NO₂ BAH). 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 $5.4 \times 10^{-1} \text{ mol dm}^{-3}$ decreases $10^{-4} \text{ k(S}^{-1})$ from 4.22 to 0.15 for BAH at 25°C and 0.43 to 0.055 for p-Nitro BAH at 25°C . Increase in $[Cl^-]$ from 7×10^{-2} to $5.4 \times 10^{-1} \text{ mol dm}^{-3}$ decreases $10^{-4} \text{ k(S}^{-1})$ from 2.80 to 0.095 for BAH at 25°C and 0.69 to 0.076 for p-Nitro BAH at 25°C . 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.

Added acrylonitrile in the concentration range 0.5 to 2.5 vol.% by keeping concentrations of oxidant, reductant, perchloric acid, hydrochloric acid and ionic strength fixed did not produce any precipitate due to polymerization of the added acrylonitrile on the pseudofirst order rate constants indicating absence of free radicals.

Since there is no formation of free radicals in the reaction, the reaction proceeds with two-electron transfer step. The order in thallium (III) was found to be unity and the order in hydrazide was found to be fractional. Such fractional order in substrate concentration is due to



Scheme 1

the prior complex formation equilibrium between the reactants. The Michealis - Menten plots of $1/k_{\text{obs}}$ versus $1/[Hydrazide]$ were linear with an intercept in support of the complex formation. Therefore, in agreement with the results obtained the mechanism of the reaction can be represented as in Scheme 1. Equation 2 gives the rate according to Scheme 1. Since, total $[Tl^{III}]$ exists in the form of

free [Tl^{III}] and the complex (Equation 3) therefore, the [Tl^{III}] free is given by Equation 6. The overall rate law is now expressed by Equation 7 and the Pseudo-first order rate constant k_{obs} , by Eq. 8.

$$\text{Rate} = k_1 [\text{Complex}] = k_1 K_c [\text{Hydrazide}]_{\text{free}} [\text{Tl}^{\text{III}}]_{\text{free}} \quad \dots(2)$$

$$[\text{Tl}^{\text{III}}]_{\text{total}} = [\text{Tl}^{\text{III}}]_{\text{free}} + [\text{Complex}] \quad \dots(3)$$

$$[\text{Tl}^{\text{III}}]_{\text{total}} = [\text{Tl}^{\text{III}}]_{\text{free}} + K_c [\text{Hydrazide}] [\text{Tl}^{\text{III}}]_{\text{free}} \quad \dots(5)$$

$$[\text{Tl}^{\text{III}}]_{\text{free}} = [\text{Tl}^{\text{III}}]_{\text{total}} / (1 + K_c [\text{Hydrazide}]) \quad \dots(6)$$

$$\text{Rate} = k_1 K_c [\text{Hydrazide}] [\text{Tl}^{\text{III}}]_{\text{free}} \quad \dots(7)$$

$$k_{\text{obs}} = k_1 K_c [\text{Hydrazide}] / (1 + K_c [\text{Hydrazide}]) \quad \dots(8)$$

Rate law 8 is verified by plotting $1/k_{obs}$ against $1/[\text{Hydrazide}]$ at four different temperatures and from the slopes and intercepts of these plots the values of k_1 and K_c were calculated and are given in Table 1.

The effect of hydrogen and chloride ion concentrations on the reaction is due to the protonation of hydrazides⁷ and different chloro – complexes⁸ of thallium (III) present in the solution. Hydrazides are known to be protonated in acid medium according to Equation 9. Therefore, total [Hydrazide] can be expressed by Equation 10 and thereby the fact that there was no effect of Free [Hydrazide] by Eq. 12. Since the rates of reaction decreases as the $[\text{H}^+]$ increases, free hydrazide is the active species



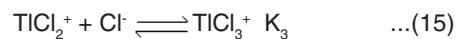
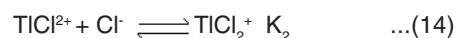
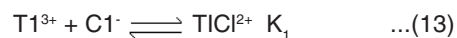
$$[\text{Hydrazide}]_{\text{total}} = [\text{Hydrazide}]_{\text{free}} + [\text{Hydrazide}]_{\text{protonated}} \quad \dots(10)$$

$$[\text{Hydrazide}]_{\text{total}} = [\text{Hydrazide}]_{\text{free}} + K_H [\text{Hydrazide}]_{\text{free}} \quad \dots(11)$$

$$[\text{Hydrazide}]_{\text{free}} = [\text{Hydrazide}]_{\text{total}} / (1 + K_H [\text{H}^+]) \quad \dots(12)$$

This is in support of ionic strength on the reactions indicating one of the reactant is neutral.

