

Oxidation of benzoic and n- Butyric acid hydrazides by Thallium (III) in Acidic Medium- A Kinetic and Mechanistic approach

Hrushikesh Deokar¹, Amit Varale^{2*}

¹Karmveer Bhaurao Patil College, Vashi, Maharashtra, India

²A.S.P. College, Devrukh Dist-Ratnagiri Maharashtra State, India

Corresponding author amitvarale@gmail.com

Abstract

The reaction between Thallium (III) and benzoic, n-butyric acid hydrazides is carried out in a mixture of perchloric and hydrochloric acid medium. The reaction proceeds through formation of complex with reactant, which decomposes in subsequent steps to give product. Effect of acrylonitrile shows, that there is no formation of free radicals. The increase in $[H^+]$ and $[Cl^-]$ decreases the rate of the reaction. The increase in ionic strength does not affect the rate of reaction. The effect of temperature was studied at four different temperatures ranging from 15°C to 30°C. The activation parameters were also determined and a mechanism is predicted.

Keywords: kinetics, Thallium(III), Oxidation, benzoic and n-butyric acid hydrazides.

1. Introduction

Chemical kinetics, also known as reaction kinetics, is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It is to be contrasted with thermodynamics, which deals with the direction in which a process occurs but in itself tells nothing about its rate. Chemical kinetics includes investigations of how experimental conditions influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that also can describe the characteristics of a chemical reaction.

Thallium, as well as its compounds of high purity, is widely used in many fields of science and technology. Today it is difficult to call the field of technology that would not use rare metals, their alloys and various compounds. Due to its physical-chemical properties, thallium, as well as its compounds of high purity, is widely used in many fields of science and technology. In particular, metal thallium is used to obtain bearing and low-melting alloys, in semiconductors, as a source of β - radiation it is used in radioisotope devices^{1,2,3}. Alloys containing thallium have increased resistance, inertness with respect to acids, low melting point. It is known that thallium is used as a catalyst in the obtaining of special alloys, optical lenses, jewelry, and the creation of low temperature thermometers. Thallium compounds are also used as medicines against rodents and insecticides^{4,5,6}.

The hydrazides are pharmaceutically important compounds used as antitubercular⁷ and antibacterial agents; some of them have been reported to possess anti-inflammatory⁸ and diuretic⁹ activities. Interest in the use of thallium (III) in the oxidation of organic compounds has increased only recently and research in this regard has not been extensive. The thallium(III) oxidations of several other aliphatic, aryl aliphatic and cyclic ketones have been examined¹⁰. The oxidation of phenol by thallium(III) acetate in aqueous acetic acid leads to

formation of dione as a major product¹¹. It is clear that little information is available regarding the oxidation of benzoic and n-butyric acid hydrazides by thallium (III). Hence, the present work deals with the kinetics and mechanism of oxidation benzoic and n-butyric acid hydrazides by Thallium (III) in acidic medium.

2. Materials and Methods

Thallium (III) solution was prepared by dissolving Tl_2O_3 (ACROS) in 1.0 mol dm^{-3} HCl and the concentration was ascertained by iodometric titration. The benzoic and n-butyric acid hydrazides was prepared from reported procedure and characterized by determining their melting points. Stock solution of benzoic and n-butyric acid hydrazides was prepared in 50 % v/v, 1, 4-dioxan. Ionic strength was kept constant.

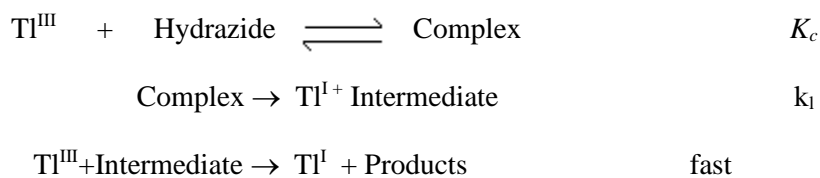
3. Results and Discussion

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 $6.4 \times 10^{-3} \text{ mol dm}^{-3}$ keeping the $[hydrazide]$ constant at $1 \times 10^{-1} \text{ mol dm}^{-3}$. Since, the pseudo first order rate constants were fairly constant ($3.6 \pm 0.1 \times 10^{-4} \text{ s}^{-1}$ for benzoic and n-butyric acid hydrazides (n-BuAH) at $25^\circ C$, 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.