Thallium (III) forms strong complexes with chloride ions of the formula TlCl_n^{3-n} where n is the number of chlorides complexes with thallium (III) as represented in equilibrium 13 to 16. The values of respective stability constants⁸ are $K_1 = 1.38 \times 10^8$, $K_2 = 3.98 \times 10^{13}$, $K_3 = 6.02 \times 10^{15}$ and $K_4 = 1.0 \times 10^{18} \text{ mol}^{-1} \text{ dm}^3$. The presence of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ chloride ion concentration (which is the minimum $[\text{Cl}^-]$ used in the present study) all the



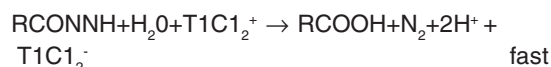
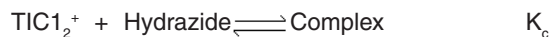
Thallium (III) will exist as TlCl_2^+ and its concentration can be expressed by Equation 17. The $[\text{TlCl}_2^+]_{\text{free}}$ can now be given by eq. 19 where, $\beta_1 = K_3/K_2 = 151$ and $\beta_2 = K_4/K_3 = 166$, further, using Equations 18 and 19 the concentrations of $[\text{TlCl}_2^+]_{\text{free}}$, TlCl_3 and TlCl_4^- were calculated at different chloride ion concentrations and

$$[\text{Tl}(\text{III})]_{\text{total}} = [\text{TlCl}_2^+]_{\text{total}} = [\text{TlCl}_2^+]_{\text{free}} + [\text{TlCl}_3] + [\text{TlCl}_4] \quad \dots(17)$$

$$[\text{TlCl}_2^+]_{\text{total}} = [\text{TlCl}_2^+]_{\text{free}} (1 + \beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2) \quad \dots(18)$$

$$[\text{TlCl}_2^+]_{\text{free}} = [\text{TlCl}_2^+]_{\text{total}} / (1 + \beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2) \quad \dots(19)$$

compared with the change in rate constant as the chloride ion concentration varied. The concentration of both of $[\text{TlCl}_2^+]_{\text{free}}$ and TlCl_3 parallel the values of rate constants as $[\text{Cl}^-]$ changes but the order $[\text{Cl}^-]$ is -1.5 , which makes $[\text{TlCl}_2^+]_{\text{free}}$ as the only active species.



Scheme 2

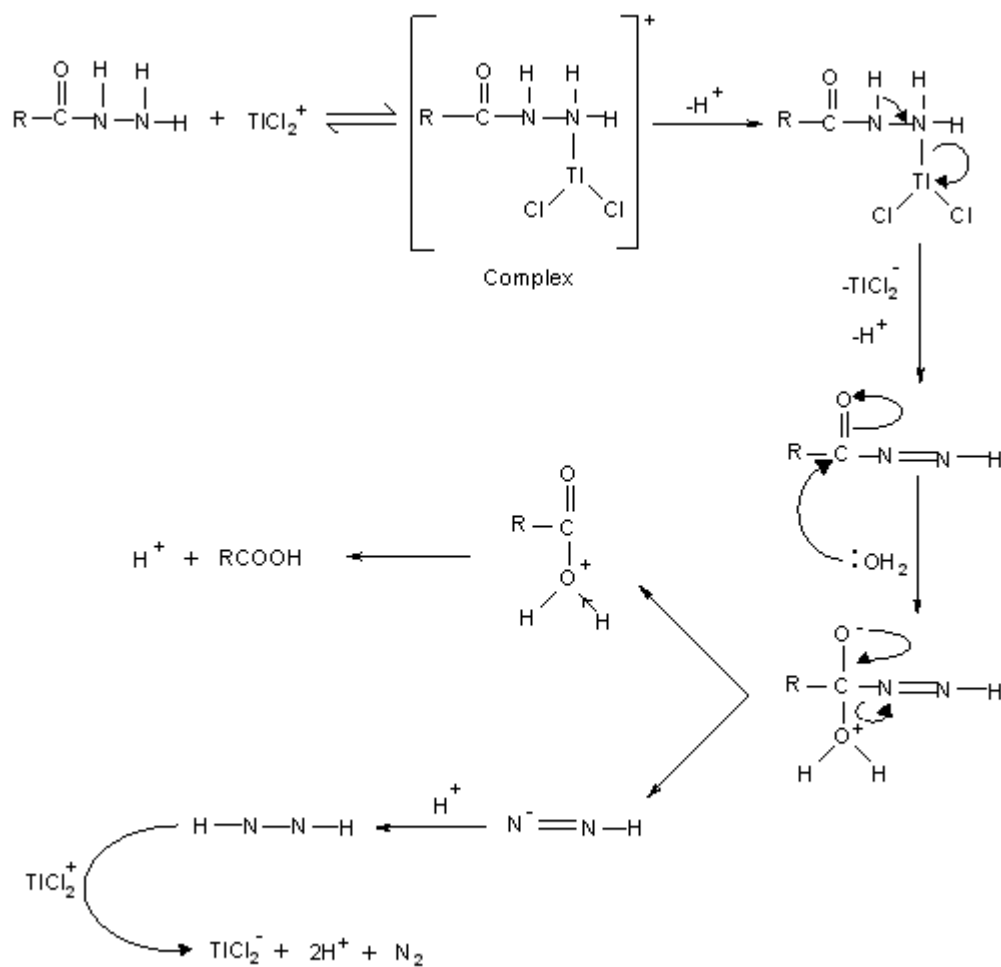
where $R = C_6H_5$ for benzoic acid hydrazide and $C_6H_5NO_2$ for p-Nitro benzoic acid hydrazide

The mechanism considering $TiCl_2^+$ of oxidant and free hydrazide of the substrate as the active species can now be represented by scheme 2 with respective rate law and the expression for

the pseudo-first order rate constants by Equations 20 and 21. The rate law 21 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.

$$\text{Rate} = \frac{k_1 K_c [\text{Hydrazide}]_{\text{total}} [TiCl_2^+]_{\text{total}}}{(1 + K_c [\text{Hydrazide}]) (1 + K_H [H^+]) (1 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2)} \quad \dots(20)$$

$$\text{Rate} = \frac{k_1 K_c [\text{Hydrazide}]_{\text{total}}}{(1 + K_c [\text{Hydrazide}]) (1 + K_H [H^+]) (1 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2)} \quad \dots(21)$$



$R = C_6H_5$ for benzoic acid hydrazide and $C_6H_5NO_2$ for p-Nitro benzoic acid hydrazide

Scheme 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 dm³ for benzoic and p-NO₂ benzoic acid hydrazides respectively. The electrophilic character of $TiCl_2^+$ among the thallium (III) chlorocomplexes is highest thus making it the reactive species.

Table 1 – values of K_c and k_1 [HCl] = 0.1 mol dm⁻³, [HClO₄] = 0.1 mol dm⁻³, [T^{III}] = 3.0 X 10⁻³ mol dm⁻³, I = 0.6 mol dm⁻³

The detailed mechanism involves electrophilic substitution on the nitrogen of the hydrazide with the formation of N-Tl bond, which decomposes in the subsequent step with, direct two-electron transfer from hydrazide to thallium to give an intermediate followed by fast steps. (Scheme 3). Such N-Tl bond formation has been postulated during thallium (III) oxidation of nitrogen⁹ containing compounds.