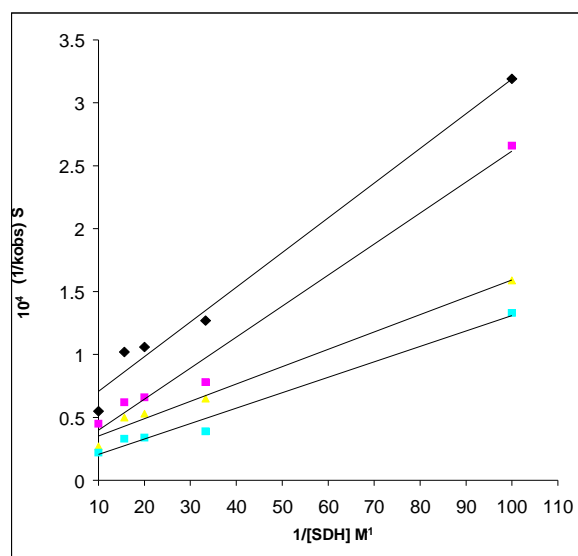
To study the effect of $[H^+]$ and $[Cl^-]$, $[oxidant]$, $[hydrazide]$ and ionic strength were kept as 3.0×10^{-3} , 1×10^{-1} and 0.6 mol dm^{-3} respectively. To vary $[H^+]$ and $[Cl^-]$, $HClO_4$ and $NaCl$ were used. Increase in $[H^+]$ from 0.13 to 0.60 mol dm^{-3} decreases $10^4 k(s^{-1})$ from 4.20 to 0.15 for BAH at $25^\circ C$ and 28.71 to $0.31 \times 10^{-4} \text{ s}^{-1}$ for n-BuAH at $25^\circ C$. Increase in $[Cl^-]$ from 0.13 to 0.60 mol dm^{-3} decreases from 2.80 to 0.085 for BAH at $25^\circ C$ and 4.13 to $0.15 \times 10^{-4} \text{ s}^{-1}$ for n-BuAH. 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 % did not produce any precipitate due to polymerization of the added acrylonitrile on the pseudo first order rate constants indicating absence of free radical

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.



Scheme 1



3.1 Michalie's-Menten plot for BAH

The Michealis - Menten plots of $1/k_{obs}$ versus $1/[Hydrazide]$ were linear with an intercept in support of the complex formation.

$$\text{Rate} = k_1 [\text{Complex}] = k_1 K_c [\text{Hydrazide}]_{\text{free}} [\text{TI}^{\text{III}}]_{\text{free}} \quad (1)$$

$$[\text{TI}^{\text{III}}]_{\text{total}} = [\text{TI}^{\text{III}}]_{\text{free}} + [\text{Complex}] \quad (2)$$

$$[\text{TI}^{\text{III}}]_{\text{total}} = [\text{TI}^{\text{III}}]_{\text{free}} + K_c [\text{Hydrazide}] [\text{TI}^{\text{III}}]_{\text{free}} \quad (3)$$

$$[\text{TI}^{\text{III}}]_{\text{free}} = [\text{TI}^{\text{III}}]_{\text{total}} / (1 + K_c [\text{Hydrazide}]) \quad (4)$$

$$\text{Rate} = k_1 K_c [\text{Hydrazide}] [\text{TI}^{\text{III}}]_{\text{free}} \quad (5)$$

$$k_{obs} = k_1 K_c [\text{Hydrazide}] / (1 + K_c [\text{Hydrazide}]) \quad (6)$$

Rate law 8 is verified by plotting $1/k_{obs}$ against $1/[Hydrazide]$ 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.

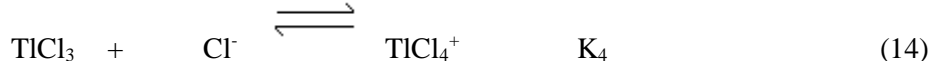
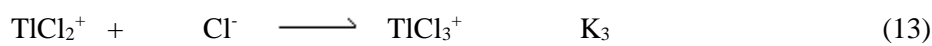
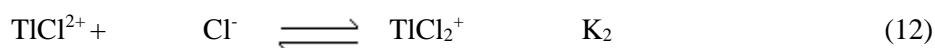
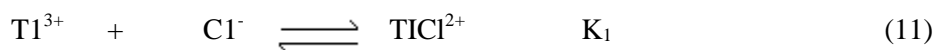


$$[\text{Hydrazide}]_{\text{total}} = [\text{Hydrazide}]_{\text{free}} + [\text{Hydrazide}]_{\text{protonated}} \quad (8)$$

$$[\text{Hydrazide}]_{\text{total}} = [\text{Hydrazide}]_{\text{free}} + K_H [\text{Hydrazide}]_{\text{free}} \quad (9)$$

$$[\text{Hydrazide}]_{\text{free}} = [\text{Hydrazide}]_{\text{total}} / (1 + K_H [\text{H}^+]) \quad (10)$$

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 constants are $K_1 = 1.38 \times 10^8$, $K_2 = 3.98 \times 10^{13}$, $K_3 = 6.02 \times 10^{15}$ and $K_4 = 1.0 \times 10^{18} \text{ mol}^{-1} \text{ dm}^3$.