Table 1: Values of K_c and k_1

Temp in °C	K_c (mol ⁻¹ dm ³)		$10^4 \times k_1$ (S ⁻¹)	
	BAH	p-NO ₂ BAH	BAH	p-NO ₂ BAH
15	9.33	9.60	3.57	1.11
20	9.60	9.40	4.16	1.66
25	9.33	9.60	7.14	2.5
30	9.00	9.60	8.33	3.33

The activation parameters, with respect to slow step, k_1 , ΔH^\ddagger (KJ mol⁻¹), ΔG^\ddagger (KJ mol⁻¹) and ΔS^\ddagger (JK⁻¹mol⁻¹) were found to be 37.20, 40.11 and -82.38 respectively for benzoic acid hydrazide and 19.27, 81.81 and -209.89 for p-Nitro benzoic acid hydrazide. Considerable decrease in the entropy of activation is due to formation of more ordered transition state as shown in scheme 3. The mechanism involves neutral hydrazide as the active substrate thus the reaction is unaffected by the change in the ionic strength. The increase in 1,4-dioxan content in the reaction medium decreases;

the rate such an effect of the solvent is due to the stabilization of the complex formed between reactants¹⁰ in a medium of low relative permittivity.

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REFERENCES

- Ho T.L., Ho H. C. and Wong C. M., *Synthesis.*, 562 (1972).
 - Schnyder, J. and Rittenberg M, *Helv. Chim. Acta.*, **58**: 521 (1975).
 - Tsuji, J., Takayanagi H and Toshida Y, *Chem. Lett.*, 147 (1976).
- Aylward, R. J and Norman, R. O. C *J. Chem. Soc.*, 2399 (1968).
 - Tsuji J., Hayakawa S, Takayanagi H. *Chem. Lett.*, 437 (1975).
 - Tsuji J., Anathema T, Qui N. T. and Takayanagi H., *Tetrahedron.*, **36**: 1180 (1913).

- d) Hoffman R. V., Kumar A. J., *J. Org. Chem.*, **49**: 4014 (1984).
3. Mckillop A., Taylor E. C., *Organic synthesis by oxidation with metal compounds.*, W.J. Mijs, C. R. H. J. de Jonge, Plenum: New York, 695 (1986).
4. Vogel A. I., *Textbook of practical organic chemistry.*, (Longman, New York) 5th Edn 66 (1989).
5. (a) Mckillop A., Hunt J. D and Taylor E. C., *J. Am. Chem. Soc.*, **93**: 4918 (1971).
b) Butler R. N., Morris G. J and O'Donohue A.M, *J. Chem. Res.(S.)*, 61 (1981).
c) Taylor E. C., Robey R.L and Mckillop A., *Angew.Chem. Int. Ed., Engl.*, **11**: 48 (1972).
d) Taylor, E. C., Robey R.L., Mckillop A, *J. Org. Chem.*, **37**: 2797 (1972).
e) Silveria A, Jr., Angelastro M., Israel R., Totino F and Williamsen P.J, *J. Org. Chem.*, **45**: 3522 (1980).
6. Vogel A. I., *Textbook of practical organic chemistry.*, (ELBS & Longman Group) 4th Edn 1125 (1975).
7. Handbook of chemistry and physics, edited by R C Weast, 50th edn., (CRC) (1970).
8. (a) Kazo K, Hirakazo T., Hisashi K and Zenzo T, *Chem. Pharm. Bull.*, **11**: 797 (1963).
(b) Krishnarao P.V., Frank M. S. and Ramaih A. K, *React. Kinet. Cata. Lett.*, **9**: 59 (1978).
(c) Krishnarao P.V., Frank M. S. and Ramaih A.K, *Indian J. Chem.*, **16A**: 418 (1978).
(d) Ramaih A.K., Frank M. S., Baburao G and Krishnarao P.V, *Indian J. Chem.*, **18A**, 416 (1979).
9. Lee A. G, *The Chemistry of Thallium.*, (Elsevier, London) 48 (1971).
10. (a) Mckillop A., Hunt J.D., Naylor R. D. and Taylor E. C, *J. Am. Chem. Soc.*, **93**, 4918 (1971).
(b) Buttler R.N., Morris G. J. and O' Donohue A. M., *J. Chem. Res. (s)*, 61 (1981).
11. Varale A.S., Hilage N.P., *Oxidation Communications.*, (2008). In Press
12. Varale A.S., Hilage N.P., *Asian Journal of Chemistry*, **20** (2008). In Press.