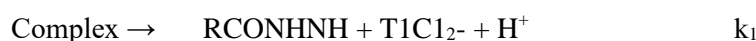
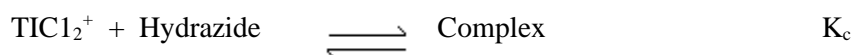
All the thallium (III) will exist as TlCl_2^+ and its concentration can be expressed by Equation 17. The $[\text{TlCl}_2^+]_{\text{free}}$ can now be given by eq. 19 where, $\beta_1 = K_3/K_2 = 151$ and $\beta_2 = K_4/K_3 = 166$, further, using Equations 18 and 19 the concentrations of $[\text{TlCl}_2^+]_{\text{free}}$,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

$$[\text{TI (III)}]_{\text{total}} = [\text{TlCl}_2^+]_{\text{total}} = [\text{TlCl}_2^+]_{\text{free}} + [\text{TlCl}_3] + [\text{TlCl}_4] \quad (15)$$

$$[\text{TlCl}_2^+]_{\text{total}} = [\text{TlCl}_2^+]_{\text{free}} (1 + \beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2) \quad (16)$$

$$[\text{TlCl}_2^+]_{\text{free}} = [\text{TlCl}_2^+]_{\text{total}} / (1 + \beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2) \quad (17)$$

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.



where R –Alkyl group

Scheme 2

Plotting $1/k_{\text{obs}}$ against $1/[\text{Hydrazide}]$ and $1/k_{\text{obs}}$ against $[\text{H}^+]$ which were found to be linear. From the slopes and intercepts of these plots the values of K_c and K_H were determined. The values of K_c are given in Table 1 and those of K_H were found to be 13 and 16 $\text{mol}^{-1} \text{dm}^3$ for benzoic and n-butyric acid hydrazides respectively.

$$\text{Rate} = \frac{k_1 K_c [\text{Hydrazide}]_{\text{total}} [\text{TlCl}_2^+]_{\text{total}}}{(1 + K_c [\text{Hydrazide}]) (1 + K_H [\text{H}^+]) (1 + \beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2)} \quad (18)$$

$$K_{\text{obs}} = \frac{k_1 K_c [\text{Hydrazide}]_{\text{total}}}{(1 + K_c [\text{Hydrazide}]) (1 + K_H [\text{H}^+]) (1 + \beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2)} \quad (19)$$

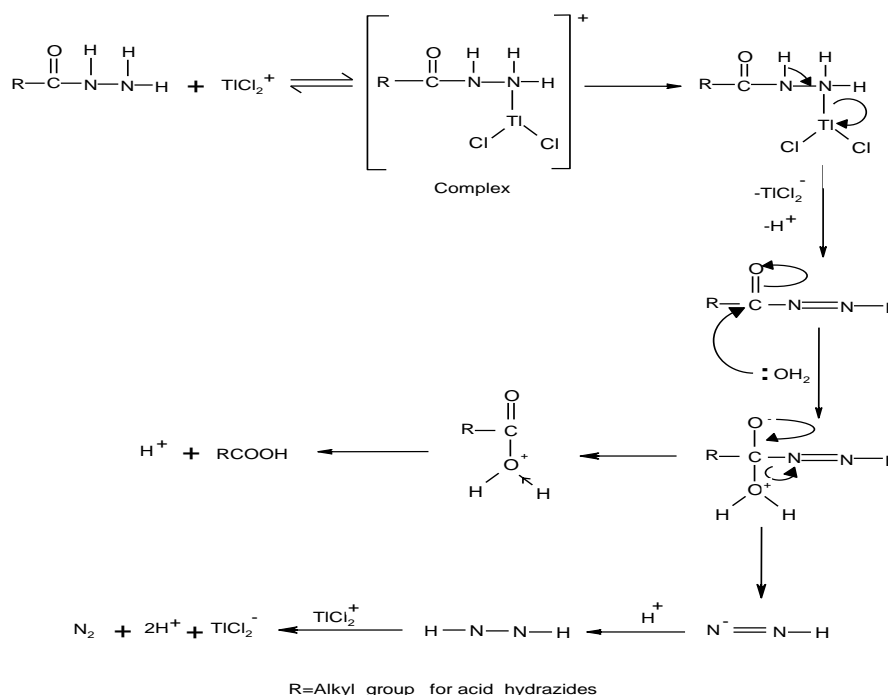
Table 1 – Values of Kc and k₁

$$[\text{HCl}] = 0.1 \text{ mol dm}^{-3}, [\text{HClO}_4] = 0.1 \text{ mol dm}^{-3}$$

$$[\text{Tl}^{\text{III}}] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}, I = 0.6 \text{ mol dm}^{-3}$$

Hydrazide	Kc. (mol dm ⁻³)				10 ⁴ x k ₁ (s ⁻¹)			
	15°C	20°C	25°C	30°C	15°C	20°C	25°C	30°C
BAH	59.09	55.50	47.69	40.00	1.23	2.05	2.58	4.44
n-BuAH	9.20	9.22	9.23	9.25	1.25	2.38	3.33	10.00

Mechanism



Scheme 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 nitrogen containing compounds.

The activation parameters are shown in Table 2. 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 reactants in a medium of low relative permittivity¹².

Table No. 2 Activation Parameters

Hydrazide	Ea (KJ mol ⁻¹)	ΔH^\ddagger (KJ mol ⁻¹)	ΔG^\ddagger (KJ mol ⁻¹)	ΔS^\ddagger (KJ mol ⁻¹)
BAH	67.45	59.74	87.94	-94.64
n-BuAH	54.45	38.54	118.16	-107.50

4. Conclusion

The order of reactivities of Benzoic and benzoic and n-butyric acid hydrazides under investigation is -



The rate of oxidation of n-butyric acid hydrazide decreases as compared with benzoic acid hydrazide.

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